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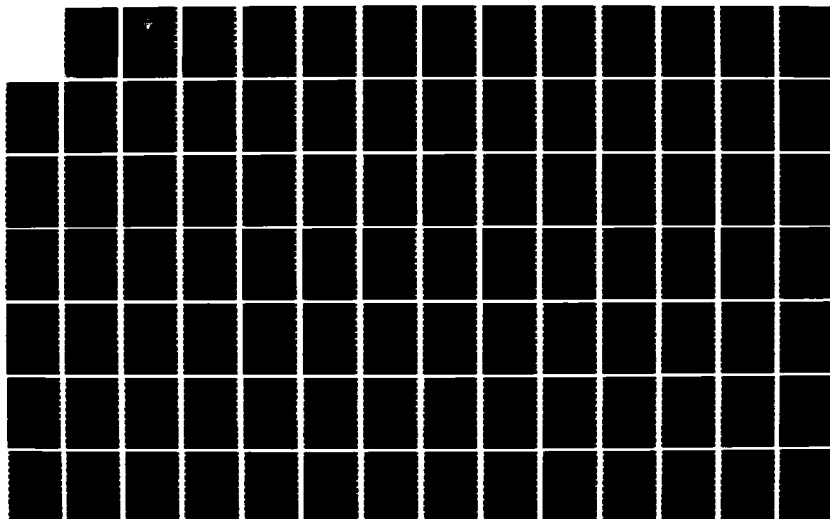
FLASH PHOTOLYSIS AND ITS APPLICATIONS MEETING IN
HONOUR OF SIR GEORGE PO (U) ROYAL INSTITUTION OF GREAT
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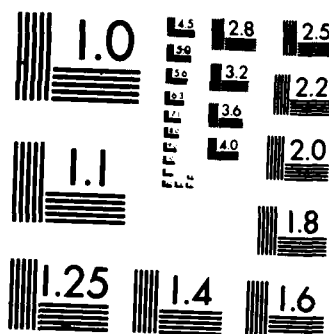
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FLASH PHOTOLYSIS AND ITS APPLICATIONS

MEETING IN HONOUR OF SIR GEORGE PORTER, P.R.S.

14th - 16th July, 1986

PREPRINTS

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MONDAY 14 JULY 1986

09.00-10.30 REGISTRATION AND COFFEE : Entrance Hall
10.30-10.45 PROFESSOR DAVID PHILLIPS: Welcoming Remarks

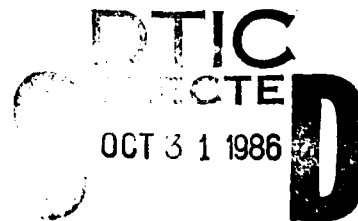
SESSION A: DEVELOPMENT OF THE TECHNIQUE

Chairman: M. W. WINDSOR

10.45-11.00 G.R. FLEMING: Picosecond and femtosecond studies of the influence of solvent on reaction dynamics
11.00-11.15 F. WILKINSON: Diffuse reflectance flash photolysis
11.15-11.30 M.A. WEST: Time-resolved IR Spectroscopy
11.30-11.45 P. GOUDMAND: Flash photolysis using IR lasers
11.45-12.00 D. PHILLIPS: Time-resolved resonance Raman spectroscopy
12.00-12.15 J. WIRZ: Application of flash photolysis to the determination of keto-enol equilibria in the ground state
12.15-12.30 R.J. CHERRY: Measurement of slow rotational diffusion of biological macromolecules by transient dichroism of triplet probes
12.30 LUNCH in the Royal Institution
13.40 PHOTOCALL in the Main Lecture Theatre

POSTERS associated with Session A :

T.A.M. DOUST and B.L. GORE: Design and construction of a picosecond flash spectroscope
G. LEARY: A photoacoustic mercury detector
D.J. MORANTZ and J.W. WIGLEY: Substrate interactions with organic triplet states
A. ROOD: Combined flash photolysis and gas phase electron diffraction studies of small molecules
F. SKUSE: Little things might mean a lot
G.J. SMITH: OSSA - an erythematous radiation actinometer



Picosecond and Femtosecond Studies of the Influence of Solvent
on Reaction Dynamics.

Graham R. Fleming, Scott Courtney, Soeng Kim,
Silvio Canonica and Michael Balk
The University of Chicago
Department of Chemistry
Chicago, Illinois 60637

It is now possible to perform flash photolysis experiments with better than 100 fs resolution. An amplified colliding pulse ring laser system will be described and experiments to study the isomerization and reorientational dynamics of trans and cis stilbenes discussed. The isomerization of trans stilbene has also been studied from isolated microcanonical ensembles all the way to the liquid state in both normal and deuterated stilbene. The implications of these data for current theories of reactions in solution will be discussed. The relaxation of solvent molecules around newly created charges or dipoles is an area of current interest. Fluorescence up-conversion with subpicosecond resolution has been used to time resolve Stokes shifts and to relate these to models and molecular dynamics simulations of solvent dynamics.

DIFFUSE REFLECTANCE FLASH PHOTOLYSIS

Francis Wilkinson

Department of Chemistry, University of Technology
Loughborough, Leics., United Kingdom

One reason why flash photolysis is such a powerful technique well worthy of the award of the Nobel Prize in Chemistry is that it can be applied to any transparent sample e.g. to gases, to fluid and rigid solutions etc.⁽¹⁾ Recently there has been considerable interest in the photochemical properties of heterogeneous systems many of which are opaque, including examples in photobiology. It is a pleasure to report at this meeting, which is to honour Sir George Porter, recent progress which extends to opaque, heterogeneous, and often highly scattering samples, the advantages of being able to subject them to flash photolysis investigations by using diffuse reflected light in place of transmitted light as the analysing source on timescales extending from several seconds to picoseconds. Photoinduced transient spectra and decay kinetics have been observed from a wide variety of opaque samples including :- fractions of monolayers of organic molecules adsorbed on catalytic oxide surfaces^(2,3) and included within the hydrophobic zeolite silicalite⁽⁴⁾ - semiconductor powders and sintered porous electrodes doped and undoped^(5,6) - organic microcrystals^(7,8) - powdered inorganic phosphors⁽⁹⁾ and dyes adsorbed on fabrics and chemically bound to polymers^(10,11). These examples clearly demonstrate that flash photolysis in diffuse reflectance mode should be as invaluable to the understanding of heterogeneous photoreactions as the transmittance mode has been for homogeneous photoreactions.

The first successful demonstration of diffuse reflectance laser flash photolysis on picosecond time scales has been obtained using xanthone adsorbed on a high surface area powdered silica gel. The results obtained at the Rutherford-Appleton Laboratory are shown in the upper section of the figure. This sample was also studied using nanosecond laser photolysis exciting at 354 nm and the decay of triplet-triplet absorption spectrum with $\lambda_{\text{max}} = 590$ nm is also shown in the figure. The sensitivity of the technique is demonstrated by these results since only 1% of a monolayer of xanthone is being excited. The figure also illustrates that spectral and kinetic information can now be obtained using the diffuse reflectance mode with much the same precision as in the transmission mode. The fact that the growth of the transient measured with 6 ps pump pulses at 295 nm and variably delayed probe pulses at 590 nm has a risetime of about 500 ps demonstrates that S_1-T_1 intersystem crossing in xanthone is very sensitive to environment since the risetime of triplet xanthone in benzene is <9 ps.⁽¹²⁾ Large changes in non-radiative transitions have been reported previously for aromatic hydrocarbons adsorbed on several surfaces⁽¹³⁾. It is well known⁽¹⁴⁾ that λ_{max} for the xanthone triplet is a sensitive probe of the polarity of the environment being 655, 610, 590 nm in carbon tetrachloride, cyclohexane and 10% aq. ethanol respectively. A λ_{max} value of 590 nm demonstrates the polar nature of the silica gel surface.

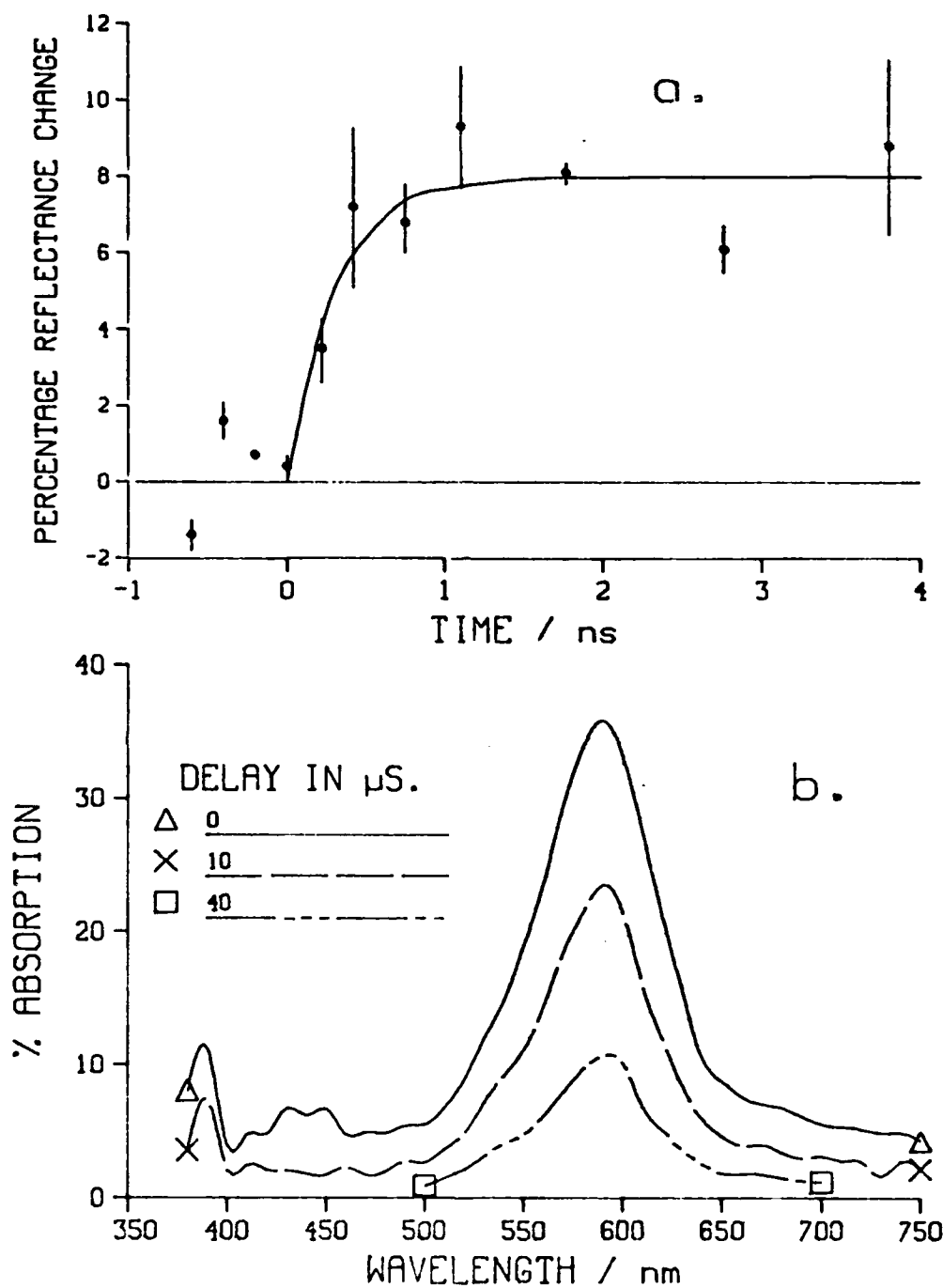
For samples composed of randomly distributed absorbers Kubelka-Munk theory has been proved to hold in practice for many opaque diffuse reflectors. In this theory two light fluxes in opposite directions, I and J, are considered perpendicular to the irradiated surface at $x = 0$. If K and S are the absorption and scattering coefficients with dimension, (distance)⁻¹, then the attenuation of the incident flux I is given by

$$dI(x) = -I(x)(K+S)dx + J(x)S dx \quad (1)$$

and

$$dJ(x) = J(x)(K+S)dx - I(x)S dx \quad (2).$$

For transparent media $S = 0$ and (1) becomes $dI = -KI(x)dx$ i.e. Lambert's Law where $K = 2.303\epsilon C$. The reflectance R is measured at the surface thus $R = J(o)/I(o)$. In flash photolysis experiments what is measured is $\Delta R(t)/R_b = (R(t)-R_b)/R_b$ as a function of time where R_b is the reflectance before and $R(t)$ after excitation.



Diffuse reflectance laser flash photolysis of xanthone adsorbed on silica gel. (a) Growth in absorbance of 6 ps probe pulses at 590 nm due to increased delay from pump pulses at 295 nm (b) transient decay following excitation with a 20 ns laser pulse at 354 nm.

Equations (1) and (2) can be used to predict the distribution of excited species initially formed below the irradiated surface and ΔR expected for any transient. Computer calculations based on (1) and (2) and measured values for K and S for ground state species and for the laser energy density; together with estimates of extinction coefficients of triplet states of adsorbed species or within microcrystals based on solution values give good agreement with experiment. For example in the case of acridine on powdered silica the calculated reflectance is reduced to 5% of its value before excitation i.e. the transient absorption is effectively 95% and this is within experimental error of what is found in practice. In addition the dependence on laser energy and ground state concentration found experimentally conform with the theoretical expectations. It is also possible to predict temperature rises of several hundred degrees, detected experimentally, when micro-crystals are excited into highly absorbing transitions.⁽¹⁵⁾

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TIME-RESOLVED IR SPECTROSCOPY

M. Poliakoff and P.M. Hodges

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, England

M.A. West

The Royal Institution, 21, Albemarle Street, London W1X 3BS, England

This lecture will describe apparatus for recording time-resolved IR spectra on a microsecond time scale and its application to organometallic photochemistry.

Many catalytic reactions involve organometallic compounds and a full understanding of the mechanisms requires the identification of short-lived intermediates. Unfortunately, conventional flash photolysis is only of limited use in this context, because the UV-visible absorption bands of organometallic compounds are generally broad and contain little information. By contrast, IR spectra, particularly of transition metal carbonyls, can provide detailed information about the structures of intermediates. We are therefore developing equipment to record the IR spectra of these transient species.¹

Our apparatus combines a UV flash with a line-tunable cw CO laser to monitor transient IR absorptions over the range 2020 to 1700 cm^{-1} . IR spectra are reconstructed point-by-point from kinetic traces recorded at different IR wavelengths. With a liquid N_2 -cooled photo-conductive HgCdTe detector we can detect an absorbance change of 2×10^{-3} with a S/N of 5 on single shot.² Initially, we used a 50J flash lamp, for generating the transient species, and the lifetime of the flash has proved to be the major limitation to the time resolution of the apparatus.³ This limitation is being overcome by use of an excimer laser. Ultimately a time resolution of 30 nsec can be anticipated.

In this lecture we shall describe some of the problems involved in such equipment⁴ and survey the chemical systems which we have studied so far.^{2,3}

1. For a general review of time-resolved IR of organometallics; see M. Poliakoff and E. Weitz, Adv.Organometallic.Chem., (F.G.A. Stone, Ed.) 25 (1986) 277.
2. B.D. Moore, M. Poliakoff and J.J. Turner, J.Am.Chem.Soc., 108 (1986) 000.
3. B.D. Moore, M.B. Simpson, M. Poliakoff and J.J. Turner, J.Chem.Soc., Chem.Comm., (1984) 972.
4. The performance of our equipment will be compared with apparatus based on a global IR source, e.g. S.P. Church, H. Hermann, F-W. Grevels and K. Schaffner, J.Chem.Soc., Chem.Comm., (1984) 785.

TIME RESOLVED RESONANCE RAMAN SPECTROSCOPY

David Phillips

The Davy Faraday Research Laboratory
The Royal Institution
21 Albemarle Street
London W1X 4BS

The technique of flash photolysis relies on the monitoring of absorption spectra of transient species following pulsed excitation of a photochemical system. While this technique leads to information of great kinetic importance, in general the electronic spectra produced do not give rise to structural information about the transients. Recording the vibrational spectrum of a transient is potentially much more revealing, and we will describe an experimental system for taking resonantly enhanced Raman spectra of transient species on the nanosecond timescale.

As an example of the use of the technique, the anthraquinone photochemical system will be revisited.

Time-resolved absorption spectroscopy [1] has led to the proposal of a complicated mechanism for the aqueous solution photochemistry of the so-called 'strong' sensitizers, shown in Figure 1, and the triplet state has been observed to decay with the production of three different transient species including two different complexes with water, B and C. The correlation of these transients with hydroxylated derivatives obtained as permanent products on steady-state irradiation is shown in Figure 1.

Time-resolved resonance Raman spectroscopy (TR³) has been used to characterise structures in a number of the transients shown in Figure 1. [2,3] Vibrational assignments are shown in Table 1.

The pattern of wavenumber shifts demonstrates clearly that the structural and bonding perturbation in the excited triplet state and its photosolvates B and C, as well as in the free radical reduction products, is heavily concentrated in the carbonyl groups. The data also supports the identification of transients B and C as strong charge-transfer complexes. In transient B, the water is attached via the carbonyl group whereas in transient C, the water molecule is presumed to be attached to a side ring via the oxygen atom.

Figure 1 Kinetic Scheme

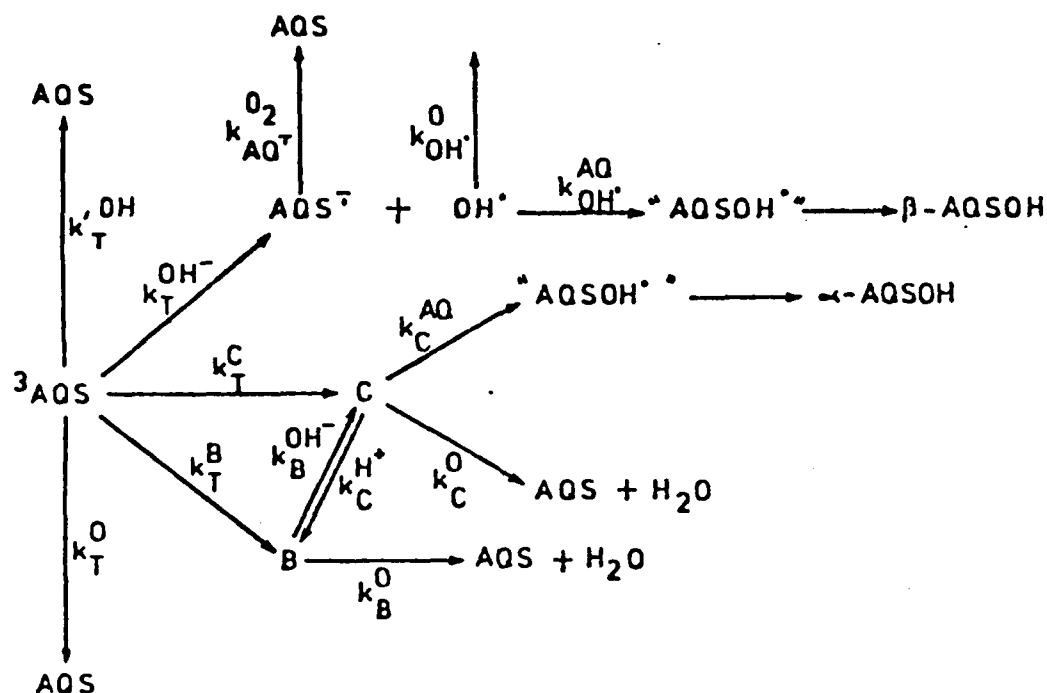


Table 1. Resonance Raman bands (cm⁻¹) from anthraquinone-2,6-disulphonate (AQ26DS) and derived photoreaction intermediates.[4]

Parent AQ26DS	Radical AQ26DSH	Anion AQ26DS	Triplet $^3\text{AQ26DS}$	Transient photosolvates AQ26DS (B)	Transient photosolvates AQ26DS (C)	C _{2h} assignments
1668	-	1496	-	-	-	b _u (C=O) asym
1669	1605	1347	1210	1347	1345	a _g (C=O) sym
1625	-	1598	1597	1598	1595	b _g (C-C) str
1596	1576	1498	1556	1555	1513	a _g (C-C) str
-	-	-	1490	1521	1485	(C-C) str
-	-	-	-	-	1286	(C-O) str
1177	1177*	1182*	1182*	1180*	-	a _g (C-H) ip bend
-	-	1101	1126	-	-	(C-C) str/ (C-C) def

Key: * bands also observed in ground state spectra

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J.N.Moore, D.Phillips, N.Nakashima and K.Yoshihara. J.C.S.Faraday I
(in press.)
- [2] J.N.Moore, G.H.Atkinson, D.Phillips, P.M.Killough and
R.E.Hester. Chem.Phys.Lett., **107**, 381 (1984).
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Time-resolved Vibrational Spectroscopy (A.Lauberau and M.Stockburger,
eds.), Springer (1985).
- [4] J.N.Moore, Ph.D. Thesis, London University, 1986.

Application of Flash Photolysis to the Determination of
Keto-Enol Equilibria in the Ground State.

Jakob Wirz

Institut für Physikalische Chemie der Universität
Basel, Klingelbergstrasse 80, CH-4056 Basel

Thermodynamically unstable tautomers are generated by flash photolysis of suitable precursors in order to determine the rate of conversion to the stable isomer in aqueous solution as a function of pH (pH-profile). By combination with the rate of the reverse reaction, determined independently by conventional techniques, this method has yielded the first purely experimental and accurate equilibrium constants both for the tautomerization and for the dissociation of C-H acids in aqueous solution. Applications of the method to prototype keto-enol equilibria (acetaldehyde, acetone, acetophenone, phenol) will be reported.

MEASUREMENT OF SLOW ROTATIONAL DIFFUSION OF BIOLOGICAL MACRO- MOLECULES BY TRANSIENT DICHOISM OF TRIPLET PROBES

R.J. CHERRY

Dept. of Chemistry, University of Essex,
Colchester, Essex CO4 3SQ

Rotational relaxation times of proteins embedded in biological membranes are typically in the microsecond-millisecond time range, due to the high viscosity of the lipid bilayer. Similar long relaxation times are also observed for large macromolecular assemblies such as ribosomes and multienzyme complexes. Such slow rotation can be measured by exploiting the long lifetime of the triplet state of suitable probe molecules (Razi Naqui et al., *Nature New Biol.* 245, 249 (1973)). Flash photolysis provides a convenient method of triplet state detection, either by direct observation of triplet-triplet absorption or indirectly by observation of ground state depletion. In either case, rotational diffusion may be determined by measurement of transient dichroism following excitation by a linearly polarised light pulse.

Following the development of suitable probes with reactive groups for covalent attachment to proteins, the method was first applied to the investigation of protein rotational diffusion in the human red blood cell membrane (Cherry et al., *Nature* 263, 389 (1976)). Subsequently the technique has been applied to a wide range of membrane proteins, both in cell membranes and in reconstituted systems. Studies with ribosomes and other macromolecular assemblies have also been reported.

Recent work has concentrated on the information on membrane structure and function which can be obtained from rotational diffusion measurements. Since rotational relaxation times are very sensitive to the size of the rotating particle, protein rotation measurements prove to be a valuable way of investigating protein-protein interactions in membranes. This approach has yielded much information on the architecture of the human red blood cell membrane, as well as on structural perturbations by toxic agents such as the bee venom polypeptide, melittin.

DESIGN AND CONSTRUCTION OF A PICOSECOND FLASH SPECTROSCOPE

T.A.M. Doust* and B.L. Gore

Davy Faraday Research Laboratory, The Royal Institution,
21 Albemarle Street, London W1X 4BS, U.K.

*Perkin-Elmer Limited, Post Office Lane, Beaconsfield,
Buckinghamshire HP9 1QA, U.K.

The two fundamental requirements of a flash spectroscopic apparatus are the initial excitation of the chemical system by a short pulse of light, followed by a similarly short pulse of 'white' light to determine the transient optical spectrum of the excited system.

The original flash photolysis apparatus (1) had a time resolution of several milliseconds, determined by the use of high power flash lamps to initiate the photolysis of substances such as Acetone and NO_2 , with a pulse of light in the u.v. region of the spectrum. Due to the much lower light intensities required to record the transient spectrum, small microsecond duration flashlamps could be used.

From the time of its introduction until the late 1960s the time resolution of flash spectroscopy was determined by the advances in the design of fast, powerful, excitation flash lamps. By 1967 the use of pulsed, Q switched, laser sources was feasible and both Ruby & Neodymium lasers, as well as gas discharge lasers, allowed excitation within times as short as a few nanoseconds.

The time limitation of flash spectroscopy now reversed and the need to provide short pulses of white light to record the transient spectrum became the determining factor. As the use of mode-locked laser pulses, with pulse widths of a few picoseconds, became relatively common the use of spark gaps and other nanosecond white light sources was superseded by the discovery of continuum generation (2). The application of the pulses from a CPM laser (3) now allows for measurements with time resolution as low as 50fs with detection throughout the entire visible region.

We shall present the design and results from the current flash spectroscopic system at the R.I. A hybrid mode-locked, cavity dumped dye laser is used to seed a Neodymium:YAG pumped, four stage amplifier chain. This produces several millijoules of light at ca. 600nm in a pulse less than 1ps in duration. By continuum generation in water, a white light pulse with the same duration as the pump pulse provides light from 380-1000nm. Detection and analysis of the transmitted probe is performed by a vidicon camera electronic light detector and a micro computer. This system allows for the collection and conversion of raw data to transient optical density spectra in a matter of minutes. Overall, the design considerations of a modern flash spectroscope will be presented in the light of the developments that have allowed an increase in time resolution by a factor of 10^{11} in just 36 years.

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A PHOTOACOUSTIC MERCURY DETECTOR.

Gordon Leary

Chemistry Division, DSIR,
New Zealand.

Quenching of atomic fluorescence in mercury vapour produces sound at the modulation frequency of the light source. The effect is substantial and has resulted in the design of a practical analytical instrument for the detection of trace quantities of mercury vapour as low as 0.01 ng. The response varies also as a function of quench gas concentration in a suitable inert carrier such as argon and this may be described by a modified Stern Volmer equation if mercury concentrations are held constant. This characteristic may form the basis of a very sensitive hydrocarbon detector for gas chromatography.

Substrate interactions with organic triplet states

D. J. Morantz and J. W. Wigley

The London College of Printing of The London Institute
at the Elephant & Castle, London SE1 6SB, U.K.

Short lived excited states are extensively studied by flash photolysis. Longer lived species, surviving up to fractions of a second, may be studied using non-pulsed light sources; however, complex kinetics yield more readily to laser flash photolysis methods (1,2). Thus, only a limited number of phosphorescent organic species in dilute solutions in polymer matrices have been found by us to decay exponentially at ambient temperatures; At 77 K, exponential decays are commonly found. We explore the interpretations of such non-exponential decays for these not-so-short lived systems. We rule out T-T annihilation and excimer formation which arise through higher concentrations of 'guest' chromophoric species; quenching by oxygen and other impurity species may also be ruled out in these studies. Triplet states do not appear to be the only reacting species present. A hydrogen abstraction quenching mechanism (2) is discussed and the systems to be considered include mono- and diketones. The several species which we find to decay exponentially at room temperature are biacetyl and camphorquinone. In poly(methylmethacrylate) and polystyrene matrices the decay rates range from 850 to 800 sec^{-1} for biacetyl and 1000 to 950 sec^{-1} for camphorquinone, at 298 K.

(1) K. Horie and I. Mita, Polymer Journal (1985) 17 3 517-524.

(2) D.J.Morantz and J.W.Wigley, Polymer Communications (1985) 26 170-171.

COMBINED FLASH-PHOTOLYSIS AND GAS-PHASE
ELECTRON-DIFFRACTION STUDIES OF SMALL MOLECULES

DR. ANTHONY ROOD

HEALTH & SAFETY EXECUTIVE

403, EDGWARE ROAD, LONDON NW2 6LN, UK

Apparatus has been constructed to observe the electron-diffraction pattern from short-lived species in the gas phase generated by the technique of flash photolysis. The operational characteristics of the system have been established by a study of the flash photolysis of chlorine dioxide and biacetyl. A channel plate electron amplifier and a photographic recording system have been used in this work. Recently, a photodiode array has been tested as a data acquisition device: it may improve the quality of the initial diffraction signal, but is prone to accidental electron beam damage.

OSSA: An Erythemat Radiation Actinometer

Gerald J. Smith

Department of Physical Chemistry

University of Melbourne, Melbourne, Australia

A dramatic increase in the incidence of skin cancer in recent years has prompted a number of countries to adopt solar uv exposure guidelines for "at risk" occupational groups (1). However, existing dosimeters for the measurement of erythemat (sunburn) uv radiation are either too expensive to attract widespread usage or their wavelength response does not accurately match the erythemat response of white skin to solar radiation (2,3,4).

Recognizing the need for an inexpensive but accurate device for measuring solar erythemat radiation, an actinometer has been developed, based on the photodissociation of an alkyl-disulphide in anoxic solution. The action spectrum for cleaving such disulphide bonds is very similar to that for erythema (1).

Flash photolysis studies of (5,6) alkyl-disulphides has shown that in addition to sulphur-sulphur bond cleavage there is also carbon-sulphur bond cleavage and this leads to the formation of tri and higher polysulphides (7). Because these sulphides absorb light in the solar erythemat wavelength range, they would introduce internal filtering with consequent non-linearities in dose measurements if they were formed in an actinometer.

In the photolysis of anoxic solutions of alkyl-disulphides in a hydrocarbon solvent consisting of molecules containing a weak C-H bond (eg. methylcyclopentane), it is found that the thiyl and dithio radicals produced react so rapidly with

solvent molecules that the free radical reactions producing tri and higher polysulphides are effectively eliminated. GC-MS product analysis shows the single sulphur products are the alkylthiol and alkyl-S-M where MH is the solvent molecule. The uv absorption spectra of extensively irradiated disulphide solutions show no sign of tri and higher polysulphide products.

In recent field trials of the actinometer conducted in association with the New Zealand Cancer Society, the Queensland (Aust.) Cancer Fund and ICI(NZ) Ltd., the yield of alkylthiol was found to be related to the solar erythema dose and independent of sun angle (i.e. solar spectrum) and length of actinometer exposure.

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SESSION B: GAS-PHASE STUDIES

Chairman: LORD TEDDER

- 14.00-14.30 **Keynote Lecture B.A. THRUSH:** Spectroscopic and kinetic studies of free radicals in the infra-red
- 14.30-14.45 **R.N. DIXON:** Vector correlations between the motions of a photofragment
- 14.45-15.00 **J.P. SIMONS:** Photodissociation dynamics of H O via Doppler photofragment spectroscopy
- 15.00-15.15 **J.I. STEINFELD:** Laser flash photolysis of organosilanes
- 15.15-15.30 **L.E. HARRIS:** CARS spectroscopy of the reaction zone of methane-nitrous oxide and nitramine flames
- 15.30 **TEA**

POSTERS associated with Session B:

G. BLACK and L.E. JUSINSKI: Laser-induced fluorescence studies of the CH S radical

A.C. JONES, A.G. TAYLOR and E.M. GIBSON Supersonic jet spectroscopy of complexes of carbazole and N-ethyl carbazole with alkyl cyanides

T. ICHIMURA: Picosecond and nanosecond laser flash photolysis study of some halogenated benzene derivatives

L.J. STIEF, W.A. PAYNE and D.F. NAVA: Flash photolysis studies of atoms and free radical reactions with phosphine

J.M. TEDDER: The reactions of reactive intermediates (radicals and cations) with alkanes, alkenes and alkynes

Spectroscopic and Kinetic Studies of Free
Radicals in the Infra-Red

B.A. Thrush

Department of Physical Chemistry
University of Cambridge
Lensfield Road
Cambridge CB2 1EP

The success of flash photolysis has been based on the large number of free radicals and other transient species — such as excited states — which have discrete spectra in the visible and ultraviolet regions of the spectrum. However, the structures and reactivities of many small free radicals and free atoms which are of interest in gas processes cannot be studied in the readily accessible visible and near ultraviolet regions where efficient spectroscopic sources and detectors are readily available.

In recent years, the advent of tunable diode lasers has provided rapidly tunable infrared sources with high brightness and very narrow spectral linewidth. Such sources can in theory be used to monitor any transient molecule, except for a homonuclear diatomic, in flash photolysis experiments. They are particularly useful for small polyatomic species such as HO_2 . Diode lasers can also be used to measure the rate of formation of products (or loss of reactant) in such systems. The construction and application of a flash photolysis apparatus with infrared detection is described and its performance is compared with other techniques for studying free radicals in the infrared. These mainly use electron paramagnetic resonance, laser magnetic resonance or other tunable infrared lasers in conjunction with discharge flow systems.

Vector Correlations Between the Motions of
a Photofragment

Richard N. Dixon

University of Bristol

School of Chemistry, The University
Cantock's Close, Bristol BS8 1TS, U.K.

The distribution of the available energy between the various degrees of freedom of the fragments from a photochemical decomposition is an important indicator of the detailed reaction dynamics. When the parent is photoselected by a polarised laser beam the optical transition moment is preferentially aligned parallel to the $\mathbf{g}$ vector of the exciting radiation. If the parent then fragments on a time-scale fast compared with molecular rotation this anisotropy is carried over to the product motions, and particularly to translational recoil and rotational anisotropy. Translational anisotropy can be studied through the measurement of angular distributions, and rotational anisotropy from the polarisation of product chemiluminescence or laser induced fluorescence excitation as appropriate. The spectral profiles of recoil Doppler-broadened lines, and the polarisation dependence of these profiles and the relative line intensities, provides a method for the simultaneous determination of both anisotropies. Furthermore, any mutual correlation between translation and rotation can also be determined.

The application of such measurements will be described for the photodissociation of HONO and H_2O_2 , determining the correlations of $\mathbf{V}$ and $\mathbf{J}$ (fragment) with each other and with $\mathbf{g}$ (parent).

Photodissociation Dynamics of H_2O_2 via Doppler Photofragment
Spectroscopy

M P Docker, A Hodgson and J P Simons

Department of Chemistry

The University, Nottingham NG7 2RD

Featureless dissociation continua, beyond indicating rapid molecular fragmentation in the electronically excited state, provide no detailed information on the dynamics in the excited state. Other methods must be employed to probe this secret behaviour. If the dissociation is not too rapid, i.e. if the Franck-Condon region on the upper potential surface that is initially accessed is not too steep, laser excited resonance Raman spectroscopy of the dissociating molecule can provide resolved spectral data from which dynamical information can be extracted [1]. Alternatively, the dissociation dynamics may be probed on a longer time scale through photofragment spectroscopy following laser flash photolysis [2]. If the fragments are fluorescent, Doppler resolved laser induced fluorescence techniques can reveal their internal state distributions, their translational distributions and in addition the anisotropies in the scattered fragment vector distributions - both translational and rotational.

The photodissociation of H_2O_2 by KrF laser radiation at 248 nm provides an ideal system for this kind of approach. Its near u.-v absorption is totally featureless and the primary fragments, $\text{OH}(X)$, are generated in the ground vibrational state with relatively low rotational excitation but necessarily, very high translation. This behaviour is tailor made for Doppler spectroscopic probing which, in combination with polarisation measurements, provides a unique way of examining both the detailed scalar and vectorial aspects of the dissociation dynamics. In particular, any correlation between the fragment recoil velocity v and its rotational angular momentum J can be exposed through Doppler resolved polarisation spectroscopy since selection of a

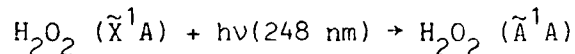
particular velocity component v_k along the probe beam axis $\underline{k}^{\text{probe}}$ (with the Doppler shift $\Delta\nu_D = \underline{v}_k \cdot \underline{k}^{\text{probe}} / c$) destroys the axial symmetry of the scattering system [3].

Translational Alignment

The excess energy of $125 \text{ kJ mol}^{-1}/\text{OH}$ appears in translation giving a centre of mass recoil velocity of 4.06 km s^{-1} and dramatically split Doppler profiles. For a single fragment recoil and coaxial photolysis-probe beam geometry, the Doppler profile is given by [4]

$$\begin{aligned} S(\Delta\nu) &= (1/\Delta\nu_D) [1 - \frac{1}{2}\beta P_2(\Delta\nu/\Delta\nu_D)] & : \Delta\nu < \Delta\nu_D \\ S(\Delta\nu) &= 0 & : \Delta\nu > \Delta\nu_D \end{aligned}$$

where $\Delta\nu_D = \underline{v}_0 \cdot \underline{k}^{\text{probe}} / c$ is the Doppler shift, $\Delta\nu$ is the displacement from the line centre ν_0 and β , the anisotropy parameter, takes the values $+2$ or -1 in the limits of fast dissociation parallel or perpendicular to the parent absorption dipole. The measured profile for the $R_2(1)$ line in the LIF spectrum is double peaked: its contour is accurately reproduced by choosing $\beta = -1$, consistent with an absorption transition, polarised along the 2-fold symmetry axis



and fast axial recoil along the O-O bond. The predicted transition has the character $6b(\pi) \rightarrow 7b(\sigma^*)$, $^1\text{A} \rightarrow ^1\text{A}$ [5].

Correlation between $\underline{J}_{\text{OH}}$ and $\underline{v}$

As the quantum number N_{OH} increases the (P,R) and Q lineshapes show different behaviour. Using an unpolarised photolysis beam, there is an increasing contrast in the central minimum for the P and R features while that for the Q features shows a steady reduction. The dependence on (a) the choice of rotational branch and (b) the subsequent use of polarised photolysis beam, aligned either $//$ or $\perp$ to $\underline{\epsilon}^{\text{probe}}$ identifies the cause of this behaviour as a correlation between $\underline{J}_{\text{OH}}$ and $\underline{v}$. A model which assumes a helical motion for the recoiling, rotationally excited fragments, with their rotational angular momenta tending to point along the recoil velocity vector $\underline{v}$ explains the observations. As the limit of high rotation is approached the transition moment in the OH fragments tends to lie parallel to $\underline{J}_{\text{OH}}$ for Q branch lines but in the rotation plane for P,R branch lines; any correlation between $\underline{v}$ and $\underline{J}_{\text{OH}}$ leads to complementary changes in the Doppler profiles. A quantitative classical analysis of the limiting profiles which assumes (i) an axially symmetric distribution of $\underline{J}_{\text{OH}}$ about $\underline{v}$ characterised by a single cone angle $(\underline{J}_{\text{OH}} \cdot \underline{v})$ (ii) axial recoil along the O-O bond ($\beta = -1$) and (iii) a symmetrical disposal of rotation into both of the OH fragments (i.e. $N_1 = N_2$) reproduces the general

trends observed [6]. Finally the model is confirmed by more detailed experiments utilising polarized photolysis and probe beams, directed coaxially or perpendicular to each other [7].

Summary Laser photodissociation of H_2O_2 at 248 nm generates translationally excited OH fragments, which recoil rapidly along the parent O-O axis and which tend to be rotationally aligned with their rotation planes lying perpendicular to the recoil direction. The rotational excitation can be ascribed therefore to production of torsionally excited parent molecules in the photo-excited state, rather than to any torque generated by their rapid recoil along the O-O axis.

The support of SERC is gratefully acknowledged

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Laser Flash Photolysis of Organosilanes

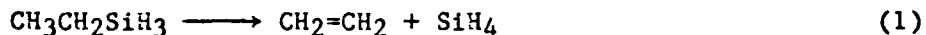
Jeffrey I. Steinfeld and Joseph S. Francisco*

Department of Chemistry, Massachusetts Institute of
Technology, Cambridge, Massachusetts 02139, U.S.A.

Introduction

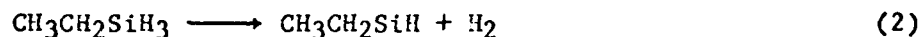
The first multiphoton molecular dissociation process was discovered in Sir George Porter's laboratory twenty years ago [1]. Since that time, multiphoton dissociation (MPD), using both visible/u.v. and infrared laser excitation, has been the subject of numerous studies; laser isotope separation and photochemical reactions at the gas-surface interface are among the important applications of this technique.

During the course of our investigations of laser-driven vapor deposition of semiconductor materials, we found that CO₂ laser photolysis of organosilanes led to deposition of amorphous silicon on adjacent surfaces, along with formation of gaseous products including olefins, silane, and molecular hydrogen [2]. The mechanism proposed for this decomposition was a four-center elimination reaction, e.g. in ethylsilane

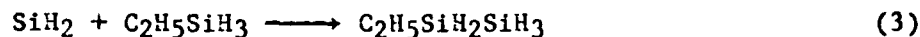


followed by secondary IRMPD of the vibrationally "hot" silane produced in (1) to yield SiH₂ and hydrogen. The SiH₂ has been observed by laser-induced fluorescence (LIF) on the visible $\tilde{A}^1\text{B}_1 - \tilde{X}^1\text{A}_1$ transition, following IRMPD of butyl- and phenylsilane [3] or of ethylsilane [4]. In the latter work, an alternative dissociation mechanism was proposed, namely, a three-center elimination

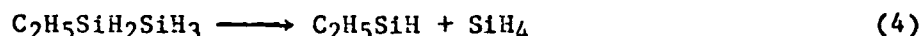
*Present address: Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.



followed by decomposition of the organosilylene to form olefin and SiH_2 . In this mechanism, the silane is formed by secondary post-pulse reactions such as



and



SiH_2 has also been observed by LIF following the u.v. flash photolysis of phenylsilane with the 193 nm ArF excimer laser [5]. Subsequent work at other u.v. wavelengths [6], however, suggests that as is the case in IRMPD, SiH_2 may be a secondary photoproduct in the u.v.-initiated process as well.

Radiative Lifetimes of SiH_2 ($\tilde{\text{A}}^1\text{B}_1$)

During the course of the LIF measurements, we observed a wide variation in decay times among individual ro-vibronic levels of the SiH_2 $\tilde{\text{A}}$ state, ranging from ca. 10 nsec for many of the levels to nearly 1 μsec for some. The variation is quite irregular, with neighboring transitions having lifetimes that may vary by over an order of magnitude. SiH_2 appears to be an extreme case of the anomalous lifetimes predicted by Douglas [7], which result from mixing of the electronically excited state with background levels of the ground ($\tilde{\text{X}}^1\text{A}_1$) or neighboring triplet ($\tilde{\text{a}}^3\text{B}_1$). These perturbations may be responsible for the difficulties encountered in assigning the SiH_2 $\tilde{\text{A}} \leftarrow \tilde{\text{X}}$ spectrum observed in flash kinetic absorption spectroscopy [8]. The wide variation in lifetimes doubtless results from the sparse level structure of the dihydride, which in turn leads to an irregular distribution of detunings between levels having the correct symmetry to mix with each other. Work is currently in progress on identifying the perturbed transitions and on modeling the distribution of lifetimes, possibly based on one of the algebraic models for distribution of molecular energy-level spacings [9].

The variation in lifetimes can have important practical consequences, if LIF is used for quantitative detection of SiH_2 in rate constant measurements or in establishing concentration profiles in silane CVD reactors. For example, a recent measurement of the reaction rate of SiH_2 with hydrogen using LIF [10] differs by a factor of 30 from a corresponding measurement using flash-kinetic absorption spectroscopy to detect SiH_2 [11]. Some or all of this discrepancy may be attributable to use of an incorrect radiative lifetime in interpreting the LIF measurements.

Comparison of Three- and Four-Center Elimination Mechanisms

In order to assess the relative importance of the three- and

four-center elimination mechanisms represented by reactions (2) and (1), respectively, we have carried out theoretical calculations of the energies and RRKM rates for each of these pathways. Overall heats of reaction were estimated using Benson's empirical rules [12] and the group additivities given by O'Neal and Ring [13], and also calculated by a MNDO technique [14]. The MNDO calculations are in reasonable agreement with the empirical results, and give a value of $\Delta H^\circ \approx +60$ kcal/mole for production of $\text{CH}_3\text{CH}_2\text{SiH}+\text{H}_2$ by the three-center elimination (1), and $\Delta H^\circ \approx +35$ kcal/mole for production of $\text{C}_2\text{H}_4 + \text{SiH}_4$ via the four-center elimination (2).

To evaluate the decomposition kinetics, calculations were carried out on the transition-state configurations for each of the two pathways. Barrier heights were calculated by empirical and MNDO approaches, with the following results:

Reaction	E_{act} , kcal/mole		
	empirical	MNDO	experimental
(2) (3-center)	58.5	70.7	63-65 [13]
(1) (4-center)	35.0	42.7	33-41 [15]

Thus, the activation energy for the four-center elimination is estimated to lie 20-25 kcal/mole below that for the three-center elimination.

RRKM rates were calculated for each of the two pathways. Activation energies of 42.7 and 65 kcal/mole were used for reactions (1) and (2), respectively, and transition-state frequencies and moments of inertia were estimated using Benson's rules [12]. On the basis of these preliminary estimates, we find that over range of 40-150 kcal/mole (12-48 CO_2 laser photons absorbed by the parent molecule), the rate for the four-center reaction exceeds that for the three-center reaction at any assumed level of excitation.

The two mechanisms cannot be readily distinguished on the basis of SiH_2 production rates; this species is a secondary photoproduct in both mechanisms and, in both cases is formed during the IR photolysis pulse [3,4]. The principal distinction between the two mechanisms is that the four-center process involves direct production of a stable primary product, SiH_4 ; this species is formed by secondary reactions (3) and (4) in the three-center elimination mechanism. Direct observation of SiH_4 in a crossed laser-molecular beam experiment [16], or monitoring its formation kinetics by spectroscopic probes such as Raman scattering or diode laser absorption, would be necessary to distinguish between the two mechanisms.

Acknowledgments

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CARS Spectroscopy of the Reaction Zone of
Methane-Nitrous Oxide and Nitramine Flames

L.E. Harris*

US Army Armament Research and Development Engineering Center
Dover, New Jersey

Abstract

Coherent Anti-Stokes Raman Scattering spectra were obtained for a $\phi = 3.2$ $\text{CH}_4/\text{N}_2\text{O}$ model and nitramine propellant flames throughout the reaction and postflame zones in order to assess kinetic mechanisms occurring in these flames. Spectra were obtained in the regions 4200-3900, 2400-2050, and 1900-1200 cm^{-1} . The reaction zone of the rich $\text{CH}_4/\text{N}_2\text{O}$ flame was studied primarily to provide a stationary flame analog to the transient propellant flame. In the $\text{CH}_4/\text{N}_2\text{O}$ flame, the decay of the initial produces was observed through the Q branch of the ν_1 and ν_3 modes of N_2O and Q, O, and S branches of the ν_2 and $2\nu_2$ modes of CH_4 . The formation of the produces N_2 , H_2 [Q($v'' = 0$ and $v'' = 1$) and S(5)-S(9)], CO, and CO_2 (ν_1) were also observed. Temperatures were obtained from both the H_2 and N_2 Q branches. In the nitramine propellant flame, the upper bound of the gas-surface interface temperature was measured as 900 ± 100 K from the H_2 Q branch. Near the surface of the propellant, reactant RDX (1599 cm^{-1} tentatively assigned as asymmetric NO_2 stretch) and transients HCN (ν_1) and NO are observed at moderate concentration ($>1\%$). The final produce N_2 is observed at low concentration ($<1\%$); H_2 (Q and S branches) and CO are observed at higher concentration ($>10\%$). RDX and HCN decay within 2mm of the propellant surface, while NO remains constant until 4mm, where it decays with a concomitant rise in N_2 concentration and temperature. H_2 and CO also increase in temperature and concentration. The nitramine reaction zone is seen to consist of two regions characterized by the reaction of RDX and HCN near the surface, consistent with the high-temperature mechanism of RDX decomposition, and the conversion of NO to N_2 to generate the luminous flame further above the surface.

ABSTRACT

LASER-INDUCED FLUORESCENCE STUDIES OF THE CH_3S RADICAL

Graham Black and Leonard E. Jusinski

Chemical Physics Laboratory

SRI International

Menlo Park, CA 94025 USA

Alkyl thiyl radicals (RS) are intermediates in combustion and atmospheric chemistry of organosulfur compounds of both natural and anthropogenic origins. These compounds, although minor constituents, may play a role in the atmospheric sulfur cycle and contribute to the acid precipitation problem. It is, therefore, important to determine the atmospheric chemistry of these radicals.

Until recently, the only reported absolute rate coefficient studies involved the HS radical.¹⁻³ Recently, the emission and laser-induced fluorescence (LIF) spectra of CH_3S were reported.^{4,5} This has led to the first measurements⁶ of the rate coefficients for the reactions of CH_3S with NO , NO_2 and O_2 . This paper reports further LIF studies of CH_3S and a study of its reaction with O_3 . CH_3S radicals were generated by the 248 nm photodissociation of dimethyl disulfide $[(\text{CH}_3)_2\text{S}_2]$ and 193 nm photodissociation of methyl mercaptan (CH_3SH). Fluorescence was excited on the $\tilde{\text{A}}^2\text{A}_1 \sim \tilde{\text{X}}^2\Sigma$ transition using a Nd:Yag-pumped dye laser. The transitions excited were 3_0^2 at 366.0 nm, 3_0^1 at 371.3 nm and 0_0^0 at 377.0 nm. Vibrational relaxation and electronic quenching of the upper state have been studied and the results are summarized in Table I (estimated errors are $\pm 10\%$ for $v_3' = 2$ and 0 and $\pm 20\%$ for $v_3' = 1$).

Table 1

RATE COEFFICIENTS FOR REMOVING $\text{CH}_3\text{S}(\tilde{\text{A}}^2\text{A}_1)$ in $\nu_3' = 2, 1$ and 0

Gas	Rate Coefficients ($\text{cm}^3\text{molec}^{-1} \text{ s}^{-1}$)		
	$\nu_3' = 2$	$\nu_3' = 1$	$\nu_3' = 0$
He	7.6×10^{-12}	2.0×10^{-12}	$<1 \times 10^{-13}$
Ar	4.9×10^{-12}	1.7×10^{-12}	$<1 \times 10^{-13}$
H_2	8.4×10^{-11}	5.9×10^{-11}	5.3×10^{-11}
N_2	2.3×10^{-11}	1.3×10^{-11}	6.9×10^{-12}
O_2	2.1×10^{-11}	1.4×10^{-11}	5.7×10^{-12}
CO_2	4.7×10^{-11}	2.4×10^{-11}	$<1 \times 10^{-13}$
CH_4	8.2×10^{-11}	4.7×10^{-11}	2.1×10^{-11}
SF_6	2.3×10^{-11}	1.0×10^{-11}	$<1 \times 10^{-13}$

For He, Ar, CO_2 and SF_6 , removal of $\nu_3' = 2$ with these gases results in $\nu_3' = 0$ emission confirming that only vibrational relaxation can occur with these gases. For H_2 , N_2 , O_2 and CH_4 vibrational relaxation and electronic quenching are both occurring.

By varying the delay between the excimer and dye laser pulses, it was also possible to measure a rate coefficient for vibrational relaxation into the ground state ($\nu_3' = 0$) of CH_3S . These results are summarized in Table 2 (estimated errors are $\pm 10\%$).

Table 2

VIBRATIONAL RELAXATION INTO GROUND STATE ($\nu_3'' = 0$) OF CH_3S

Gas	Rate Coefficient ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)
He	2.3×10^{-12}
Ar	2.9×10^{-12}
N_2	5.3×10^{-12}
O_2	9.7×10^{-12}
H_2	2.2×10^{-11}
CO_2	1.4×10^{-11}
CH_4	1.8×10^{-11}
SF_6	3.0×10^{-11}

Experiments were then performed to measure the rate coefficient for CH_3S reacting with several gases. Most of the experiments involved photodissociation of CH_3SH at 193 nm in a high pressure of SF_6 . This avoided problems with O_3 absorption at 248 nm. The 3_0^2 transition was pumped at 366.0 nm and 0_0^0 reemission was monitored at 449 nm (3_6^0 transition). The time delay between the excimer and dye lasers was varied to determine the decay of the CH_3S radical. No reaction with either O_2 or O_3 could be found ($k_{\text{O}_3} < 8 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) and the fast reaction⁶ with NO_2 was confirmed.

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SUPERSONIC JET SPECTROSCOPY OF COMPLEXES OF CARBAZOLE AND N-ETHYL CARBAZOLE WITH ALKYL CYANIDES.

Anita C. Jones, Alan. G. Taylor and Elizabeth M. Gibson

Davy Faraday Research Laboratory
The Royal Institution
21 Albemarle Street
London W1X 4BS

The fluorescence excitation spectra of 1:1 complexes of carbazole and N-ethylcarbazole with a series of six alkyl cyanides (CH_3CN , $\text{C}_2\text{H}_5\text{CN}$, $n\text{-C}_3\text{H}_7\text{CN}$, $i\text{-C}_3\text{H}_7\text{CN}$, $n\text{-C}_4\text{H}_9\text{CN}$, $t\text{-C}_4\text{H}_9\text{CN}$) have been investigated in a supersonic jet. In all cases complexation leads to a substantial red shift ($\geq 316 \text{ cm}^{-1}$) of excitation energy, indicating a stabilisation of the S_1 state of the complex relative to its ground state.

Carbazole is expected to hydrogen bond with these ligands, through the N-H proton with the nitriles acting as proton acceptors. That this is the case is confirmed by the good correlation between the observed red shifts of the complex origins, relative to that of the bare molecule, with the gas phase proton affinities of the cyanides. N-ethylation of carbazole prevents this hydrogen bonding interaction; in this case the binding energy of the complex is attributed to a dipole-dipole interaction: both carbazole and N-ethylcarbazole have a ground state dipole moment of $\sim 2\text{D}$ directed along the short (C_2) axis of the molecule, the cyanides all have dipole moments of $\sim 3.5\text{D}$. The $S_1 \leftarrow S_0$ transition in carbazole and N-ethylcarbazole is short axis polarised and is accompanied by

considerable charge transfer from the nitrogen to the ring system, leading to an increase in dipole moment to $\sim 3D$ in the excited state. Thus the hydrogen bonding in the carbazole-RCN complexes is strengthened in the excited state, as a result of the increased acidity of the N-H proton, and the dipolar interaction in the N-ethylcarbazole-RCN is also enhanced, leading to the observed red shifts in both cases.

With the exception of carbazole- CH_3CN , the excitation spectra of all the complexes contain low frequency, intermolecular modes. In most cases a prominent progression in a mode of $\sim 15\text{ cm}^{-1}$ (probably due to bending or torsion of the intermolecular bond) dominates the spectrum, indicating a change in geometry of the complex along this co-ordinate between ground and excited states. The absence of intermolecular vibronic transitions in the spectrum of carbazole- CH_3CN can be accounted for by symmetry arguments.

Pico-second and Nano-second Laser Flash Photolysis
Study on Some Halogenated Benzene Derivatives

Teijiro Ichimura

Department of Chemistry, Tokyo Institute of Technology,
Ohokayama, Meguro-ku, Tokyo, 152, Japan

(1) Direct Measurement of Benzyl Chloride Photodecomposition Rate

Excited at 266 nm in the Vapour Phase

Picosecond laser photolysis of benzyl chloride vapour has been examined by monitoring the absorption time profile of benzyl radicals formed in the 266 nm photodecomposition. The time-resolved absorption of benzyl radicals obtained in the photolysis of benzyl chloride(0.5 Torr) is illustrated in Fig. 1. The rise time of benzyl radical absorption, 6 ns, was attributed to the decomposition rate of benzyl chloride molecules under collision free conditions.

(2) Intramolecular Hydrogen Transfer in the o-Tolyl Radical

Studied by Time Resolved Absorption Measurements

The intramolecular hydrogen transfer rate of o-tolyl radicals has been examined by monitoring the absorption time profile of benzyl radicals formed in the picosecond 266 nm laser photolysis of o-chlorotoluene. The rise time of the benzyl radical absorption, 6.5 ns, was attributed mostly to the rearrangement rate of o-tolyl radicals to benzyl radicals.

(3) Formation and Collisional Deactivation of Vibrationally Highly

Excited Hexafluorobenzene Molecules

The formation and collisional deactivation of the excited HFB molecules was studied directly by monitoring ultraviolet absorption spectra of vibrationally highly excited hexafluorobenzene(HFB) molecules

produced by excitation with an ArF(193 nm) laser. The absorption spectrum observed at the time $t=0$ is attributed to S_0^* (hot hexafluorobenzene with an internal energy of 639 kJ/mol). This transient absorption spectrum can be simulated as a part of the spectrum of the $S_3(^1E_{1u}) + S_0$ transition at 3050 K. The decay time profile of the internal energy was calculated from the observed absorption decay profile of the hot molecule using the relation between the absorbance by hot molecules and the internal energy. Thus the average energy $\langle \Delta E \rangle$ transferred per collision was estimated by two different models; energy-independent and energy-dependent function for the decay of the internal energy. The obtained values of $\langle \Delta E \rangle$ (Table 1) indicate that the energy-dependent model may give reasonable values for $\langle \Delta E \rangle$, but as far as the value of $\langle \Delta E \rangle$ is concerned, the energy-independent model is more unambiguous than the energy dependent model.

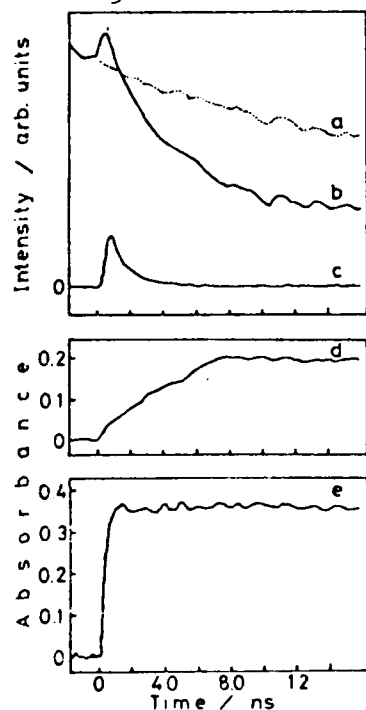


TABLE 1 Energy transferred per collision at $t=0$ ($\Delta E(E_0)$) obtained by two models for various foreign gases.

Quencher	$\Delta E(E_0)$ (kJ·mol ⁻¹)		
	E Indep. ^a	E Dep. ^b	(N_T) ^c
HFB	11.3	14.8	(43.1)
Ar	2.9	4.3	(148.0)
N ₂	2.8	3.5	(183.3)
O ₂	2.9	4.1	(155.2)

^a Fitted value using $E(t) = E_0 - Z \cdot \Delta E \cdot t$ where E_0 is initial energy, Z is collision frequency and ΔE is not varying with time.

^{b, c} First fitting N_T using $E(t) = E_0 \exp(-Z \cdot t / N_T)$ and then $\Delta E(E_0)$ is derived by relation $E_0 = N_T \cdot \Delta E_0$.

FIG. 1 Time-resolved absorption of benzyl radicals in the 266 nm laser photolysis of benzyl chloride; time evolution of (a) the probe light intensity at 305 nm (I_0), (b) the probe light intensity at 305 nm (I_k) when benzyl chloride vapor (0.5 Torr) was irradiated by the laser pulse, (c) the fluorescence intensity (I_f) excited by the laser pulse and observed at 305 nm, (d) the benzyl radical absorption $\log_{10}[I_0/(I_k - I_f)]$, and (e) rise of the benzyl radical absorption in 3-methyl pentane observed at 316 nm.

Flash Photolysis Studies of Atoms and Free
Radical Reactions with Phosphine

L. J. Stief, W. A. Payne, and D. F. Nava

Astrochemistry Branch, Laboratory for Extraterrestrial Physics,
NASA/Goddard Space Flight Center Greenbelt, Maryland 20771, USA

The reactions of atomic and free radical species with phosphine have been of considerable interest for a variety of reasons. The oxidation of phosphine was among the first reactions shown to involve a branched chain mechanism. The reactions of phosphine and phosphorous with atomic oxygen produce intense chemiluminescence. The phosphorous/oxygen system has been investigated as a potential chemical laser for the 200-400 nm region. Our interest in the reactions of phosphine is not related to any of these, but rather for the role of phosphine reactions in the photochemistry or aeronomy of phosphine in the giant planets Jupiter and Saturn.^{1,2} We have previously studied the reactions $H + PH_3$ ³ and $NH_2 + PH_3$ ⁴ and are now examining the kinetics of the reaction $O(^3P) + PH_3$. These reactions play prominent roles in models attempting to account for the origin and nature of the Great Red Spot on Jupiter and the stability of NH_3 in the atmospheres of Jupiter and Saturn.

The reactions $\text{H} + \text{PH}_3$ and $\text{O} + \text{PH}_3$ are studied by flash photolysis of PH_3 or N_2O (to produce H and $\text{O}(^3\text{P})$ respectively) combined with time resolved detection of H and $\text{O}(^3\text{P})$ via resonance fluorescence. For the reaction $\text{NH}_2 + \text{PH}_3$, the source of NH_2 was flash photolysis of ammonia and detection of NH_2 was via laser induced fluorescence. In these experiments, $[\text{PH}_3]$ was $\sim 10^{13}$ to 10^{15} cm^{-3} while $[\text{X}] \sim 10^{11} \text{ cm}^{-3}$ where $\text{X} = \text{H}, \text{NH}_2$ or O . Thus pseudo-first-order conditions were achieved with $[\text{PH}_3] \gg [\text{X}]$ and the decay of the atomic or free radical species X is given by

$$\ln [\text{X}] = -k_{\text{observed}} t + \ln [\text{X}]_0 \quad (1)$$

The observed pseudo-first-order rate constant is represented by

$$k_{\text{observed}} = k_{\text{bi}} [\text{PH}_3] + k_{\text{d}} \quad (2)$$

where k_{bi} is the bimolecular rate constant for the reaction $\text{X} + \text{PH}_3$ and k_{d} is the first-order rate constant for diffusional loss of X from the reaction volume viewed by the photomultiplier. Accumulated fluorescent counts are proportional to $[\text{X}]$ and plots of $\ln (\text{counts-background})$ versus time were linear as required by equation (1). Value of k_{observed} , determined from the slope of such plots, were graphed as a function of $[\text{PH}_3]$. In accordance with equation (2), this yields a straight line with slope equal to k_{bi} . Variations in $[\text{PH}_3]$, total pressure (Ar) and flash intensity (i.e., initial atom or radical concentration) were performed to test for possible kinetic problems due to secondary reactions. No dependence of k_{bi} on any of these parameters was observed. Experiments were performed at 209-459 K for $\text{H} + \text{PH}_3$, 218-456 K for $\text{NH}_2 + \text{PH}_3$ and 298 K for $\text{O} + \text{PH}_3$. The results are summarized in the table along with results for $\text{OH} + \text{PH}_3$.⁵

Table. Comparison of k (298 K) and Arrhenius Parameters for reaction of NH_2 , H, OH and O with PH_3

Reactant	k (298 K)/ $\text{cm}^3 \text{ s}^{-1}$	$A/\text{cm}^3 \text{ s}^{-1}$	$E/\text{kcal mole}^{-1}$
NH_2	6.1×10^{-14}	1.5×10^{-12}	1.84
H	3.4×10^{-12}	4.5×10^{-11}	1.47
OH	1.6×10^{-11}	2.7×10^{-11}	0.31
O	3.2×10^{-11}	-----	-----

Comparison of our rate constant results for H, NH_2 and O will be made with the few other published values; there is one for H + PH_3 ⁶, two for O + PH_3 (both at 298 K only)^{6,7} and none for NH_2 + PH_3 . The reaction mechanisms will be discussed with emphasis on the evidence for the O + PH_3 reaction occurring via a different mechanism from the other reactions. Implications of these results for the photochemistry of PH_3 and NH_3 in the atmosphere of Jupiter will be discussed.

This work was supported by the NASA Planetary Atmospheres Program.

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THE REACTIONS OF REACTIVE INTERMEDIATES (RADICALS AND CATIONS) WITH ALKANES, ALKENES AND ALKYNES

J. M. TEDDER,

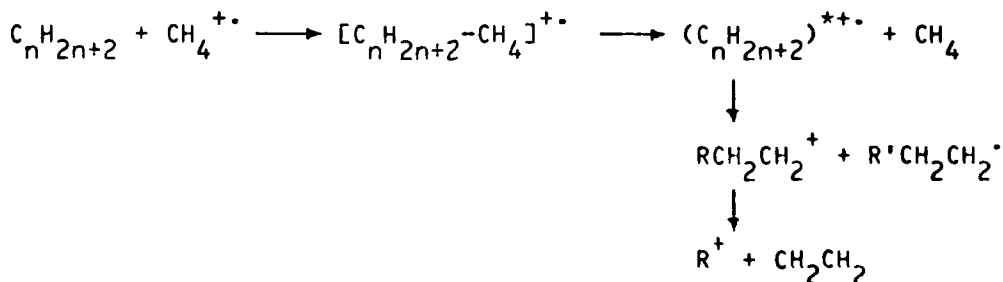
Department of Chemistry, University of St. Andrews,

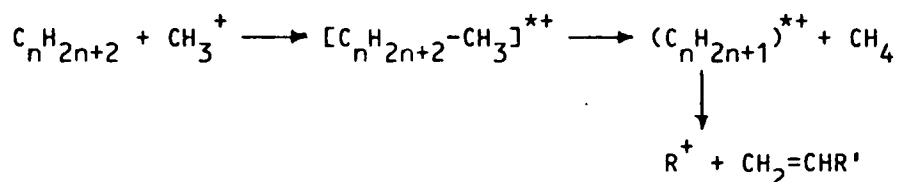
ST. ANDREWS, Fife KY16 9ST

The present study of reactive intermediates in the gas phase was commenced at Sheffield University in 1956. The first paper reported quantitative data for the fluorination, chlorination and bromination of alkanes in the gas phase. The paper concluded with an acknowledgment of the advice given to the authors by Professor Porter. His encouragement was crucial in persuading the authors that it was possible to obtain quantitative kinetic data in the form of Arrhenius Parameters rather than qualitative data at one temperature. This work was the starting point of a series of papers on Free Radical Substitution (mostly in *J. Chem. Soc.*). Developing out of this work was a second series of papers on the study of Free Radical Addition (mostly in the *Trans. Faraday Soc.*). The present work, which developed directly out of these earlier studies, is concerned with the reactions of carbocations with alkanes, alkenes and alkynes in the gas phase.

(a) The Reactions of Alkane and Alkyl Cations with Alkanes

Alkane cations react with alkanes by simple charge exchange while reactions with alkyl cations involve hydride transfer. The

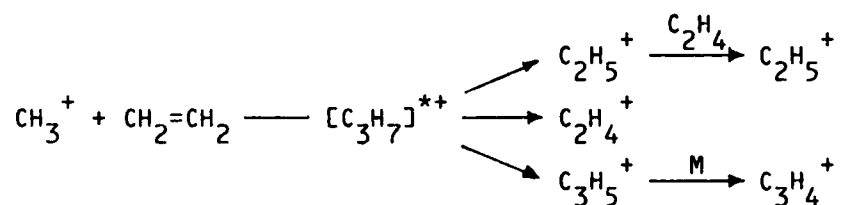




resulting cations fragment by similar sequences.

(b) The Reactions of Alkyl Cations with Alkenes

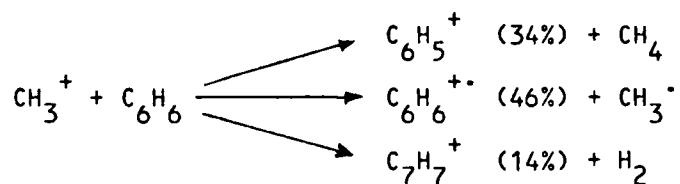
The initial process in the reaction of alkyl cations with alkenes is the formation of a thermally excited adduct which then fragments. Thus methyl cations react with ethene to yield five products:



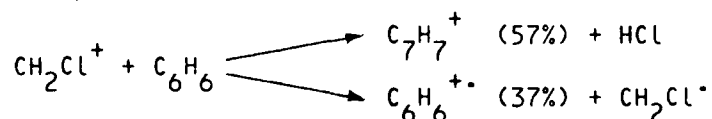
The corresponding reactions involving more elaborate initial cations and olefins become more complex.

(c) The Reactions of Alkyl Cations with Arenes

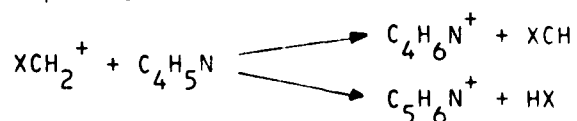
Benzene reacts with CH_3^+ to yield three principal ionic products:



The chloromethyl cation reacts with benzene to give $C_7H_7^+$ as the principal ionic product.

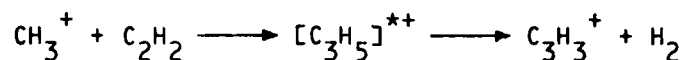


Ring enlargement is also observed in the reactions of pyrrole (also furan and thiophen).

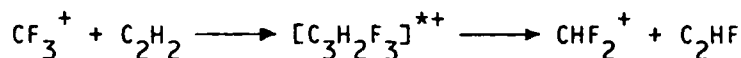


(d) The Reactions of Alkyl Cations with Ethyne

Methyl cations react with ethyne to form cyclopropenium ions in very high yield.

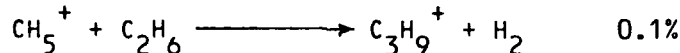
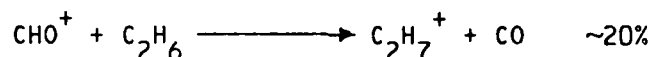


Trifluoromethyl cations are less reactive and on reaction with ethyne yield CHF_2^+ as the main product.



(e) The Formation of Carbocations $(\text{C}_n\text{H}_{2n+3})^+$

CH_5^+ and similar ions are formed in simple hydrogen transfer reactions.



All this work has been done using multiple stage mass spectrometers (specifically a tandem magnetic sector; a triple quadrupole and just recently a quinquequadrupole).

We are grateful of this opportunity to acknowledge our debt to Sir George Porter. Sheffield was an exciting place to work in the late 50s and early 60s and all of us who were there owe a great deal to him. His willingness when asked to take an interest in junior colleagues' work helped promote the enthusiasm for research characteristic of Sheffield at that time.

SESSION C: FREE RADICALS IN SOLUTION, MAGNETIC EFFECTS

Chairman: N.M. ATHERTON

- 16.00-16.30 **Keynote Lecture** A. WELLER: Magnetic field effects on photochemical reactions
- 16.30-17.00 **Keynote Lecture** S. NAGAKURA: External magnetic field effects upon photochemical reactions through radical pairs
- 17.00-17.15 D.I. SCHUSTER: Kinetic evidence for a reactive ground state intermediate in photocycloaddition and photorearrangement reactions of cyclohexenones
- 17.15-17.30 P. SUPPAN: Mechanism of the primary process in the photoreduction of aromatic carbonyl compounds and quinones
- 17.30-17.45 J.R. BOLTON: The mechanism of the photochemistry of p-benzoquinone in aqueous solutions
- 17.45-18.00 L.I. GROSSWEINER: Flash photolysis studies on enzyme photochemistry and photoinactivation: a brief history
- 18.00-18.15 T.G. TRUSCOTT: Porphyrins related to cancer photochemotherapy
- 18.15-18.30 E.J. LAND: Flash photolysis and pulse radiolysis studies of some semiquinones in relation to cancer induction and therapy
- 18.30-19.30 **RECEPTION** in the Royal Institution
- 19.30-21.30 **POSTER SESSION I** Posters for Sessions A, B and C to be manned

POSTERS associated with Session C:

N.M. ATHERTON, R.D.S. BLACKFORD and W.A. CROSSLAND: ENDOR spectroscopy of trapped radicals in single crystals

B. BROCKLEHURST, Singlet and triplet yields in radiolysis: magnetic field effect on fluorescence

R.W. YIP, R. GIASSON and D. GRAVEL: Photochemistry of the o-nitrobenzylic system - the reactive intermediates

Z.G. SZABO: Stabilisation of free radicals

KINETIC EVIDENCE FOR A REACTIVE GROUND STATE INTERMEDIATE IN PHOTOCYCLOADDITION AND PHOTOREARRANGEMENT REACTIONS OF CYCLOHEXENONES

David I. Schuster,* Philip C. Tucker,* Christopher A. Rhodes,* J.C. Scaiano# and Douglas Weir#

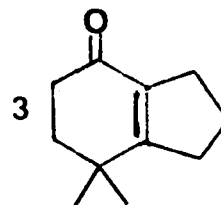
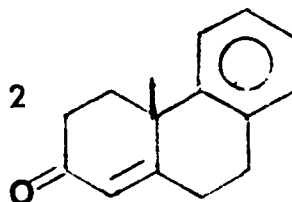
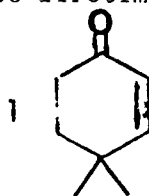
*Department of Chemistry, New York University

*Washington Square, New York, NY, USA 10003

#Chemistry Division, National Research Council

#Ottawa, Ontario Canada K1A 0R6

Laser flash excitation of cyclohexenones results in formation of transient intermediates, λ_{max} 280 - 320 nm, proposed^(1,2) to be twisted $^3\pi,\pi^*$ excited states. Transient lifetimes correlate with the anticipated ability of the enone to twist around the C=C bond, ranging from ca. 25 ns for cyclohexenone and methylated analogues such as 1 to 135 ns for phenanthrone 2, 330 ns for testosterone and ca. 1.5 μs for rigid bicyclic enones such as 3. These lifetimes vary only slightly as a function of solvent



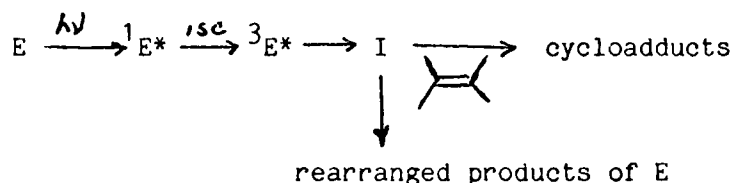
polarity. The triplet decay curves fail to return to the base line, suggesting that a long-lived species is formed under these conditions. This residual absorption is higher in nonpolar than in polar solvents, and is sharply reduced by small amounts of

trifluoroacetic acid.

We have previously reported⁽³⁾ that alkenes quench the photorearrangement of enone 1 concomitant with formation of [2 + 2] cycloadducts, indicating a common intermediate on both reaction pathways. The generally accepted mechanism for photocycloaddition of enones to alkenes (so-called photoannulation)⁽⁴⁾ involves interaction of the alkene with an enone triplet to give an exciplex, which then proceeds to a 1,4-diradical and thence to products. The proposed mechanism for photorearrangement of enones such as 1⁽⁵⁾ as well as the formation of trans-fused cycloadducts⁽⁶⁾ suggested that a twisted enone triplet $^3E^*$ was the logical intermediate intercepted by alkenes. However, this mechanism is incompatible with recent laser flash studies which show that tetramethylethylene (TME) at concentrations up to 4 M in acetonitrile or methanol has no effect on the rate of decay of transient triplet absorption of enones 1 and 2 at 280 nm, nor on the rates of transfer of triplet excitation from these enones to 1-methylnaphthalene (MN) as measured by growth of ^3MN absorption at 420 nm. We reported previously⁽²⁾ that 1,1-dimethoxyethylene (DME) had no effect on the decay at 280 nm of transients derived from 1 and 2, although DME seemed to effect the rate of growth of triplet naphthalene (NA) absorption at 413 nm; we believe the latter result may be due to improper analysis of the ^3NA growth kinetics as a function of alkene concentrations. NA quenches rearrangement of 1 and cycloaddition of 1 to TME (giving both

cis- and trans-fused cycloadducts) to exactly the same extent, with values of $k_q \tau$ in excellent agreement with those directly measured by flash techniques. Thus, NA must be intercepting an enone triplet precursor to the species intercepted by alkenes.

We therefore propose that photoannulation of cyclohexenones such as 1 and 3 involves interaction of alkenes not with $^3E^*$ but rather with a reactive ground state species I, according to the following scheme, and that I is also on the pathway to photo-rearrangement products (lumiketones) of such enones.⁽⁵⁾ The



identity of I and its relevance to the residual absorption seen in the triplet decay curves are as yet uncertain. An intriguing candidate for I is a ground state trans-cyclohexenone, perhaps best described as a twisted diradical, which would be even more strained than trans-1-phenylcyclohexene.⁽⁷⁾ This new mechanism resolves some remarkable coincidences associated with our earlier report⁽²⁾ and is in accord with relative reactivities of alkenes in photocycloaddition to 1, which do not fit a mechanism involving formation of triplet exciplexes but are consistent with trapping of a transoid ground state enone. The original Corey-de Mayo mechanism⁽⁴⁾ probably obtains in the case of cyclic enones which are incapable of photoisomerization to a transoid species.

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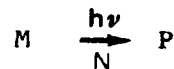
Mechanism of the primary process
in the photoreduction of aromatic
carbonyl compounds and quinones.

Paul SUPPAN

Institute of Physical Chemistry, University of Fribourg,
CH-1700 FRIBOURG, Switzerland.

The photoreduction reaction common to a wide range of aromatic ketones, aldehydes and quinones has become one of the most studied test systems for general theories of bimolecular photochemical reactivity. In particular, the reaction mechanism at the molecular level is not yet fully understood; it has been considered as a thermally-activated chemical reaction of the excited molecule (seen as a new chemical species in thermal equilibrium with its surroundings)¹, or as the result of a radiationless transition linked to the deactivation of the electronically excited molecule².

A quantitative description of the photoreactivity of a molecule M in a specified bimolecular reaction



requires a knowledge of the reaction rate constant k_r for each reactive state M^* ; in general only the reaction quantum yield

$$\phi_r = k_r [N] / (k_r [N] + k_d + k_q [Q])$$

can be measured experimentally and k_r can be obtained only if the unimolecular deactivation rate constant k_d and the bimolecular deactivation (quenching) rate constant k_q are known. In general k_d and $k_q [Q]$ are the sums of several independent terms, but this is of no importance for the relationship between ϕ_r and k_r .

The values of k_r , k_d and k_q have been determined for a wide range of substituted and unsubstituted aromatic aldehydes, ketones and quinones in various conditions of temperature, solvent and hydrogen donor partners. All these molecules follow Kasha's rule both in their photophysical (e.g. luminescence) and photochemical behaviour, so that the important excited states are simply

the lowest excited singlet S_1 and triplet T_1 . The lifetime of S_1 is limited by the unimolecular deactivation via fluorescence and intersystem crossing (sum of k_d) but the lifetime of T_1 seems to be limited largely by quenching processes ($k_q [Q]$) of which the most important may be concentration quenching by the ground state species. The temperature dependence of these unimolecular and bimolecular deactivations is quite small in the range 10 to 100°C (less than a factor 2) whereas the rate constants k_r for chemical reaction sometimes show large variations, up to a factor 10 over this temperature range. In general these variations follow an Arrhenius-type relationship $\ln k_r \propto 1/T$, there being no detectable curvature of the Arrhenius plot within the accessible temperature range.

The deuterium isotope effect is very small on k_r both for intra- and inter-molecular hydrogen abstractions



in every case under the value $k_r(H)/k_r(D) \sim 6$ which is the maximum expected from classical kinetics. This must be contrasted with the large isotope effect on the thermal hydrogen atom transfer in the enol $\rightleftharpoons$ keto tautomerization of molecules such as 2-methylbenzophenone³; in the low temperature region ($T < -20^\circ\text{C}$) the ratio $k_r(H)/k_r(D)$ increases beyond this classical limit of 6 and at the same time the Arrhenius plot flattens out as the values of k_r decrease, effects attributed to the increasing importance of nuclear tunnelling as the dominant reaction pathway. The comparison between the photochemical and the thermal hydrogen (or deuterium) atom transfer suggests that nuclear tunnelling is relatively unimportant in the photochemical process in the temperature region above $\sim 300\text{K}$. The temperature dependence of the photochemical reaction rate constant k_r is therefore interpreted as a thermal activation in the sense of the Arrhenius-Eyring transition state model.

The primary photochemical product which is a geminate radical pair or a biradical can be considered to be an excited state of the final product, so that the primary photochemical process takes place on the excited state potential energy surface and is not connected with electronic deactivation. There is no reason to expect a simple correlation between the photochemical reactivity (as defined by k_r) and the energy balance of the primary photochemical process, and indeed there is no such correlation:

excited states of very close energies show widely different reaction rate constants, and this is an illustration of the general rule that kinetics and thermodynamics are independent.

In conclusion, the temperature dependence of the reaction rate constants and the very small deuterium isotope effect suggest that photochemical hydrogen abstraction reactions cannot be considered as radiationless transitions, but rather as thermally activated chemical reactions of the excited molecules seen as new chemical species.

The nature of the activation barrier in terms of $n-\pi^*$, $\pi-\pi^*$, CT states etc. is still far from being fully understood. The role of the electrostatic charge distribution, the role of the localization of excitation in the relevant anti-bonding orbitals and other factors such as orbital symmetry conservation must all be considered. The separation of the activation energy and the activation entropy throws some light on the relative importance of these various factors.

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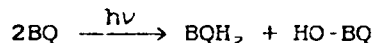
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THE MECHANISM OF THE PHOTOCHEMISTRY OF
p-BENZOQUINONE IN AQUEOUS SOLUTIONS

A.I. Ononye, A.R. McIntosh and J.R. Bolton*

Photochemistry Unit
Department of Chemistry
The University of Western Ontario
London, Ontario, Canada N6A 5B7

p-Benzoquinone (BQ) in aqueous solution at pH ~7 undergoes a fairly clean photochemical reaction with the stoichiometry

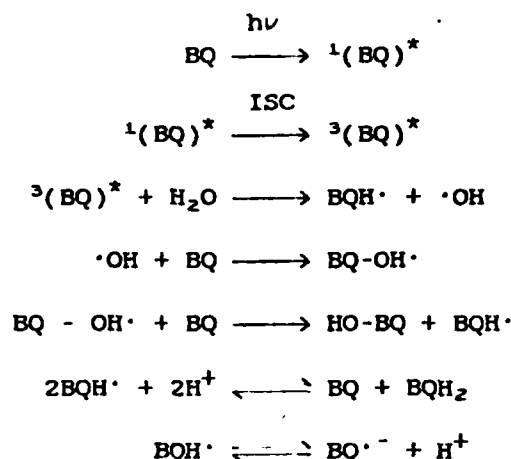


where BQH₂ is hydroquinone and HO-BQ is 2-hydroxy-p-benzoquinone. The mechanism of this reaction has been studied by several groups (1-7) since the pioneering work by Bridge and Porter (1), who first suggested that the primary step involves hydrogen abstraction from H₂O by the triplet excited state of BQ. However, an alternative mechanism has been proposed (5), namely a photosolvation of ³BQ to form a hydrated intermediate which then reacts with BQ in secondary reactions. The main problem in the previous studies has been the lack of convincing evidence to prove or disprove the presence of free ·OH in this system. Doubts have also been cast as to whether or not ³BQ has enough energy to oxidize water (7).

Our approach to the study of the mechanism of the BQ photochemistry has been to utilize the technique of spin trapping (8), first on a system known to yield free ·OH radicals (the photolysis of H₂O₂) and then on the BQ system. The spin trap used was 5,5'-dimethyl-1-pyrroline-1-oxide (DMPO) which is known to be a very effective trap for the ·OH radical.

We have also studied the formation and decay of the p-benzosemiquinone anion BQ^{·-} which is formed from the neutral semiquinone BQH[·] using both optical- and EPR-detected flash photolysis.

Our results point clearly to the presence of free ·OH as a primary photoproduct. The following mechanism accounts for all of our observations.



BQ-OH $\cdot$ is an OH adduct to BQ of unknown structure. In the presence of DMPO both $\cdot\text{OH}$ and BQ-OH $\cdot$ react to form the same product



with the latter reaction being much slower than the former.

From our optical flash photolysis studies we have determined several of the rate constants in the mechanism. In addition, we have determined the quantum yield at pH 7 to be 0.47 ± 0.04 which increases with increasing pH.

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Flash Photolysis Studies on Enzyme Photochemistry and
and Photoinactivation: A Brief History

Leonard I. Grossweiner

Biophysics Laboratory, Physics Department, Illinois Institute of
Technology, Chicago, Illinois 60616, U.S.A.

Proteins are the most abundant molecules in cells, except for water, and the most diverse of all biomolecules in size, form, and function. The exposure of proteins to ultraviolet (UV) radiation leads to changes in almost all physical and chemical properties. In "colorless" proteins, UV radiation from 240 to 320 nm is absorbed by the aromatic amino acids, cystine, and the peptide bonds. The role of the chromophores as potential initial reaction sites has motivated much research on the photochemistry of the aqueous amino acids. However, the photochemistry of a protein-bound amino acid may differ from the free state because of intramolecular energy transfer and electron transfer processes, conformation changes induced by photolysis of disulfide bonds, and stabilization of early damage by inhibition of diffusional reactions. In a quite early flash photolytic study of aqueous ovalbumin (Grossweiner, 1956), transient bands were observed near 400 nm and 500 nm, identified with the initial photolysis products of tyrosine (Tyr) and tryptophan (Trp), respectively, by comparisons with the aqueous amino acids and small glycol peptides. This work was subsequently repeated with red-sensitive spectroscopic plates (Grossweiner et al., 1963; Joschek and Grossweiner 1966). In addition to the long-lived, aromatic radical bands from Trp, Tyr, and phenylalanine, there was a superimposed short-lived, red absorption band, quenched by air. This band was attributed to the hydrated electron (e_{aq}^-), first identified by pulse radiolysis of water (Hart and Boag, 1962). It was concluded that photoionization is an important primary photolysis reaction of aqueous aromatic amino acids, a mechanism implied by flash photolytic studies on the phenolate anion (Grossweiner and Mulac, 1969). A flash photolytic study on an intact enzyme, hen lysozyme showed the e_{aq}^- absorption, the radical band identified

with photoionized Trp, and a new absorption band near 420 nm (Grossweiner and Usui, 1971), identified with the disulfide bond electron adduct (Adams et al., 1969). The disulfide electron adduct was present in oxygenated lysozyme solutions prior to approximately 1 μ s, suggesting that electrons ejected from excited aromatic residues were transferred to disulfide bonds via a fast, intramolecular process. The photoionization of Trp residues was confirmed for many proteins by Subramanyan and Tollin (1972). Detailed flash photolytic studies were made on several other well known enzymes, with the objective of relating the initial photochemical steps to permanent residue destruction and loss of enzymic activity: ribonuclease A (Volkert and Grossweiner, 1973), trypsin (Kaluskar and Grossweiner, 1974), and papain (Baugher and Grossweiner, 1975). The earlier experiments were repeated under similar conditions and re-analyzed, which led to specific photoinactivation mechanisms, based on the enzyme structure, initial product yields, permanent residue destruction, and information from biochemical and radiation chemical studies. It was deduced that photolysis of an essential chromophoric residue or an aromatic residue adjacent to an essential residue contributes to loss of enzymic activity (Grossweiner et al., 1976). The fast intramolecular electron transfer to disulfide bridges was confirmed for lysozyme, trypsin, and papain. Comparisons of the aromatic radical yields in the enzyme with equivalent amino acid mixtures led to a correlation between the number of photoionized aromatic residues and residue exposure. Subsequent work of Land and coworkers (Prutz et al., 1980) identified a slower electron transfer from intact Tyr residues to oxidized Trp, equivalent to photosensitization of Tyr damage by Trp.

By 1976, the initial Trp photolysis product was identified with a neutral radical (Trp $\cdot$), formed by photoionization at the indolic nitrogen followed by deprotonation (Santus and Grossweiner, 1972), the neutral phenoxyl-type radical from Tyr (Tyr $\cdot$) was known (Volkert and Grossweiner, 1973), and the triplet-triplet absorptions of Trp (Santus and Grossweiner, 1972) and Tyr (Bent and Hayon, 1975a) had been identified. The development of 265 nm laser flash photolysis led to improved time resolution, with the capability of measuring the electron quantum yields (ϕ_e) (Bryant et al., 1975). The assumption that photoionization is the only significant initial act led to values of the Trp $\cdot$ and Tyr $\cdot$ extinction coefficients, which are in good agreement with independent measurements based on pulse radiolysis (Grossweiner, 1976). The decay of e_{aq}^- generated by flash photolysis did not follow the expected pseudo-first order kinetics, as found for e_{aq}^- generated by pulse radiolysis of water. A new decay model was proposed, based on the formation of long-lived electron-radical pairs (Grossweiner and Baugher, 1977; Lee et al., 1979). Measurements of ϕ_e for the previously studied enzymes, plus

carboxypeptidase A (Lee and Grossweiner, 1978) and subtilisins (Blum and Grossweiner, 1982), showed that the number of aromatic radicals was approximately equal to the number of disulfide electron adducts plus hydrated electrons at 50 ns delay (Grossweiner et al., 1982).

The photoionization mechanism in aqueous aromatics has been the subject of continuing controversy. Although flash photolytic measurements indicate that e_{aq}^- production from Trp takes place from a pre-fluorescent state (Bent and Hayon, 1975b; Mialocq et al., 1982), biphotonic ionization at high laser intensities cannot be ruled out. Work in this laboratory has shown that high bromide ion, which quenches Tyr and Trp fluorescence, had no effect on ϕ_e with Trp (Baugher and Grossweiner, 1977; Grossweiner et al., 1981), Tyr (Baugher and Grossweiner, 1978), and subtilisin BPN' (Blum and Grossweiner, 1982), arguing against electron release from the fluorescent state. However, laser flash photolysis measurements on Trp showed that the photoionization yield is independent of wavelength from 280 to 300 nm, which was explained by monophotonic ionization from the fluorescent state (Bazin et al., 1983). An unambiguous biphotonic process in Trp was discovered by Finnström et al., (1980), in which the e_{aq}^- yield was increased by double-pulse excitation at 265 nm and 530 nm. This result was extended to many indolyl and tyrosyl derivatives, and some enzymes (Grossweiner et al., 1981).

These studies on aromatic amino acids and enzymes should be further studied with picosecond techniques. Although photoionization of aromatic compounds in aqueous solution has been established as an important primary act, the states responsible for electron transfer to the medium have not been identified for either monophotonic or biphotonic pathways. The values of ϕ_e measured by flash photolysis are significantly higher than the values deduced by photochemical scavenging. The atypical decay kinetics of photochemical e_{aq}^- should be further investigated; they may be involved in this apparent discrepancy. The slow electron transfer from intact Tyr to Trp' residues, demonstrated with pulse radiolysis, should be confirmed for UV excitation.

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PORPHYRINS RELATED TO CANCER PHOTOCHEMOTHERAPY

T. GEORGE TRUSCOTT

PAISLEY COLLEGE, DEPARTMENT OF CHEMISTRY, PAISLEY,
RENFREWSHIRE, PA1 2BE, SCOTLAND, U.K.

It is well-known that porphyrins cause photosensitisation in man and that the natural photosensitivity associated with various porphyric diseases is due to the excess of a porphyrin, such as protoporphyrin, in the skin. A closely related porphyrin, haematoporphyrin (Hp), or some closely related species present as an 'impurity' in the Hp has the ability to accumulate and be retained somewhat selectively by malignant tissue and the red fluorescence of the Hp, or Hp related material, has been used as a basis of tumour detection since about 1960. To improve this use and to overcome solubility problems a material called 'haematoporphyrin derivative' (HpD) was introduced, produced by treating Hp with H_2SO_4 /acetic acid and then by treating the resulting products (mainly a mixture of Hp acetates) with NaOH. It is now known that such a treatment leads to a most complex mixture and that the active component/s probably involve more than one Hp moiety linked via an ester bond. Perhaps surprisingly it is only relatively recently that the two factors of photosensitivity and selectivity for tumours have been combined in the use of Hp, and particularly HpD, as a photochemotherapeutic treatment for some cancers. Since the active component may well break down once bound to cell components to yield Hp or its dehydration products hydroxyethylvinyldeuteroporphyrin and protoporphyrin (PP) this paper will concern aspects of the photochemistry of these porphyrins as well as Hp, HpD and 'purified' forms of HpD obtained via gel chromatography. Laser flash photolysis results are presented for such systems in a range of environments ranging from homogeneous solvents to micro-heterogeneous situations such as Hp bound to human serum albumin (HSA) and when encapsulated in micelles and liposomes. The typical absorption spectra of a porphyrin such as Hp shows a strong band ~ 400 nm (Soret band) and markedly weaker bands in the

visible region. It is important to note that the wavelength used in therapy is ~ 620 nm because shorter wavelengths are ineffective due to low tissue penetration and that the Hp ground state extinction coefficient is quite low ($\sim 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at these red wavelengths. Consequently 'the hunt is on' for drugs with better red-light absorbing characteristics and particular attention is being focused on the structurally similar chlorins (dihydroporphyrins), bacteriochlorins (tetrahydroporphyrins) and the phthalocyanins - a few results on some of these systems are included. Finally in this introduction it is important to note that the porphyrins Hp and particularly HVD and PP as well as HpD components are extensively aggregated in aqueous solution but that disaggregation tends to occur in non-polar solvents and detergents.

The Triplet State: While it is generally accepted that the *in vivo* mode of action of Hp (or related material) involves singlet oxygen generation via the lowest triplet state a role for the excited singlet state cannot be entirely ruled out. Nevertheless this paper is restricted to the study of the triplet state parameters of porphyrins and to the measurement of the quantum yield of 'singlet oxygen' formation (ϕ_Δ) using a photo-diode system to monitor the 1270 nm phosphorescence of singlet oxygen $\{\text{O}_2(^1\Sigma_g) + \text{O}_2(^1\Delta_g)\}$ after laser excitation (~ 12 ns) with 347 nm (ruby), 530 nm (YAG) or longer wavelength from a YAG pumped dye laser.

In mainly organic solvents Hp has a $\Delta\epsilon_T^{\text{max}}$ (450 nm) in the range $1.3 \pm 0.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ while in mixed solvents such as methanol/water this falls as the water content of the solvent increases. This is related to aggregation and the same effect can be observed by noting the effect of Hp concentration on $\Delta\epsilon_T$ in water with values of 0.27, 0.42 and $0.83 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at concentrations of 83, 17 and $8 \times 10^{-6} \text{ mol dm}^{-3}$ respectively. A comparable result of $\Delta\epsilon_T$ for HVD is $0.33 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at $8 \times 10^{-6} \text{ mol dm}^{-3}$ reflecting the increased hydrophobic nature of HVD compared to Hp and hence its greater tendency to aggregate in water. These $\Delta\epsilon_T$ values are all obtained by the so-called 'complete conversion' of the ground state to the triplet at high laser intensities and are based on an assumed molecular weight of the ground state of 600 - clearly if aggregates have a lower (possibly near 0) triplet yield the $\Delta\epsilon_T$ value is lower than expected and may be a measure of the degree of aggregation. In detergents (CTAB, Triton X-100 and SDS) the $\Delta\epsilon_T$ values of both Hp and HVD imply that these molecules are monomeric. However, in the cell model environment of phosphatidylcholine liposomes complex behaviour is observed with multicomponent transient decays and quite low $\Delta\epsilon_T^{\text{max}}$ values (4280, 2900, 3200, 3000 and 2700 $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for HpDME, MPDME, PPDME, Hp and HVD respectively) whereas the ground state spectra imply that the porphyrins are not aggregated in this environment.

The study of HpD is of limited interest because it is such a complex mixture although some results on the purified form (DHE) will be presented, however this is also a mixture. We have prepared DHE by two routes, firstly the reported acetate route and

secondly a route involving replacing acetic acid with HBr which is more likely to give higher yields of porphyrin di-(or longer) esters. In both cases separation of the product uses gel exclusion chromatography. Laser flash photolysis of such DHE samples yield no detectable triplet absorption. These samples obey the Beer Lambert law over 1000 $\times$ dilution ($\sim 10^{-4}$ - 10^{-7} M) suggesting that 'aggregation' is so strong that it is not disrupted by dilution. This may well indicate substantial covalent (ester) links of the porphyrin rings. Indeed, allowing for the sensitivity of the laser detection equipment and assuming that the triplet yield of the non-aggregated species is similar to that of Hp leads to an implied aggregate size of > 100 Hp units. Laser flash photolysis of DHE in detergents such as Triton X-100 and CTAB does lead to the observation of triplet absorption. If we assume aggregation is substantially reduced in this detergent environment the $\Delta\epsilon_T$ value obtained from the data is directly related to the assumed molecular weight of the DHE. In the presence of Triton X-100 and assuming a molecular weight of 600, a $\Delta\epsilon_T$ value of $1000 \pm 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 440 nm was thus found. If the molecular weight is $N \times 1000$, then $\Delta\epsilon_T$ is simply $N \times (1000 \pm 100)$.

Once $\Delta\epsilon_T$ is obtained this value can be used to determine the quantum yield of triplet state formation (Φ_T) based on a comparative technique and the value of Φ_T so determined depends on $\Delta\epsilon_T$ and hence on the assumed molecular weight of the drug as described above. Assuming a drug molecular weight of 600, the Φ_T value so determined was 5.0. If the molecular weight is $N \times 600$, then Φ_T is $5.0 \times N^{-1}$.

Since $\Phi_T < 1$, it follows that the molecular weight of the DHE molecule is at least 3000 corresponding to ≥ 5 porphyrin units per molecule. In fact, because Hp contains both two hydroxyethyl substituents and two acid ($-\text{CH}_2\text{CH}_2\text{COOH}$) substituents, it is likely that the active component DHE is a mixture of chains of different length containing from two to a large number of porphyrin ring systems. Our result shows that the average molecular weight of DHE in detergent solution is ≥ 3000 and that the average number of porphyrin rings in a DHE molecule is ≥ 5 . Porphyrins bind to, and are transported through the blood stream by, serum proteins and a few results will be presented on Hp and DHE bound to HSA. The effect of increasing HSA concentration on the Soret region of the absorption spectra of Hp is to show increasing disaggregation and this is also reflected in the magnitude of the triplet transient obtained by laser flash photolysis - increasing to a maximum at $[\text{HSA}]/[\text{Hp}] = 1$ and showing no further increase, thus suggesting that HSA binds Hp in a monomeric form. However, HSA has virtually no effect on the very low ($\sim$ zero) triplet yield of DHE even though it is well established that this species is bound to HSA - thus for DHE there must be little or no disaggregation on binding.

Singlet Oxygen: Since porphyrin-sensitised photodamage is mediated mainly by singlet O_2 ($^1\Delta$) and this species can only travel ~ 100 nm in a cell the most sensitive cell targets are those containing high

concentrations of the porphyrins such as mitochondria (outer cell membrane porphyrin concentration after therapeutic incubation times are probably unimportant). The yield of $^1\Delta$ in several environments has been studied using the 1270 nm time resolved luminescence technique with mainly 355 nm excitation but some recent data on the effect of excitation wavelength will be presented. Typical results for the quantum yield of $^1\Delta$ (ϕ_Δ), ϕ_T and S_Δ ($S_\Delta = \phi_\Delta/\phi_T$ the fraction of triplet quenching reactions leading to $^1\Delta$) show an ~ 2 fold increase in ϕ_Δ and ϕ_T for both Hp and HVD in CTAB/D₂O compared to D₂O buffer environments. For 532 nm excitation M.A.J. Rodgers and co-workers have shown relatively little change in ϕ_Δ values between buffer and detergents. At this time the reasons for this wavelength dependency effect are not understood but is important because, as noted above, 620 nm is used in therapy. Preliminary results for ϕ_Δ and S_Δ using such wavelengths for Hp, and a recently synthesised ester-linked chlorin-porphyrin 'dimer' will be presented. For DHE in D₂O a very low yield of O₂ ($^1\Delta_g$) is obtained but this increased over 10 fold on CTAB addition suggesting a dramatic structural change of DHE, such as unwinding or unstacking of the porphyrin polymer on incorporation in the detergent. Interestingly Grossweiner and co-workers have found (using the RNO method for O₂ $^1\Delta_g$ estimation) a similar increase in the presence of small unilamellar vesicles.

In benzene as solvent ϕ_Δ and S_Δ values of 0.54 ± 0.05 (relative to acridine) and 0.74 ± 0.04 are obtained for a series of porphyrin esters including HpDME and PPDME. However, substantial differences are noted for these esters in DPPC liposomes, e.g. ϕ_Δ (HpDME) $\sim 3\phi_\Delta$ (PPDME); possibly related to this difference is the complex, multi-component triplet decays of such esters when in liposomes. While progress has been made in understanding the photochemistry of Hp along with other 'simple porphyrins' as well as HpD and various HpD tumour localising components, it seems likely that HpD or even DHE is such a complex mixture that further progress with such materials will be seriously limited. The long-term potential in the use of photochemotherapy to treat cancer seems to lie in the development of new, well-defined drug systems with the ability to absorb light strongly in the red, to localise selectively in tumours and to generate the necessary tumour destroying species, presumably O₂ ($^1\Delta_g$), and, of course, to be non-toxic to normal cells.

FLASH PHOTOLYSIS AND PULSE RADIOLYSIS STUDIES OF SOME
SEMIQUINONES IN RELATION TO CANCER INDUCTION AND THERAPY

E.J.LAND

Paterson Laboratories
Christie Hospital and Holt Radium Institute
Manchester M20 9BX, England, U.K.

Semiquinones may often be conveniently prepared and studied by either flash photolysis (e.g. via hydroquinone photoionisation or $H\cdot/e^-$ abstraction by triplet excited quinone), or the derived technique pulse radiolysis (e.g. via reactions of various radiolytically produced one-electron oxidising or reducing radicals). The two techniques can provide complementary information, and this paper describes their use in two projects which may have chemotherapeutic implications.

Melanin formation with regard to malignant melanoma

Transformation of the cell responsible for production of melanin, the melanocyte, leads to malignant melanoma, one of the most aggressive and intractable forms of cancer, sometimes characterised by increased melanin formation. The mechanisms whereby malignant melanoma arises are unknown, although epidemiological evidence links the development of the disease to sunlight and genetic predisposition. The disease is associated with elevated levels of 5-S-cysteinyl-dopa (5-SCD), a natural metabolite of active melanocytes, and there is increasing interest in 5-SCD as a biochemical marker of melanoma metastasis. UV-stimulated melanocytes also produce increased amounts of 5-SCD which itself is extremely photolabile. Indeed, the photochemical mechanisms operative in UV-induced malignant melanoma may involve the photochemistry of 5-SCD.

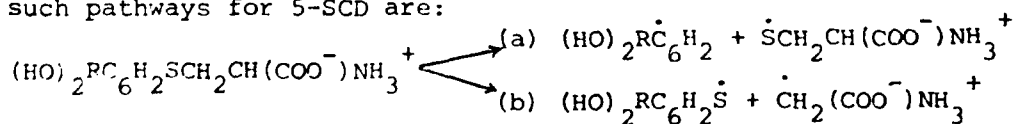
Much of what is already known about the initial stages of melanogenesis has been discovered by enzymatic oxidation studies in which slow enzyme-catalysed steps are rate-determining. Pulsed radiation methods provide a novel means of very rapidly

producing the short-lived semiquinone, quinone and subsequent intermediates of melanogenesis derived from various precursors including 3,4-dihydroxyphenylalanine (dopa), cysteinyl dopas and hydroxyindoles. Increased knowledge of the mechanism of melanin formation and of the photochemistry of melanin precursors gained by such techniques may provide information relevant to the development of malignant melanoma.

The unstable quinones of dopa and the most abundant cysteinyl dopa isomers 5-SCD, 2-SCD and 2,5-S,S'-dicysteinyl dopa (2,5-SCD) have been generated via disproportionation of their respective semiquinones prepared pulse radiolytically by one-electron oxidation of the corresponding dopas with azide radicals. Dopaquinone decays via a base-catalysed unimolecular cyclisation yielding leucodopachrome which, under the present conditions, is immediately oxidised by remaining dopaquinone to form dopachrome and reform dopa. By contrast, the cysteinyl dopa quinones decayed via an acid-catalysed unimolecular cyclisation involving the cysteine side chain to form cyclic quinone-imines which subsequently rearranged to more stable phenolic benzothiazine isomers.

Blockage of melanogenesis may be a means of killing tumour cells if, as is believed to occur with the depigmenting agent 4-hydroxyanisole, this causes a build-up of high concentrations of toxic intermediates. Cysteine and a number of related molecules with primary SH groups, although unreactive towards dopasemiquinone, combine with dopaquinone and thus prevent the formation of dopachrome and hence dopamelanin. New means of interrupting melanogenesis could ultimately lead to an improved chemotherapeutic approach towards malignant melanoma.

The photochemistries of dopa, 5-SCD and 2,5-SCD were investigated by 265 nm laser flash photolysis. The quantum yield of hydrated electron from dopa (9.1%) was about half the yield of dopasemiquinone (19.6%), implying that dopasemiquinone is formed via two primary photochemical mechanisms: photoionisation (giving e_{aq}^-) or photohomolysis (giving $H^\bullet$). In contrast, photolysis^{aq} of the cysteinyl dopas resulted in lower photoionisation quantum yields and the production of initial transient species whose absorption spectra were markedly different from their semiquinone absorption spectra determined pulse radiolytically. These observations indicate that the primary cysteinyl dopa photochemical species is not such a semiquinone, but rather results from S-C bond photohomolysis. Two possible such pathways for 5-SCD are:

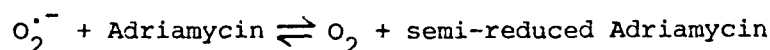


Recent ESR-spin trapping evidence obtained at Johns Hopkins University is consistent with the occurrence of reaction (b) rather than (a).

Quinone anti-tumour agents

Anthracycline antibiotics constitute a major class of chemotherapeutic agents for the treatment of many different kinds of cancer. Amongst these adriamycin has the widest spectrum of clinical antitumour activity, but its use is seriously hampered by dose related cardiotoxic side-effects. Moreover, radicals formed by enzymatic reduction have been implicated in these side effects.

The one-electron reduced radicals of adriamycin can be readily prepared by pulse radiolysis of aqueous solutions of adriamycin containing high concentrations of sodium formate. In order to determine the one-electron reduction potential of adriamycin, the semi-reduced adriamycin radical was brought into temporary equilibrium with several redox standards including duroquinone, various viologens and misonidazole. From the position of equilibrium the one-electron reduction potential at pH7 was found to be -328 mV versus the normal hydrogen electrode. Comparisons with the known one-electron reduction potential of oxygen suggest that if semi-reduced adriamycin radicals are formed in biological systems in the presence of oxygen, the position of equilibrium of the reaction

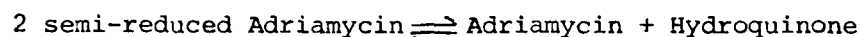


will lie well over to the left. *In vivo*, therefore, when oxygen is present, any semi-reduced adriamycin radicals formed will immediately transfer their electrons to oxygen to form $\text{O}_2^{\cdot -}$. This $\text{O}_2^{\cdot -}$ could then give rise to hydrogen peroxide and/or $\text{OH}^{\cdot}$ radicals which may cause, for example, strand scission of DNA via hydrogen abstraction from deoxyribose residues.

Pulse radiolysis studies of the variation in one-electron reduction potential of adriamycin with pH in the range 6-12 show that the net charge on semi-reduced adriamycin at pH7 is zero. Thus at this pH, the structure of the semiquinone is zwitter-ionic. This form exists between pH 2.9, below which the $\text{O}^{\cdot -}$ protonates, and pH 9.2, above which the amino group deprotonates. The fact that the semiquinone has a zwitterionic form at biological pH values is important since this influences transport through membranes and affects orientation of the species when in the vicinity of other biological molecules such as DNA which adriamycin can intercalate.

In fairly strong acid or alkaline solutions, semi-reduced

adriamycin decays by disproportionation to give the hydroquinone and the original parent quinone back again. In the approximate pH range 6-11 however, the semi-reduced adriamycin enters into a temporary equilibrium with its fully oxidised and fully reduced forms:



The highest stability of the semiquinone appears to be at about pH 9 where the equilibrium constant for the equilibrium is ≤ 1 . The main reason for the high stability, as well as the wide spread of the pK_a values of the semiquinone, is the stability of the hydrogen-bonded resonance-stabilised central naphthazarin structure. This high stability of the semiquinone means that if it is formed in regions of biological systems where the concentration of oxygen is low, it will be capable of reaction with components of the cell remote from the site of origin.

High enough concentrations of the adriamycin hydroquinone are present temporarily at certain pH values to allow the spectrum of the hydroquinone to be measured. The different spectra obtained at pH 5.0 and 11.5 show that at least one pK value occurs between these two pH values.

The equilibrium between semi-reduced adriamycin and the fully oxidised and fully reduced forms only persists for 10-20 ms. Over hundreds of milliseconds further marked changes in absorption occur which are tentatively assigned to elimination of the daunosamine sugar residue from the hydroquinone yielding a tautomer of 7-deoxyadriamycinone.

The semi-oxidised radical of the adriamycin model naphthazarin is also being studied, since molecules like adriamycin which contain hydroquinone as well as quinone moieties can form resonance stabilised semiquinone radicals by one-electron oxidation, and oxidative conditions as well as reducing situations can occur within cells.

These investigations provide a firmer basis for speculations about the role of free radicals and other unstable intermediates in the mode of action of these quinone drugs. Such studies, like those concerning melanin precursors, also illustrate that pulsed radiation methods can be used to investigate properties of transient species other than free radicals or excited states.

ENDOR Spectroscopy of Trapped Radicals in Single Crystals

N.M. Atherton, R.D.S. Blackford and W.A. Crossland

University of Sheffield

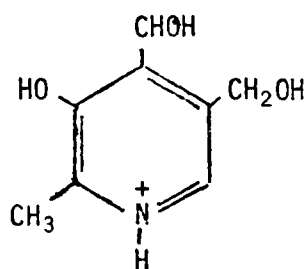
Department of Chemistry, The University, Sheffield,
S3 7HF

The value of e.s.r. spectroscopy for identifying and characterising free radicals rests almost entirely on the ability to resolve the hyperfine couplings. If the hyperfine couplings are not resolved in the e.s.r. spectra then the technique is not immediately helpful but the required information may still be obtained by using electron nuclear double resonance, (ENDOR), in which one measures the n.m.r. frequencies of the coupled nuclei.

Two reasons for lack of resolution in e.s.r. spectra are distinguished here. The first is a case where there are many coupled nuclei resulting in severe overlap of hyperfine components. The second case is where there is a small hyperfine coupling to nuclei remote from the free radical centre so the hyperfine splitting is within the relatively narrow e.s.r. linewidth: measurement of the small couplings using ENDOR gives structural information about the environment of the trapped radical.

Pyridoxine hydrochloride provides the first example. The molecule is closely related to Vitamin B₆ so its radiation chemistry is of some interest. Even a single crystal does not have usefully resolved e.s.r. spectra although they have been interpreted through resolution enhancement techniques [1]. A single crystal ENDOR study has been made to confirm the identification of the trapped radical and coupling tensors for five protons have been obtained at room temperature. Their interpretation gives strong support to the identification of the radical as

ENDOR of Trapped Radicals



The second case is exemplified by a study of the ClO_3 centre in irradiated barium perchlorate trihydrate. The e.s.r. parameters for the radical are markedly temperature dependent and this behaviour appears to reflect in some way the interaction of the radical with its environment in the crystal [2]. As a first step to clarifying this problem the proton structure of the environment of the radical at 120K has been determined from a single crystal ENDOR study. Coupling tensors to twenty four protons have been measured. Their interpretation throws light on an ambiguity in the space group of the crystal.

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Singlet and Triplet Yields in Radiolysis:

Magnetic Field Effect on Fluorescence

Brian Brocklehurst

Sheffield University

Chemistry Department, The University, Sheffield, S3 7HF

Ionization in liquid hydrocarbon is usually followed by geminate recombination: at short times (close ion pairs), the initial spin correlation is preserved; over longer periods (>10 ns, distant pairs), the correlation decays as a result of hyperfine interaction between electron and nuclear spins. The decay of initially singlet pairs into mixtures of singlets and triplets leads to magnetic field effects on fluorescence. The rate of the decay gives information about the ions involved. The magnitude of the field effect is less than theory predicts which suggests that some triplet pairs are formed initially. Also, there is evidence of very fast charge transfer (positive hole transport) in e.g. cyclohexane. These are areas of continuing controversy in radiation chemistry.

PHOTOCHEMISTRY OF THE o-NITROBENZYLIC SYSTEM - THE REACTIVE
INTERMEDIATES

R.W. Yip*, R. Giasson and D. Gravel

Div. of Chemistry, NRCC, Ottawa, Ont. K1A 0R6;

Dépt. de chimie, Univ. de Montréal, Montréal, P.Q.H3C 3V1

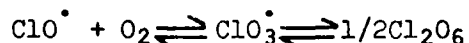
The photochemical rearrangement of o-nitrobenzylic system is a reaction of active interest in the development of photochromic compounds, photolabile protective groups, and more recently, photoresists. In order to gain a more satisfactory understanding of the factors which control the efficiency of the rearrangement, we have used ps absorption spectroscopy to probe the mechanism of a number of o-nitrobenzylic systems. We report that the o-quinonoid intermediate (arising from a transfer of a hydrogen from the o-benzylic carbon to the oxygen of the nitro group) is formed by two distinct pathways: a rapid 'concerted' pathway from the excited singlet state, and a delayed pathway via a triplet biradical. The reaction is interpreted in terms of the structure, transients, and relative quantum yields.

STABILISATION OF FREE RADICALS.

Z. G. Szabo

Institute of Inorganic & Analytical Chemistry,
L. Eotvos University,
Budapest, Hungary.

In order to explain the mechanism of freezing in of the chain process of thermal decomposition of Cl_2O or ClO_2 , I assumed (1) some forty years ago reaction between the chain carrier radical ClO and oxygen:



The detailed kinetic investigation (2) of thermal decomposition of propionaldehyde has proved that NO can decrease and increase the reaction rate, depending on its concentration, pointing to the reversible reaction $\text{R}^\cdot + \text{NO} \rightleftharpoons \text{RNO}$. The reactivity of $\text{R}^\cdot$ and RNO being rather different at the competing processes (3).

$\text{R} + \text{M} = \text{RH} + \text{M}^\cdot$ or $\text{RNO} + \text{M} = \text{RH} + \text{M}^\cdot + \text{NO}$, further $\text{R} + \text{R}^\cdot = \text{R}_2$, $\text{R}^\cdot + \text{RNO} = \text{R}_2 + \text{NO}$ finally $\text{RNO} + \text{RNO} = \text{R}_2 + 2\text{NO}$. From this scheme both the decelerating and accelerating effect can be deduced (4).

During my stay at Sheffield in Professor Porter's laboratory (5), after reproduction of some previous experiments about the iodine atom recombination in the presence of inert gases, I took nitric oxide as chaperon. Surprising has been the quite new trace on the oscilloscope indicating the presence of a rather long lived transient in fairly high concentration. This has been proved to be NOI ; not existing under common conditions contrary to NOCl and NOBr .

The experimental data show that nitric oxide is more effective as a chaperon by four orders of magnitude than neon. The discussion of collected results throws some light on the nature of the interaction and on the strength of the transient bond formed.

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TUESDAY 15 JULY 1986

SESSION F: PHOTOSYNTHESIS IN VIVO AND MODELS OF BIOLOGICAL SYSTEMS

Chairman: G.R. FLEMING

- 09.15-09.45 **Keynote Lecture** H.T. WITT: Analysis of elementary processes in photosynthesis in the range from nanoseconds to seconds
- 09.45-10.00 J. BARBER: Chlorophyll fluorescence: the basis of the plant physiologist's stethoscope
- 10.00-10.15 R.M. LEBLANC: Surface and optical properties of pure and mixed mono- and multilayer arrays of chlorophyll-a
- 10.15-10.30 D.R. KLUG: Picosecond pump-probe and plants
- 10.30-10.45 G.F.W. SEARLE: Temperature dependence of core antenna chlorophyll fluorescence kinetics in photosystem I reaction centre protein
- 10.45-11.00 S. MALKIN: Photoacoustic measurements of photosynthesis in intact leaves
- 11.00-11.30 **COFFEE**
- 11.30-12.00 **Keynote Lecture** M.W. WINDSOR: Primary events in bacterial photosynthesis
- 12.00-12.15 W.A. GIBBONS: Correlations of proton-proton, proton-chromophore and chromophore-chromophore distance measurements in biopolymers from NMR, emission spectroscopy and computational chemistry
- 12.15-12.30 G. STRAUSS: Restriction of lipid membrane mobility by saccharides: flash fluorometric studies
- 12.30-12.45 J.M. KELLY: Flash photolysis of DNA complexes
- 12.45-14.00 **LUNCH** in the Royal Institution

POSTERS associated with Session F :

- S.S. BRODY: Interactions between chlorophyll and carotenoids in a model system
- R.L. BROOKFIELD: Intramolecular excitation and electron transfer in model photosynthetic systems
- R.G. BROWN, E.H. EVANS, R. SPARROW et al.: Picosecond fluorescence and absorption properties of photosynthetic systems
- L.B. GIORGI, B.L. GORE, D.R. KLUG et al.: Picosecond transient absorption spectroscopy of photosystem I reaction centres from higher plants
- J.P. IDE, D.R. KLUG, B. CRYSTALL et al.: Detergent effects upon the picosecond dynamics of higher plant light harvesting chlorophyll complex (LHC)

Chlorophyll fluorescence: The basis of the plant physiologist's stethoscope.

J. Barber.

Department of Pure and Applied Biology,

Imperial College, London, SW7 2BB.

Since chlorophyll fluorescence competes with photosynthesis any change in its yield at room temperature gives information about the energy converting processes. In this way it acts as a sensitive non-destructive technique to explore the efficiency of photosynthesis and can rapidly detect perturbations of reactions in response to changes in environmental conditions. Time-resolved fluorescence gives information about energy transfer and photon trapping mechanisms as well as predicting organisational properties of the pigments. At very low temperatures (e.g. 77 K) or in the presence of the herbicide DCMU, transient changes in the yield of emission monitors only primary processes because secondary electron flow and CO_2 fixation are inhibited. At R.T. the fluorescence comes mainly from chlorophylls serving as a light harvesting system to photosystem two (PS2) and in the presence of DCMU the transient signals are relatively simple to analyse. After a dark pretreatment the initial fluorescence level (F_0) is low and corresponds to a condition when all PS2 reaction centres are open. Continuation of illumination in the presence of DCMU brings about a rapid rise in the fluorescence yield to a maximum level (F_m) corresponding to a reduction of the primary quinone acceptor Q_A . The kinetics of the rise and the values of F_0 and F_m vary when measured with isolated thylakoid membranes suspended in media of different salt concentrations. A thorough study of this phenomenon has indicated that a major factor in controlling the emission properties is the valency of the cation present and that the changes in yield correlate with the degree of thylakoid membrane stacking. An analysis of the data based on the electrostatic theory of double layers has given rise to a model for explaining the in vivo regulation of energy transfer by protein phosphorylation.

SURFACE AND OPTICAL PROPERTIES OF PURE AND MIXED MONO- AND MULTI-LAYER ARRAYS OF CHLOROPHYLL a

LEBLANC, Roger M.

Centre de recherche en photobiophysique, Université du
Québec à Trois-Rivières, Trois-Rivières, CANADA, G9A 5H7

The importance of membrane reconstitution techniques in the study of a large variety of membrane processes is now well established. Model planar lipid mono- and bilayers have indeed become an almost indispensable tool in the search for an understanding of the structural and functional characteristics of biological membranes and their study has contributed to major developments in almost every branch of membrane biology. The use of model systems arises from the desire to make *in vitro* structures which have the advantages that their composition is precisely known and that they can be made with macroscopic areas. It is possible to have a degree of control over a model system which cannot generally be achieved with a real membrane. In order to study the relevant photophysical and photochemical reactions performed by thylakoid membranes in photosynthesis, it is necessary to design specific molecular assemblies.

Considering the importance of chlorophyll a (chl a) in photosynthesis, it is mandatory to have a good knowledge of the way this pigment can interact with its environment. Our approach is to use the monolayer technique to obtain accurate data on the interactions prevailing between chl a and its lipidic (e.g. MGDG, DGDG) and/or proteinic (e.g. plastocyanin, stellacyanin, cytochrome f) environment(s). The surface pressure and the surface potential isotherms of mixtures of chl a with a lipid, covering the whole range of molar fractions, have been carefully measured at the air-water interface. The excess free energies of interactions have been calculated from the surface pressure isotherms. We have also studied some chl a-pigment mixtures, e.g. chl a-pheophytin a, chl a-chl b and chl a-carotenoid. We are now looking at more biologically relevant systems by studying how these interactions are modified when proteins are dissolved in the subphase and come

into contact with the chl a molecules dispersed in a mixed monolayer at the interface.

Mono- and multilayers of pure chl a, chl a-lipid, chl a-protein and chl a-pigment have been prepared by means of the Blodgett-Langmuir technique for electronic, infrared, emission, fluorescence lifetime, photoacoustic and photovoltaic studies. The nature of the interaction of chl a in the different systems is examined.

A comparative study between the absorption and photoacoustic spectra of mono- and multilayers of chl a has been made. An excellent agreement between absorption and corresponding photoacoustic spectra has been observed. The photoacoustic technique allows us to measure the thermal deactivation of the molecules following the absorption of light energy. This technique is used because of its great sensitivity to thin layers. The fluorescence lifetime was measured by two different techniques: the picosecond laser flash and the single photon counting. The chl a monolayer was mixed with one of the following diluents: dioleoyl-L-phosphatidylcholine (18:1), monogalactosyldiacylglycerol (MGDG), digalactosyldiacylglycerol (DGDG), phytol. The fluorescence lifetime varied from 4 ns to < 20 ps with both techniques, but the powerful laser pulse created a fast component due to exciton annihilation process. Fluorescence spectroscopy was also used to complete the study. The emission spectrum of pure monolayer has only one broad band at 700 nm giving evidence of aggregation

and self-absorption. The diluted monolayer of chl a has three distinct peaks at 632, 678 and 736 nm. Excitation spectra at different concentrations give the same profile with peaks at 386, 416 and 440 nm. Comparison of present results with data obtained from recent work on intact photosystems (Holgwarth et al., *Biochim. Biophys. Acta* 807, 155, 1985) leads to the following interesting analogies: a) the pure chl a monolayer has a similar fluorescence lifetime and emission spectrum as those of the fast decay process attributed to PSI; b) the emission spectrum of the chl a/PC (1:100) monolayer has the same maximum as the component with the PSII reaction center closed.

To study the role of carotenoids (e.g. canthaxanthine) in the process of photogeneration of charge carriers, the photovoltaic cell of the type (Al/monolayers of Cantha/Ag) and (Al-monolayers of Cantha + chl a/Ag) were prepared. The cells (Al/Cantha monolayers/Ag) and (Al/monolayers of Cantha + monolayers of chl a/Ag) do not show any photocurrent. The cells (Al/monolayers of mixture of chl a + Cantha (0.84:0.16)/Ag) do show photocurrent but the power conversion efficiency (calculated at 680 nm) is very low ($0.5 \times 10^{-4}\%$). The cells of the type (Al/20 monolayers of chl a + 14 monolayers of mixture of chl a + Cantha (0.84:0.16) + 10 monolayers of chl a/Ag) show photocurrent and have efficiency (at 680 nm) comparable to chl a cells. The interesting feature of the cells, however, is that one observes photocurrent in the absorption region of canthaxanthine (500 nm). This should be

compared with Cantha cells and chl a photovoltaic cells where no photocurrent in this region was observed. This suggests that there is transfer of excitation energy from carotenoid canthaxanthine to chl a and the separation of charges takes place at Al/chl a junction. The action spectra of these cells when illuminated through Al resemble closely the absorption spectra which shows that the photoactive region is at the Al/chl a region. The capacitance measurements indicate a large number of trapped charge carriers.

A technique that allows the formation of asymmetrical lipid bilayers from characterized monolayers have been developed in our laboratory. The main advantage of our experimental set-up lies indeed in the possibility to characterize fully the surface properties of the film-forming substances prior to membrane formation. Resistance and capacitance measurements on asymmetrical membranes formed from monolayers are discussed and compared to the results obtained on membranes prepared from lipid films which are not monomolecular in thickness.

PICOSECOND PUMP-PROBE AND PLANTS.

D.K. Klug, L.B. Giorgi, B.L. Gore and G. Porter

Davy Faraday Research Laboratory, The Royal Institution,
21 Albemarle Street, London W1X 4BS, U.K.

Picosecond pump-probe techniques have had considerable success over the last ten years in investigating the photobiophysics of the widely varying chromophore-protein complexes of bacteria. The most recent development has been the resolution of the initial step of charge separation in reaction centres from *Rhodospseudomonas viridis* and *Rhodospseudomonas sphaeroides* (1-3).

The more sophisticated nature of the higher plant thylakoid membrane has meant that it has only recently become possible to isolate relatively pure functional reaction centre complexes of photosystems 1 and 2 (PS1 and 2) and the major light harvesting complex LHC2. Pump-probe experiments and complimentary single photon counting techniques are sensitive to any variations in the state of these complexes, which are often indistinguishable to other techniques used in their characterization. Starting with chlorophyll *in vitro* and working up in complexity through LHC2 to PS1, we have found stimulated emission a most useful diagnostic of the photophysical state of these complexes, particularly with regard to the extent of triplet formation. Increasing familiarity with the technique and the samples has allowed us to use comparative techniques to identify a wide range of effects including stimulated emission, exciton annihilation, functionally disconnected chlorophyll, aggregation leading to formation of quenching traps, quenching of chlorophyll triplet states, and most recently, the excitation quenching of PS1 antenna chlorophylls by P700 with a rate constant $1/\tau$ where $\tau \approx 15$ ps.

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Temperature dependence of core antenna chlorophyll fluorescence kinetics in photosystem 1 reaction centre protein.

G.F.W. Searle, R. Tamkivi, A. van Hoek and
T.J. Schaafsma
Agricultural University of Wageningen, Netherlands
Dept. Molecular Physics, de Dreijen 11,
6703 BC Wageningen.

The purpose of this work was to study excitation energy transfer between chlorophyll(chl) forms in isolated chl-proteins, making use of low temperatures to affect these transfers by inhibiting endothermic reverse transfer processes. The reaction centre (RC) chl-protein of plant photosystem 1 (PS1) contains the primary donor P700 and about 50 antenna chl, and shows active charge separation and recombination. We have isolated this protein, called CP1, using the detergent sodium dodecyl sulphate and polyacrylamide gel electrophoresis, and studied excitation energy transfer between discrete chl forms by measuring chl fluorescence decay kinetics over a range of temperatures and emission wavelengths. A mode-locked argon ion laser at 458 nm was used for excitation and the pulse train was modulated with a Pockels cell (laboratory-built electronics) to give 3 microsec between pulses. Front surface emission was collected at right angles to the excitation beam and detected by single photon timing. The pulse width after detection was about 600 ps, and lifetime components as short as 30 ps can be resolved using standard deconvolution methods. Chl fluorescence from CP1 shows two discrete bands: an intense emission at 720 nm from low energy sites within the antenna (F720), and an emission at 690-695 nm which is only clearly seen in time-resolved spectra at short times and at low temperature (F695). The kinetics of the decay of both F695 and F720 fluorescence has been fitted to the sum

of three exponential components. The two longer components are in the ns range with a small relative amplitude, and have no significance for energy transfer - they will not be discussed further. The shortest component was found to vary in a complex way, depending on temperature and wavelength, between about 30 ps and 150 ps. It is these relative variations (and not the absolute values) of the lifetimes which have been used to develop the model for energy transfer processes in CP1. The lifetime of F695 was 30 ps at room temperature increasing to a maximum value of 80 ps at 150 K, decreasing again to about 30 ps at 80 K, and increasing again below 80 K. F720 emission showed a lifetime of 30 ps at 200 K and above, increasing to 160 ps at 100 K and below. When the wavelength dependence of the lifetimes is analysed, it is seen that at 200 K CP1 had a lifetime of 30-50 ps which was independent of emission wavelength, but as the temperature was lowered the lifetime developed a strong dependence on wavelength, showing a distinct minimum in the range 690-695 nm, where it remained shorter than 100 ps. Our interpretation of the data is that F695 can transfer energy to P700 even at 10 K and that it forms a core antenna close to the RC. A model for energy transfer will be presented which can explain the variation of the F695 fluorescence lifetime with temperature as due to the inhibition of endothermic transfer steps out of F720 as the temperature is lowered.

Permanent address RT: Institute of Physics, Academy of
Sciences of the Estonian S.S.R.,
202400 Tartu, Riia Str. 112,
Estonian S.S.R., U.S.S.R.

PHOTOACOUSTIC MEASUREMENTS OF PHOTOSYNTHESIS IN INTACT LEAVES.

by : Shmuel Malkin., O. Canaani, Biochemistry Department
The Weizmann Institute of Science, Rehovot 76 100, Israel.

Microphone detection of signals obtained from leaves by modulated light excitation is indicative of gas exchange and photochemical energy storage in photosynthesis. This will be briefly reviewed. A detailed study by photoacoustics, measuring the Emerson enhancement, leads to information on the light distribution pattern and interaction of the two photosystems in photosynthesis.

CORRELATIONS OF PROTON-PROTON, PROTON-CHROMOPHORE AND CHROMOPHORE-CHROMOPHORE DISTANCE MEASUREMENTS IN BIOPOLYMERS FROM NMR, EMISSION SPECTROSCOPY AND COMPUTATIONAL CHEMISTRY

W.A. Gibbons^{*}, K. Beyer^{*}, M. Kuo^{*}, L. MacLachlan^{*}, K P Mascagni^{*}, P. Murray-Rust^{**}, N Niccolai⁺, K P. Sarathy⁺⁺, A. Tonge^{*} and N. Zhou^{*},

* Department of Pharmaceutical Chemistry, University of London,
School of Pharmacy

** Glaxo Laboratories, Greenford, Middlesex

+ Department of Chemistry, Emory University, USA

++ Department of Chemistry, University of Siena, Italy

Spin excitation of single proton nuclei in biological macromolecules results in "transfer" of energy by a "through-space" dipolar mechanism to nuclei within a radius of five angstroms. These steady-state and time-dependent NOE and relaxation measurements of the excited donor and acceptor proton nuclei yielded proton-proton distances and hence the secondary conformation in solution to an accuracy of ± 0.2 angstroms.

The side chain conformations of these peptides were determined from "through-bond" scalar coupling constants, through-space chromophore effects on NMR shifts, and by fluorescence and phosphorescence spectroscopy. A remarkable agreement between the data from all three classes of measurement was obtained.

The nuclear Overhauser effect data was used as a basis for energy minimization calculations. The latter were not only consistent with the experimentally-derived backbone conformation but predicted most of the equilibria and kinetic effects observed for the ten side chains by NMR and ultraviolet emission spectroscopy.

This combination of techniques has provided hitherto unavailable information concerning the conformation and dynamics of macromolecules in solution.

RESTRICTION OF LIPID MEMBRANE MOBILITY BY SACCHARIDES:

FLASH FLUOROMETRIC STUDIES

George Strauss

Wright-Rieman Chemistry Laboratories, Rutgers University

New Brunswick, N.J. 08903, U.S.A.

Phospholipid bilayer vesicles (liposomes) are stabilized against disruption during dehydration or freezing by sucrose or other mono- and disaccharides (1). Such sugars appear to stabilize the bilayer by forming in effect a non-volatile and non-freezable replacement for the water of hydration. This model is supported by the fact that vesicles, as well as phospholipid monolayers, expand slightly in the presence of saccharides.

Mobilities of the bilayer-water interface were studied by ESR spectroscopy. The palmitic acid ester of the TEMPO nitroxide radical (2,2,6,6-tetramethylpiperidine-1-oxyl) was incorporated into egg phosphatidylcholine (EPC) vesicles at a 1:1000 probe to lipid ratio, thus placing the free radical at or near the membrane interface. At room temperature the ESR spectrum consisted of three narrow lines with a maximum hyperfine splitting $2A_{||}$ of 33 gauss. This showed rapid isotropic tumbling and indicated a rotational relaxation time of the order of 5 nanoseconds. Addition of sucrose, up to 30%, to the external aqueous phase had no significant effect on the ESR spectrum. Upon cooling, the value of $2A_{||}$ increased only slightly as the temperature fell to -25°C , both in the absence and presence of sucrose, showing that the interface had remained mobile. Below -25°C , $2A_{||}$ increased steeply to 70 gauss at -35°C , indicating immobilization. Thus, no observable difference in the mobility-temperature profile was induced by sucrose, despite its extraordinary stabilization effect on bilayers, in the time domain of a few nanoseconds.

To examine events over longer time spans, dynamic fluorescence quenching rates were measured. Pyrenesulfonyldipalmitoyl-phosphatidylethanolamine, with the fluorophore at the polar head,

was incorporated into EPC vesicles (probe to lipid, 1:100). TEMPO-palmitate was also incorporated as a collisional quencher at a quencher to lipid mole ratio of 1:10. Time-resolved fluorescence decay curves were determined with a flash fluorometer by single photon counting. Excitation was by a high voltage spark source at a 20 to 40 KHz repetition rate, with a flash half width of 3 ns. Pulses of heights representing the emission delay of single photons were stored in a multichannel analyzer. The decay curves were deconvoluted by computer. Plots of $\ln(\text{intensity})$ vs. time were non-linear. An initial rapid decay due to close-lying quenchers was followed by an approximately monoexponential decay stage, assumed to be diffusion-controlled. Quenching constants k_Q were determined from the latter stage.

In EPC vesicles in aqueous buffer solutions, k_Q was $(4.5 \pm 0.5) \times 10^{17} \text{ cm}^2 \text{ mole}^{-1} \text{ s}^{-1}$, corresponding to a diffusion coefficient of $(7 \pm 1) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. This was of the same order of magnitude as values reported from changes in ESR line shape (2) and from triplet-triplet interaction (3) in different membrane systems. Upon addition of increasing concentrations of sucrose to the external aqueous phase, k_Q was unaffected below 20%. Beyond this threshold, k_Q decreased sigmoidally and became almost zero in 60% sucrose. A sigmoidal dependence on sucrose concentration had also been observed in cryo-stabilization effects of sucrose. In control experiments sucrose had no effect on the lifetime of the pyrene-labeled phospholipid without quencher, nor on the ESR signal strength of TEMPO palmitate. When ω -pyrenestearic acid and 16-doxylstearic acid were incorporated into EPC vesicles the quenching reaction, which now occurred in the membrane interior, was completely unaffected by sucrose.

It is concluded that saccharides exert their stabilizing effects on lipid membranes by binding to the interface, without deep penetration, and stiffening the membrane structure. They suppress lateral diffusion occurring in a 50-100 ns time domain but do not affect the more rapid rotation or oscillation of probes.

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FLASH PHOTOLYSIS OF DNA COMPLEXES

John M. Kelly, Martin J. Murphy, Alessandro B. Tossi,
and Wil van der Putten

Chemistry Department, University of Dublin,
Trinity College, Dublin 2, Ireland.

Photo-induced base-specific cleavage of DNA could offer an alternative approach to DNA-sequencing which would complement the present chemical and biochemical procedures. By exciting photo-active compounds ("dyes") bound at particular sites of the DNA, it should, in appropriate cases, be possible to induce breaks in the sugar-phosphate backbone at, or near, these sites. Base selectivity can be controlled by exploiting (a) preferential binding of the photo-active compound near certain bases or base pairs; (b) selectivity of excitation at certain sites because of differences in absorption spectra when the "dye" is bound near different base pairs; (c) variations in the "dye"'s photophysical and photochemical properties at certain sites. These effects can be monitored conveniently using synthetic polynucleotides such as poly[d(G-C)] and poly[d(A-T)], while strand breaks and the base specificity of cleavage can be assayed using covalently closed circular DNA and ^{32}P -labelled DNA respectively. In this paper the results of laser (XeCl excimer or dye) flash photolysis studies of the excited state properties of polynucleotide complexes of (i) porphyrins (ii) ruthenium polypyridyl compounds and (iii) tricyclic dyes, such as methylene blue will be reported.

The porphyrins, meso-tetramethylpyridiniumporphyrin (H_2TMPyP^{4+}) and its zinc complex $ZnTMPyP^{4+}$, both bind strongly to DNA, the former by intercalation, the other mainly non-intercalatively¹⁻³. For H_2TMPyP^{4+} both the fluorescence and the triplet yield are strongly quenched when bound to poly[d(G-C)]. No evidence for products from this singlet state interaction, which might involve reversible oxidation of guanine, could be detected by flash photolysis. By contrast to the behaviour with poly[d(G-C)] the fluorescence quantum yield of H_2TMPyP^{4+} is approximately doubled upon binding to poly[d(A-T)]. In either degassed or aerated solution the lifetime of H_2TMPyP^{4+} is increased upon binding to each of the polynucleotides, presumably indicating that access to the porphyrin is restricted and implying that the H_2TMPyP^{4+} triplet state does not react efficiently with the nucleotide bases. For $ZnTMPyP^{4+}$ the fluorescence quantum yield is not affected upon binding to either polynucleotide but the fluorescence spectrum is markedly changed when bound to poly[d(A-T)] but not to poly[d(G-C)]. This suggests that this porphyrin is interacting more strongly with A-T base pairs, and this is substantiated by studies of the triplet state decay where it is observed that quenching by oxygen is much less efficient for poly[d(A-T)] than it is for poly[d(G-C)].

For methylene blue it is observed that the fluorescence and triplet yields are quenched in poly[d(G-C)] or calf thymus DNA, whereas the photophysical properties of the dye bound to poly[d(A-T)] are more similar to those of the free dye. As with H_2TMPyP^{4+} , no evidence was obtained for long-lived species, which might conceivably be formed by oxidation of guanine or other nucleic acid base and which might be intermediates in the reactions leading to single strand cleavage. Triplet lifetimes are increased on binding and the sensitivity to oxygen quenching is much reduced, indicating that polynucleotide-bound dye will be less effective as a singlet oxygen sensitiser.

For a series of ruthenium(II) complexes of polypyridyls {e.g. 1,10-phenanthroline (phen), 2,2'-bipyridyl (bpy), 2,2',2''-terpyridyl

(terpy), and 1,4,5,8-tetraazaphenanthrene (TAP)}, it has been found that the nature of binding and its effect on the photophysical properties is very dependent on the nature of the polypyridyl ligand^{4,5}. Thus, although both $[\text{Ru}(\text{TAP})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ intercalate (at low ionic strengths and in the absence of divalent cations) the emission quantum yield in aerated solutions of $[\text{Ru}(\text{TAP})_3]^{2+}$ is quenched and that of $[\text{Ru}(\text{phen})_3]^{2+}$ is enhanced. Other complexes such as $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{terpy})_2]^{2+}$ bind externally and their photophysical properties are less changed on binding. Flash photolysis experiments reveal that the rate of oxygen quenching is less when $[\text{Ru}(\text{phen})_3]^{2+}$ is bound to poly[d(A-T)] than when bound to poly[d(G-C)], consistent with other findings that there is a stronger binding to A-T-rich regions of DNA. Addition of Mg^{2+} , which is known to prevent intercalation of the ruthenium complex, enhances the rate of oxygen quenching.

In conclusion, these studies have shown that the photophysical properties of porphyrins, ruthenium polypyridyl complexes and dyes are markedly affected by binding to DNA. Furthermore the excited state properties depend upon the type of nucleic acid base near which the compound is bound and upon whether the species is intercalated or externally bound. Further experiments are in progress using other quenchers, such as quinones.

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Interactions between Chlorophyll and Carotenoids

Interactions between Chlorophyll and Carotenoids in a Model System

Seymour Steven Brody

New York University

Dept. of Biology, Washington Sq. New York, NY 10003

The interaction of chlorophyll *a*, with various carotenes and xanthophylls, was investigated in a liposomal system. By varying the temperature the fluidity of the lipid (composed of a mixture of fatty acids) could be varied. Interaction between the pigments is assayed by measuring both the temperature induced changes in absorption spectra, and transfer of triplet excitation from chlorophyll to carotenoids using flash photolysis.

To clearly demonstrate the interaction between chlorophyll and carotenoids, liposomes composed solely of soy bean lecithin and one of the pigments was studied. The effects of temperature on their spectral properties was determined. The carotenoids incorporated into the liposomes include alpha and beta carotene, diketocarotene (canthaxanthin), as well as the polar dihydroxy-diketo carotene (astaxanthin), and dihydroxy carotene (zeaxanthin and lutein). As temperature is lowered the carotenoids undergo blue spectral shifts; on increasing the temperature there are red shifts of the absorption spectra. There are similar temperature induced spectral shifts with liposomes composed solely of lecithin and chlorophyll.

Upon addition of chlorophyll into the liposome, the carotene absorption bands undergo a spectral shift, indicating that some of the carotene interact or form a complex with chlorophyll. There is invariably a red shift of the absorption maxima of the carotenoids. Liposomes composed of chlorophyll and a carotenoid appears to be a good model for

Interactions between Chlorophyll and Carotenoids

studying pigment interactions in vivo. This is indicated by the similarity between the spectral data obtained with liposome, and the data obtained with both chloroplasts and intact photosynthetic organisms.

Of particular interest in the present study is the large temperature induced change in absorption at 520 nm, observed in liposomes containing chlorophyll and dihydroxyl-carotene (zeaxanthin). The other carotenoids, used in this study, registered much smaller spectral changes under similar conditions. Changes in absorption, reported in vivo, at 510 nm, have been ascribed to electrochromic effects, associated with a carotenoid.

The observation that high concentrations of ionophores (valinomycin, nigericin or gramicidin) do not modify the temperature induced spectral changes indicate that the changes are not associated with electrical potentials of the bilayers or ion transport. In addition, the spectral changes are not due to temperature induced shifts in population of the vibrational states. Such shifts should be completely reversible with respect to temperature. All the spectral changes observed in vivo and in model systems, on the contrary, are not exactly reversible; there is usually a large hysteresis effect associated with the spectral changes.

The spectral shifts could arise from changes in the local electric fields of the pigments. This could result from interaction between similar or different pigments, or perhaps a phase change of the lipids. In the latter case, because of the heterogenous composition of fatty acids in the soy bean lecithin the surface of the liposome could well be divided into several lipid domains. The lipid phase is determined by the fatty acid residues and to a certain extent by materials dissolved in the lipid phase. Since lecithin is composed of a wide range of fatty acids, the phase changes in the various domains occur over a wide temperature range. The results of transfer of triplet energy are interpreted in terms of this model.

The triplet states of zeaxanthin and chlorophyll are observed at 525 nm and at 780 nm, respectively. There is considerable overlap of the chlorophyll triplet at 525 nm. This results in a biphasic (fast and slow) increase in absorption at 525 nm. The fast increase in absorption is less than 50 ns. The slow increase is interpreted as the time required for a molecule of chlorophyll, in the triplet excited state, to encounter and transfer its excitation

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energy to a molecule of zeaxanthin. At low temperature, when much of the lipid is in the solid phase so that fluidity in the liposome is low, the rate and efficiency of energy transfer is also low. The result is a small contribution of the slow change in absorption, at 525 nm. As temperature is raised, the opposite is true.

When utilizing high concentrations of pigments in the liposome, complexes appear to form between chlorophyll and zeaxanthin. The observed increase in intensity, of the fast rise in absorption, would be consistent with complex formation. The presence of such complexes markedly increase the rate of triplet-triplet transfer and, in addition, make the process relatively independent of temperature.

As temperature or the relative concentration of zeaxanthin are increased, the triplet measured at 780 nm decays faster. The rate of decay of absorption at 780 nm (which is 2 to 20 us) does not appear to be related to the slow rise time at 525 nm (which is of the order of 0.2 us). It is proposed that there are at least two different groups of lipid domains. One group of domains might contain both chlorophyll and zeaxanthin, while the another group might contain primarily chlorophyll. In the former group, there could be efficient triplet-triplet transfer. In the latter group, one would observe primarily, the slow decay of the chlorophyll triplet.

INTRAMOLECULAR EXCITATION AND ELECTRON TRANSFER IN MODEL
PHOTOSYNTHETIC SYSTEMS.

R. L. Brookfield

Perkin Elmer Limited,

Post Office Lane, Beaconsfield, Buckinghamshire.

Time resolved fluorescence kinetic and spectroscopic results which demonstrate intramolecular nonradiative excitation transfer in mixed-metal bisporphyrins are presented. The fluorescence data are supported by subnanosecond flash photolysis results obtained independently by other workers. Rate constants for excitation transfer are in the range $\sim 10^{10} \text{ s}^{-1}$.

Porphyrin fluorescence quenching observed in porphyrin-viologen compounds is complemented by independent flash photolysis results that indicate picosecond electron transfer from the porphyrin excited singlet state.

Picosecond fluorescence and absorption properties of
photosynthetic systems

R.G. Brown*, E.H. Evans*, R. Sparrow*, D. Shaw⁺, J. Barr[±],
M. Smith[±] and W. Toner[±].

*Lancashire Polytechnic, Preston

⁺SERC Daresbury Laboratory, Warrington

[±]SERC Rutherford-Appleton Laboratory, Didcot

We are studying the fluorescence and absorption properties of preparations from cyanobacteria and higher plants in the first few nanoseconds following excitation. Fluorescence decay profiles are being determined by the single-photon counting technique using the Synchrotron Radiation Source at Daresbury as the excitation source, and rapid absorption measurements are being performed at the Central Laser Facility of the Rutherford-Appleton Laboratory. The latter experiments involve excitation with a 4 psec. pulse from a Nd/YAG pumped dye laser followed by a probe pulse in the wavelength range 675-730 nm. The probe pulse is generated from the excitation pulse by Raman shifting and/or self-phase modulation and may be shifted temporally with respect to the excitation pulse such that the absorbance of the sample may be determined at any chosen time following excitation.

All the fluorescence decay profiles measured to date require a sum of at least three exponentials to achieve an acceptable fit. Lettuce chloroplasts exhibit decay times of 100 psec., 500-600 psec. and 1.5-2.0 nsec. in the wavelength range 680-720 nm. The greatest contribution to the total decay is from the fastest component, followed by the middle and slow components. The origin of the various components is a matter of considerable speculation; but our results appear to agree with the assignments of Holzwarth et al [1], namely that

- (a) the fast component originates in the antenna pigments of both photosystems
- (b) the middle component is due to the reaction centre of photosystem 2, and

- (c) the slow component results from reexcitation of photosystem 2 antenna pigments.

The effect of the addition of potassium ferricyanide and DCMU (dichlorophenyldimethylurea) on the decay profiles will be discussed, as may be the properties of other lettuce preparations.

A PS1 preparation from the cyanobacterium Chlorogloea Fritschii, which has been thoroughly characterised previously [2] and which has been shown to exhibit good long term stability, has been chosen for measurements of both fluorescence and absorption as described earlier. The preparation exhibits fluorescence decay times of 50 psec., 800 psec. and 4.0 nsec., with a much smaller contribution from the fast component, and more dominant contributions from the other two components.

Initial measurements of the absorption bleaching at 705 nm on this sample indicate that the decay of the bleaching is at least biphasic, including one component of approximately 50 psec. The profile is very similar to that observed by Il'ina et al [3] for a PS1 preparation under 'continuous saturating light conditions' where the 50 psec component was ascribed to light-harvesting chlorophyll-a. We have not attempted to influence the redox state of our sample, however, so the agreement with previous work may simply be fortuitous.

Further experiments are in progress which should provide more data on which to base an analysis of the PS1 fluorescence and absorption changes, and we hope to be able to present these.

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PICOSECOND TRANSIENT ABSORPTION SPECTROSCOPY OF PHOTOSYSTEM 1
REACTION CENTRES FROM HIGHER PLANTS.

L.B.Giorgi,B.L.Gore,D.R.Klug,J.P.Ide,J.Barber* and
G.Porter

Davy Faraday Research Laboratory, The Royal Institution,
21 Albemarle Street, London W1X 4BS, U.K.

*Department of Pure & Applied Biology, Imperial College,
Prince Consort Road, London SW7 2BB, U.K.

Picosecond time resolved absorption spectra of Photosystem 1 (PS1) reaction centres, isolated from pea chloroplasts, have been obtained in the 625nm-765nm spectral region, at room temperature. Excitation of samples is with a 10ps 600nm pulse, while the probe pulse is a white light continuum, also of 10ps duration. Typical absorption spectra, for reaction centres with a chl/P700 ratio of 50, indicate two main spectral features, one at 690nm and one at 700nm. The one at 690nm is dominant at early times, is present in the spectra of samples with P700 either chemically oxidised or chemically reduced, and decays with a lifetime of approximately 15-20ps. This feature undergoes a blue shift as it decays, finally being centred at 675nm. Previous experiments (1) have shown that the residual bleach at 675nm decays with a lifetime of between 1 and 2ns; it is believed that this signal is due to residual triplet chlorophyll molecules which are quenched by carotenoid molecules within the antenna. The decay of the 690nm signal is, within the resolution of these experiments, independent of the redox state of P700. The second main spectral feature, centred at 700nm, is very much narrower than the 690nm signal and occurs only in the spectra of samples with P700 chemically reduced. The signal at 690nm can be attributed to the excitation of the antenna chlorophyll to the singlet state while the signal at 700nm can be attributed to the photooxidation of P700 molecules.

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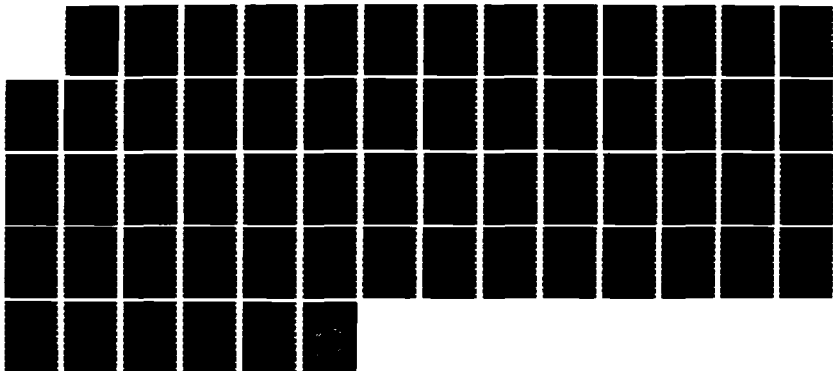
FLASH PHOTOLYSIS AND ITS APPLICATIONS MEETING IN
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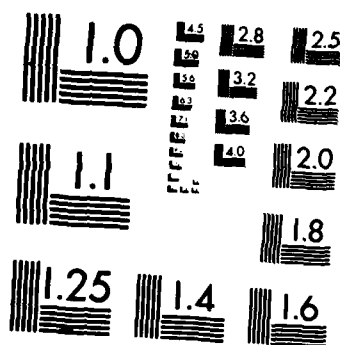
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By studying the difference between the oxidised and reduced spectra at each time delay it is possible to follow the rise of the P700 signal as the 690nm signal decays. Despite the short antenna decay lifetime and the spectral overlap of the 690nm and P700 signals, there is a clear delay in the appearance of the P700 signal relative to the rise of the 690nm signal. The rise time of the P700 signal is similar to the decay time of the 690nm signal, with the P700 signal reaching 80% of its final value within 20ps.

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DETERGENT EFFECTS UPON THE PICOSECOND DYNAMICS OF HIGHER PLANT
LIGHT HARVESTING CHLOROPHYLL COMPLEX (LHC2)

J.P.Ide, D.R.Klug, B.Crystall, B.L.Gore, L.B.Giorgi,
W.Kuhlbrandt*, J.Barber* and G. Porter
Davy Faraday Research Laboratory, The Royal Institution,
21 Albemarle Street, London W1X 4BS, U.K.
*Department of Pure & Applied Biology, Imperial College,
Prince Consort Road, London SW7 2BB, U.K.

Resolubilization of detergent extracted higher plant light harvesting complex (LHC2) from pea thylakoid membranes, is shown to produce a sample which is heterogeneous in terms of its aggregation state. The dependence of the degree of aggregation upon the chlorophyll:detergent molar ratio is monitored using the techniques of single photon counting, circular dichroic absorption spectroscopy and fluorescence spectroscopy. In general, greater aggregation is shown to lead to shorter fluorescence lifetimes and extra exciton features which can be compared with the known symmetry of the crystallized LHC2 previously determined to a resolution of $16\text{\AA}$ (Kuhlbrandt, 1984).

For the purposes of interpretation, the kinetics of energy transfer can be divided into three regimes of solubilization. A 'high' chlorophyll to detergent molar ratio leads to the formation of aggregates which show identical exciton features to crystals of an ordering equivalent to those used in determining the $16\text{\AA}$ structure. These features are a C_3 symmetric chlorophyll-b associated exciton, a chlorophyll-a/b exciton, and a dimeric exciton again associated with chlorophyll-b and indicative of significant fluorescence quenching. These 'crystals' are found to have fluorescence lifetimes of $\sim 300\text{ps}$. The 'medium' molar ratio condition produces the same exciton features as for the 'high' molar ratio, but with a much reduced 'quenching' exciton. The fluorescence decay kinetics of the medium molar ratio regime provide good fits to a biexponential decay with lifetimes of $\sim 1\text{ns}$ and $\sim 3\text{ns}$. In the 'low' molar ratio regime, all energy transfer from chlorophyll-b to chlorophyll-a is stopped, all circular dichroic exciton features are lost, and the major component of the chlorophyll-a fluorescence lifetime becomes $5.7 \pm 0.3\text{ns}$, which is the lifetime of chlorophyll-a in a micelle.

Two other detergent dependent effects have also been found. Firstly, a moderately low chlorophyll:detergent molar ratio causes a gradual collapse of chlorophyll-b to chlorophyll-a energy transfer, over a period of a few hours. However, the C₃ symmetric chlorophyll-b exciton is largely lost within five minutes followed by a gradual decline in the chlorophyll-a/b exciton, which follows the course of the collapse of energy transfer. Secondly, resolubilization of the LHC2 with SDS (as opposed to resolubilization using dioctyl-glucoside) causes an apparently immediate loss of the chlorophyll-a/b exciton, whereas both energy transfer and the C₃ symmetric chlorophyll-b exciton are retained over a period of hours. The circular dichroism spectra in the presence of SDS are identical to those previously produced by other workers (Van Metter, 1977; Shepanski and Knox 1981).

Our data provides circumstantial evidence that the C₃ symmetric exciton is due to the C₃ symmetry of the (crystallized) LHC2 trimer and that the LHC2 protein is not stable if the trimer structure is lost, which results in the eventual loss of energy transfer. Thus while none of the exciton features are necessary for the retention of energy transfer *per se*, they do represent different chromophore configurations. We conclude that the minimum stable functional unit of LHC2 *in vitro* is a trimer.

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SESSION G: SOLAR PHOTOCHEMISTRY

Chairman: B. STEVENS

- 14.00-14.30 **Keynote Lecture** A. HARRIMAN: Model systems for conversion and storage of solar energy
- 14.30-14.45 M.Z. HOFFMAN: Photodynamics of ion-pair electron donor-acceptor complexes. Methyl viologen, oxalate and EDTA
- 14.45-15.00 A. MILLS: Photoreduction of water using rose bengal and other xanthene dyes
- 15.00-15.15 M-C. RICHOUX: The stability of metalloporphyrin radical cations and anions in water
- 15.15-15.30 M.D. ARCHER: Solvent dependence of photochemical electron transfer rates in a covalently-linked porphyrin-quinone molecule
- 15.30-15.45 J.R. DARWENT: Photochemical reactions in semiconductor dispersions and colloids
- 15.45-16.00 **TEA**
- 16.00-18.30 **POSTER SESSION II** Posters associated with Sessions D, E, F and G to be manned
- 19.00-23.30 **BANQUET** at The Washington Hotel, Curzon Street, London W.1.
- 19.00-19.30 Sherry Reception
- 19.30-22.30 Dinner
- 23.30 Cash Bar closes

POSTERS associated with Session G:

- Z. ABOU-GAMRA and A. HARRIMAN: Photoredox reactions of gold (III) porphyrins
- H. ELLUL and A. HARRIMAN: Photoinduced intramolecular electron transfer processes in porphyrins
- A. HARRIMAN and X-J. LUO: Luminescence of copper porphyrins

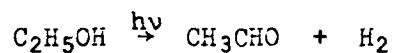
MODEL SYSTEMS FOR CONVERSION AND STORAGE OF SOLAR ENERGY.

Anthony Harriman,

Davy Faraday Research Laboratory, The Royal Institution,

21 Albemarle Street, London W1X 4BS, U.K.

Without doubt, the most realistic means of achieving efficient storage of solar energy involves the use of amorphous silicon based photovoltaic arrays. The future for homogeneous and heterogeneous photochemical systems does not look promising but this realisation does not mean that research into the development of such systems should be abandoned. Rather, it implies that future research should be concentrated on developing extremely simple and robust photosystems that can operate under quite primitive conditions. With this in mind, we have focussed attention upon the photo-dehydrogenation of ethanol:



$$\Delta G^\circ = + 42 \text{ kJ mol}^{-1}$$

Work has been restricted to low concentrations (<2% v/v) of ethanol in water, as might easily be obtained from low grade fermentation processes. The other essential ingredients needed for a successful device are a photosensitiser, a catalyst (usually metallic Pt) and (possibly) an electron relay. Potential compounds have been tested and several promising systems have been developed.

As a catalyst, ultrafine Pt colloids (radius 10-13Å) have been prepared and characterised. By high resolution electron microscopy, it has been found that these colloids are crystalline with well-ordered metallic structures. Even for particles containing only about 200 Pt atoms, the bulk and surface structure are closely related to those of bulk Pt electrodes. Thus, the particles can function as microelectrodes.

The choice of photosensitiser depends upon the overall reaction mechanism and several alternatives have been considered. Water-soluble benzophenones have been prepared which abstract a hydrogen atom from ethanol under illumination. The Pt colloid then recycles the ketyl radical before dimerisation or disproportionation occurs. Enzymes are able to oxidise ethanol quite easily, the electrons being used to reduce NADP to NADPH. Many metalloporphyrins will drive the oxidation of NADPH and the resultant reduced porphyrins can be used for H_2 generation. This cycle has been exploited to devise very efficient photosystems for the dehydrogenation of ethanol. Semiconductor systems have also been studied in some detail and several new materials have been identified.

A wide variety of electron relays has been investigated using cyclic voltammetry and pulse radiolysis techniques. In water, most organic radical anions protonate and subsequently undergo bimolecular destructive reactions. Stable radical anions are difficult to locate but we have identified and tested a few promising systems.

Overall, the photochemical dehydrogenation of ethanol has been achieved with modest efficiency in such a way that solar energy can be stored as H_2 fuel. Of course, this is not the perfect solution to the real problem but it is a practical approach to a difficult task.

PHOTODYNAMICS OF ION-PAIR ELECTRON DONOR-ACCEPTOR COMPLEXES.

METHYL VIOLOGEN, OXALATE, AND EDTA

Dasari R. Prasad and Morton Z. Hoffman

Department of Chemistry, Boston University

Boston, Massachusetts 02215, U.S.A.

Methyl viologen (1,1'-dimethyl-4,4'-bipyridinium dication; MV^{2+}) forms photochemically active ion-pair complexes with anionic species in aqueous solution. This interaction manifests as new absorption bands with discrete maxima or increased tail absorption from the near-uv into the visible spectral region to the red of the absorption bands of the uncomplexed components; the absorption can be attributed to a change in the radial electronic distribution between the pairs. The formation of the one-electron reduction product, $MV^{\cdot+}$, in flash photolysis demonstrates that the absorptions are charge-transfer in nature.

MV^{2+} forms a 1:1 complex ($K_{eq} = 21 \text{ M}^{-1}$) with $C_2O_4^{2-}$ at ambient pH (7.1). The continuous photolysis of deaerated solutions of this system at 254-380 nm generates $MV^{\cdot+}$ initially linearly with increasing irradiation time from which values of $\phi(MV^{\cdot+})$ are obtained. $\phi(MV^{\cdot+})$ is a function of the excitation wavelength and the fraction of light absorbed by the complex and the uncomplexed substrates; there is no evidence that light absorbed by uncomplexed MV^{2+} and $C_2O_4^{2-}$ results in any net photochemistry. Inasmuch as the oxidation of $C_2O_4^{2-}$ yields strongly reducing $CO_2^{\cdot-}$ (via the decarboxylation of ephemeral $C_2O_4^{\cdot-}$) which generates a second equivalent

Photodynamics of Ion-Pair Electron Donor-Acceptor Complexes

of $MV^{\cdot+}$, η_{cr} , the efficiency of release of redox products from the initially populated charge-transfer excited state can be calculated; η_{cr} exhibits a long-wavelength plateau (0.12 at 340-380 nm), and rises smoothly to 0.25 at 254 nm. Pulsed-laser excitation of mixtures of MV^{2+} and $C_2O_4^{2-}$ at 355 nm generates initially a transient absorption that is not that of free $MV^{\cdot+}$; its enhanced absorption in the 450-500 nm region is reminiscent of that displayed by reduced-viologen dimers and aggregates; no secondary formation of $MV^{\cdot+}$ due to the reduction of MV^{2+} by $CO_2^{\cdot-}$ is observed. Rather, the conversion of the initial absorption to that of free $MV^{\cdot+}$ occurs via $[MV^{2+}]$ -independent first-order kinetics in the μs time frame; k_{obs} decreases with increasing $[C_2O_4^{2-}]$. Under these conditions, where $[MV^{2+}] \gg 1$ mM, MV^{2+} can be visualized as existing as an aggregate in a hydrophobic core surrounded by a hydrophilic sheath of $C_2O_4^{2-}$; excitation of an ion-pair eventually results in the existence of two $MV^{\cdot+}$ species within a "pseudo-micelle." The final absorption change represents the formation of $MV^{\cdot+}$ in its equilibrated state in bulk solution.

The values of K_{eq} for 1:1 complexes between MV^{2+} and EDTA are 1.3, 13, 13, and 18 M^{-1} at pH 4.7, 8.0, 10.0, and 11.2, respectively; in highly alkaline solution, there is evidence for the existence of 2:1 complexes. Continuous photolysis of the system yields $MV^{\cdot+}$ with values of $\phi(MV^{\cdot+})$ that are a function of pH, excitation wavelength, and the [donor]/[acceptor] ratio. Under the conditions of constant substrate concentration and λ_{ex} , $\phi(MV^{\cdot+})$ decreases with increasing pH, showing the effect of the acid-base behaviour of EDTA ($pK_a = 0.0, 1.5, 2.0, 2.7, 6.1, \text{ and } 10.2$). At pH 10.0 with $[MV^{2+}] = 20$ mM and $[C_2O_4^{2-}] = 0.1$ M, $\phi(MV^{\cdot+})$ exhibits a long-wavelength (400-450 nm) plateau value of 0.01, rising smoothly to 0.13 at 290 nm. When solutions containing 0.1 M $C_2O_4^{2-}$ at pH 10.0 are irradiated at 320 nm, $\phi(MV^{\cdot+})$ increases as $[MV^{2+}]$ is increased to 20 mM, and then decreases, showing the effect of higher aggregates. The 355-nm pulsed laser excitation of the system generates initial-

Photodynamics of Ion-Pair Electron Donor-Acceptor Complexes

ly the spectrum of $MV^{+\cdot}$ species; as in the case of the $MV^{2+}/C_2O_4^{2-}$ system, the secondary reduction of MV^{2+} is not observed. Instead, a small increase in the absorption occurs via $[MV^{2+}]$ -independent kinetics in the μs time frame. The value of k_{obs} decreases as $[EDTA]$ and pH are increased.

In summary, it appears that ion-pair complexes of MV^{2+} exist as "pseudo-micelle" aggregates, so that the absorption of light by the complex does not initially generate $MV^{+\cdot}$ in its free, monomeric form. Rather, the reducing radicals formed from the oxidation of the donor (via decarboxylation, deprotonation, etc.) generate another equivalent of $MV^{+\cdot}$ within the aggregate; the $MV^{+\cdot}$ species therein would exist in an unstable environment, leading to the rearrangement of the aggregate structure as $MV^{+\cdot}$ is released into bulk solution in its final relaxed, equilibrated condition. The value of $\phi(MV^{+\cdot})$ in continuous photolysis reflects the competition within the aggregate among internal modes of decay of the initially formed excited states, back electron transfer, and the degradation of the oxidized donor radical.

"PHOTOREDUCTION OF WATER USING ROSE BENGAL AND OTHER XANTHENE DYES"

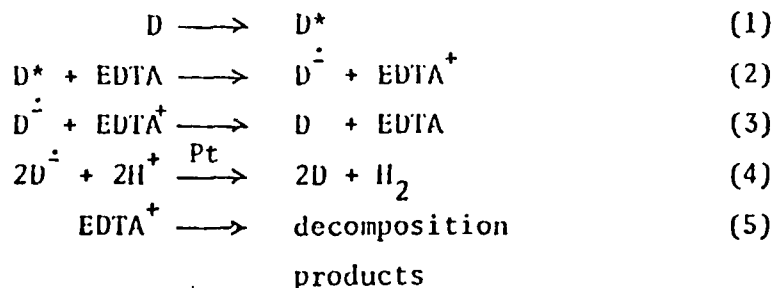
Andrew Mills* and Carl Lawrence

University College of Swansea

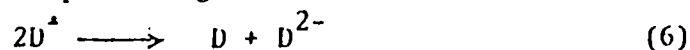
Department of Chemistry, Singleton Park, Swansea SA2 8PP

Xanthene dyes such as Rose Bengal and Eosin have several properties of interest to the photochemists working on the photo-reduction of water to hydrogen. These properties include large quantum yields for the formation of the triplet state (usually > 0.7) which are long-lived ($t_1 > 150\mu s$) and reactive ($(E^0 D_T^*/d^+) > -0.7$ V vs. SCE). Since the dyes absorb in the visible region of the electromagnetic spectrum, they appear ideal for sensitising the photoreduction of water using sunlight.

We have found that it is possible to photoreduce water via two distinct mechanisms using Xanthene dyes. The first mechanism is a photo-reductive quenching mechanism:

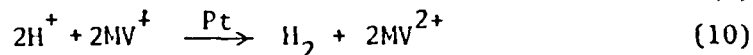
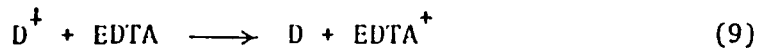
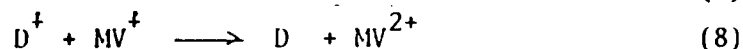
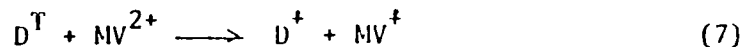


in this case EDTA is used as a sacrificial electron donor, however reaction (2) is slow (for example, with Rose Bengal k_2 ca. $20 \text{ M}^{-1} \text{ s}^{-1}$), and other complicating reactions occur such as

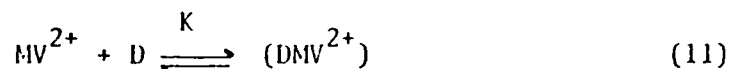


(where D^{2-} represent a permanently bleached reduced form of the dye). These latter reactions lead to the rapid destruction of the dye. In contrast, if methylviologen (MV^{2+}) is added to the reaction mixture then photooxidative quenching occurs very eff-

iciently (k_7 ca., $10^9 \text{ M}^{-1} \text{ s}^{-1}$) for all Xanthene dyes.



The addition of methyl viologen (10^{-4} M) increases the photostability of all the Xanthene dyes, however the cage escape yield for reaction (7) is usually low ($\ll 20\%$) and methyl viologen readily complexes with these dyes ($K > 5000 \text{ M}^{-1}$).



The complexed forms of the Xanthene dyes i.e. (DMV^{2+}) are able to sensitise the sacrificial reduction of methyl viologen, albeit inefficiently and appear very photostable.

In the above reactions ((1) - (11)) we have found the choice of solvent to be crucial. In water, a fine precipitate of (Xanthene/EDTA) forms slowly but the addition of a small amount of ethanol (5%) appears to prevent this.

The Stability of Metalloporphyrin Radical Cations and Anions in
Water

Marie-Claude Richoux

Photogeneration of O_2 from water is an integral part of green plant photosynthesis and represents the most natural means of storage of solar energy into chemical energy. Many laboratories have tried to mimic this natural process using model systems. For the same aim we have used metalloporphyrins to harvest light, creating excited species able to act as oxidising agents for the oxidation of water to O_2 .

We have studied the redox properties of several different metalloporphyrins, varying the central metal ion and the water solubilising groups.

The main technique used for producing porphyrin radical cations was pulse radiolysis. Under pulse-radiolytic conditions Br_2^- oxidises most of water soluble metalloporphyrins.

The stability of the resultant porphyrin radical cations depends upon the electron density residing on the porphyrin ring, which is controlled by the nature of the water-solubilising groups. Decreasing the electron density by attaching positively charged groups at the meso positions, or by replacing the central metal ion with a cation possessing a higher ionisation potential renders the radical cation unstable with respect to disproportionation. With negatively charged groups the radical cations are much more stable and good

examples are ZnTSPP and MgTSPP which possess long half-life and these two radical cations are able to generate O_2 from water when an adequate catalyst such as $RuO_2 \cdot 2H_2O$ is used. The rate of oxygen evolution was found to be dependent upon pH and the optimum was obtained for both MgTSPP and ZnTSPP at pH 12, with respective quantum efficiency of 27% and 50%.

In the same way we have tried to evaluate the factors that influence the stability of metalloporphyrin radical anions in aqueous solution.

Reduction of metal TMPyP complexes in aqueous solution gives rise to the corresponding radical anions. The lifetimes of these radical anions were found to vary greatly; those of Sb(V) and Sn(IV) are completely stable while those derived from most other metal ions decay on the ms timescale. In neutral solutions, the stability decreases in the order Sb(V) Sn(IV) In(III) Ge(IV) Ga(III) Al(III) Zn(II) which was found to correspond to the order of the porphyrin ring reduction potentials determined under identical conditions. Increased stability of the radical anions upon increasing the electronegativity of the central metal ion was found to be due to inhibition of porphyrin ring protonation, which is a necessary step in the formation of the final products. The final two-electron reduction products are mainly phlorins.

**SOLVENT DEPENDENCE OF PHOTOCHEMICAL ELECTRON TRANSFER
RATES IN A COVALENTLY-LINKED PORPHYRIN-QUINONE MOLECULE**

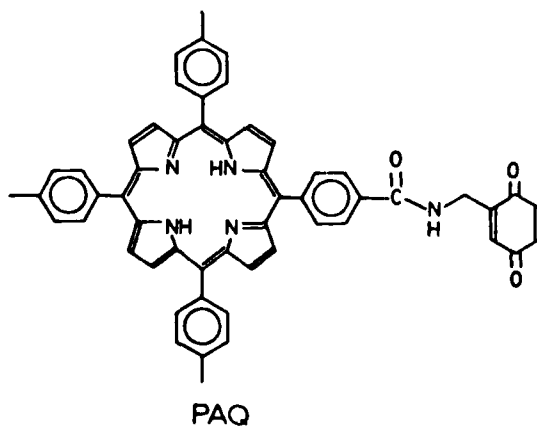
Mary D. Archer and Victor P.Y. Gadzekpo

Department of Physical Chemistry, University of Cambridge,
Lensfield Road, Cambridge CB2 1EP, U.K.

James R. Bolton, John A. Schmidt and Alan C. Weedon

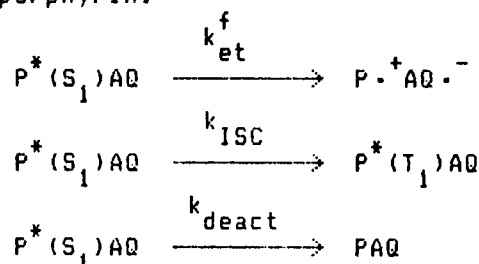
Photochemistry Unit, Department of Chemistry,
University of Western Ontario, London, Canada N6A 5B7

It is well known that the primary energy storage step of photosynthesis is a photochemical electron transfer from the singlet excited state of a chlorophyll donor to an acceptor. Many simple models of the photosynthetic reaction centre have been made by covalent linkage of an electron donor D to an acceptor A.¹ Covalent attachment confers special features not readily attainable in intermolecular D + A systems. The effective concentration of the quencher is sufficiently high for reaction from short-lived singlet states to be possible. Moreover, D and A may be held in a more or less rigid molecular framework at a defined distance. We have examined the amide-linked molecule PAQ shown below, in which the P-Q centre-to-centre distance is 1.5 nm.



We have determined the thermodynamics and kinetics of intramolecular photochemical electron transfer in PAQ in more than twenty solvents of widely varying static and optical dielectric constant D_s and D_{op} . The data have been tested for conformity both with Marcus theory and with various semi-empirical theories of solvent polarity.

Fluorescence quenching² and other studies of PAQ and related molecules provide strong evidence for the following decay channels of $P^*(S_1)AQ$ following its production by irradiation in the Q band region of the porphyrin:



The lifetime of the charge-separated state P^+AQ^- , which is also reached via intramolecular electron transfer from the triplet, is 1 - 10 ns. It undergoes rapid ($k_{et}^b > k_{et}^f$) back electron transfer to the ground state.³ The charge-separated state, although transient, is assumed sufficiently long-lived to acquire its equilibrium conformation and solvation in each solvent.



The rate constant k_{et}^f , calculated from the fluorescence lifetimes τ_1 and τ_2 of $P^*(S_1)AQ$ and the corresponding hydroquinone-containing compound P^*AQH_2 , lies in the wide range $(1 - 230) \times 10^7 s^{-1}$, depending on the solvent. Electron transfer is impossible in $P^*(S_1)AQH_2$ so, provided that k_{ISC} and k_{deact} are each the same for $P^*(S_1)AQ$ and $P^*(S_2)AQH_2$ in a given solvent,

$$k_{et}^f = 1/\tau_1 - 1/\tau_2$$

The Gibbs energy $\Delta G_{\pm}$ of the charge-separated state with respect to the ground state may be assessed from the difference between the first porphyrin ring oxidation potential O_1 and the first quinone reduction potential Q_1

$$\Delta G_{\pm} = e(Q_1 - Q_1) - U_{\text{corr}}$$

where U_{corr} is a correction term expressing the stabilization by charge and spin interaction of P^+AQ^- with respect to the electrochemically-produced species P^+AQ and PAQ^- . The Gibbs energy change of the forward electron transfer reaction is given by

$$\Delta G^0 = U_{0-0} - \Delta G_{\pm}$$

where U_{0-0} is the singlet energy of the porphyrin, provided that ΔS^0 , $\Delta V^0 = 0$ for the porphyrin excitation. By measuring Q_1 and Q_1 in various carefully-purified solvents, we find that $\Delta G_{\pm}$ lies in the range 1.3 to 1.6 eV, and ΔG^0 in the range -0.3 to -0.6 eV.⁴

Marcus theory⁵ gives the Gibbs energy of activation $\Delta G^{\ddagger}$ of an outer-sphere bimolecular electron transfer reaction as

$$\Delta G^{\ddagger} = (\lambda/4)(1 + \Delta G^0/\lambda)^2$$

where the reorganisation energy $\lambda = \lambda_{\text{in}} + \lambda_{\text{out}}$; λ_{in} is a solvent-independent contribution from structural changes within the reacting species and λ_{out} , which is a known function of D_s and D_{op} , is the contribution from the difference in the orientation and polarisation of the solvent around the reagent and product. The rate constant is related to $\Delta G^{\ddagger}$ by the transition state expression

$$\ln k_{\text{et}}^{\ddagger} = \ln A - \Delta G^{\ddagger}/kT$$

Our data are in fair accord with Marcus theory, for which it is important to take the ΔG^0 value appropriate to each solvent.

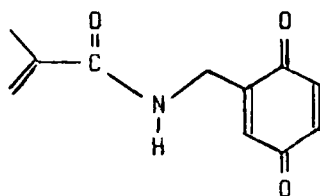
Several 'solvent polarity' scales, containing 1-4 independent parameters, have been proposed (e.g. Kosower's Z , Kamlet and Taft's π^* , α , β .) These scales are intended to provide linear correlations of the general form⁶

$$\ln k_{\text{et}} = \alpha + \beta f(D_s) + \gamma f(D_{\text{op}}) + SA + eC$$

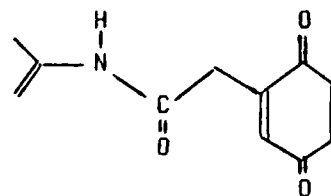
where A and C are anion-solvating (electron acceptor) and cation-solvating (electron donor) terms, respectively. The terms $f(D_s)$ and $f(D_{\text{op}})$ represent the respective contributions of orientation and distortion polarisation of the solvent continuum around the reacting species. We find very poor correlation of $\ln k_{\text{et}}^{\ddagger}$ with $f(D_s)$ and with all the A, C scales, but fair correlation with

$f(D_{op})$, which indicates the importance of solvent polarisability in determining the electron transfer rate.

There are obvious difficulties in applying any solvent parametric theory to intramolecular reactions, not least that the solvent cannot be 'between' the species that are about to react and that no role is assigned to the remainder of the molecule except via the Marcus parameter λ_{in} . However, it is widely thought that the interior of a successful D-A molecule may provide a favourable route, e.g. via π orbitals, for transduction of the electron. This appears to be so in P-Q molecules. Our values of k_{et}^f for PAQ in a given solvent are about an order of magnitude lower than those for the very similar molecule PA'Q synthesised by Gust et al.⁷



PAQ



PA'Q

PA'Q is identical with PAQ except for the direction of the amide linkage. Thus it is possible that the symmetrically placed C=O group assists forward electron transfer in a way not expressible by the theories outlined above.

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PHOTOCHEMICAL REACTIONS IN SEMICONDUCTOR DISPERSIONS
AND COLLOIDS

J.R. Darwent

Department of Chemistry

Birkbeck College, University of London

In the last ten years considerable academic attention has focused on model systems for artificial photosynthesis, with the aim of trapping solar energy by converting light into stored chemical potential.(1) One target of this research is the use of visible light to split water into hydrogen and oxygen. This requires the photochemical generation and separation of strong oxidising and reducing agents, followed by their transfer to additional redox catalysts where the oxidation and reduction of water can occur. This new research has lead to the development of a range of novel chemical systems which should find applications in areas other than solar energy conversion, for example in the development of photobacteriocides, photobleaches, and photo-imaging devices.

A particularly successful area of this research has been the development of "photocatalysts" based on semiconductor particles such as CdS and TiO_2 . These have the advantage of being integrated systems; the semiconductor absorbs light creating electron-hole pairs, which can then transfer rapidly through the semiconductor conduction and valence bands to catalysts such as Pt or RuO_2 adsorbed on the surface of the particles.(1) By integrating the system, in this way, it is possible to avoid many of the unwanted back reactions that plague photoredox reactions in homogeneous solution. As a result a number of efficient systems have been developed for the reduction and oxidation of water, as well as for photosynthetic organic and inorganic reactions, such as the production of amino acids and the oxidation

of halide ions to halogens.(1)

The semiconductor "photocatalysts" in these systems are usually of a few microns in diameter and the experiments are carried out on dispersions of semiconductor powders. As a result they are restricted to the measurement of product yields or trapping reactive intermediates - in much the style of the classical kineticists studying slow reactions - however recent work has focused on particles of colloidal dimensions (ca. 1-100nm in diameter).(2) These semiconductor colloids can be optically transparent and they are ideally suited to studies using fast reaction techniques, such as flash photolysis, time resolved Raman spectroscopy, and stopped flow. Such studies can lead to a more detailed understanding of the reactions involved and hence more efficient "photocatalysts". They can also lead to new fundamental information about the mechanism of interfacial charge transfer and the reactivity of radicals formed on the surface of semiconductor particles. The very fast time resolution, which is possible with flash photolysis, opens up a new method of studying the species which are involved in electrochemical processes.

This talk will include examples of work on both types of semiconductor system; macroscopic particles (diameter > 1 micron) and colloidal systems (diameter < 100nm). The results will deal mainly with work from our laboratory and should illustrate the attractions, advantages and pit falls of these types of systems.(3)

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PHOTOREDOX REACTIONS OF GOLD (III) PORPHYRINS

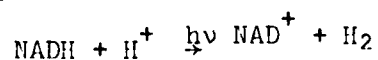
Z. Abou-Gamra and A. Harriman.

Davy Faraday Research Laboratory, The Royal Institution,
21 Albemarle Street, London W1X 4BS, U.K.

Water-soluble gold (III) porphyrins have been synthesized and their redox properties studied by a variety of techniques. The compounds exhibit hypso absorption spectra and they are stable over a wide pH range, being quite resistant to acid catalysed demetallation. No fluorescence could be detected from aqueous solutions of the gold (III) porphyrins but low temperature phosphorescence was readily observed. In outgassed aqueous solution, laser flash photolysis studies showed that the lifetimes of the first excited triplet states were ca. 2 μ s.

Cyclic voltammetry showed that the compounds were easily reduced to the corresponding π -radical anions. The electrochemical behaviour was quasireversible, suggesting that the π -radical anions were quite long-lived. In contrast, no peaks corresponding to one electron oxidation of the compounds could be resolved.

Steady-state irradiation of the various porphyrins ($\lambda > 400\text{nm}$) in aqueous solution containing NADH results in efficient reduction of the porphyrin ring. At short irradiation times, the observed product is the gold (III) porphyrin π -radical anion. Further irradiation results in formation of the phlorin (a monoprotonated porphyrin π -dianion). Aeration of the photolysed solution causes immediate reformation of the original porphyrin, with very little byproduct formation. Similarly, if colloidal Pt is added to a photolysed solution, both the π -radical anion and the phlorin transfer electrons to the colloid particles. Discharge of the particles causes reduction of water to H_2 . Consequently, the overall reaction may be written:



The system is extremely stable and, at pH 3.6, H₂ formation can be efficient. Since it is easy to reduce NAD⁺ to NADH using ethanol as electron donor, the overall system represents a modest means of storing energy.

Irradiation of the porphyrins in aqueous solution containing sodium persulphate as electron acceptor results in formation of 5,6-dihydroxyphorphyrins. The intermediate π -radical cations could not be observed as stable species and, even in the presence of a suitable catalyst, O₂ liberation did not occur.

PHOTOINDUCED INTRAMOLECULAR ELECTRON TRANSFER PROCESSES IN
PORPHYRINS

H. Ellul and A. Harriman

Davy Faraday Research Laboratory, The Royal Institution,
21 Albemarle Street, London W1X 4BS

Porphyrins, by virtue of their absorption profiles and photophysical properties, have attracted considerable attention as possible photosensitisers in solar energy storage devices. Accepting that such a device must operate on the basis of spatial charge separation, it is a necessary feature that the first chemical step in the overall process involves rapid electron transfer to or from the singlet excited state of the porphyrin to a suitable donor or acceptor. Because of the limited lifetime of such excited singlet states (typically <10 ns) and the relative slowness of mass diffusion, it is desirable to design systems in which the donor and acceptor groups are held in close proximity. However, there must be some barrier (spatial or kinetic) to reverse electron transfer or else geminate recombination will dominate. In our work, two classes of compound have been studied; namely porphyrins covalently linked to crownether moieties and porphyrins substituted at each of the four meso C atoms with alkyl viologens.

In the former case, octaethylporphyrins covalently bridged to two N_2O_4 crownethers have been synthesized by J.M. Lehn and coworkers. The crownethers are held in place by either a bridging biphenyl or a second porphyrin molecule so that the overall molecule has a well defined structure. Photophysical properties have been evaluated for the various compounds in several solvents. Inserting silver (I) ions into the crownether void results in extremely efficient quenching of the porphyrin fluorescence. On the basis of flash photolysis studies, the quenching mechanism is believed to involve electron transfer to the metal cation.

The porphyrin viologen complexes have a flexible alkyl chain connecting the reactants. This ensures a large number of conformations existing in equilibrium but, because there are four viologens attached to each porphyrin, there will always be fairly close contact between the reactants. As above, the singlet excited state of the porphyrin is highly quenched due to rapid electron transfer to a viologen molecule. The efficiency of both forward and reverse electron transfers depends markedly upon the average distribution of conformations. In turn, this depends upon the solvent and hydroxylic solvents (e.g. water or methanol) tend to give very fast electron transfer steps. Aprotic solvents (e.g. N,N-dimethylformamide) give slower forward electron transfer but the redox ion products live for several hundred nanoseconds.

Luminescence of Copper Porphyrins

A. Harriman and X. Luo

Davy Faraday Research Laboratory

The Royal Institution, 21 Albemarle Street,

London W1X 4BS

The photophysical properties for a large number of metalloporphyrins have been evaluated in recent years, primarily because of the possible use of such compounds as photosensitisers in solar energy storage devices. Most attention has focussed upon diamagnetic metalloporphyrins, such as zinc(II) meso-tetraphenylporphyrin (ZnTPP), which possess long-lived triplet excited states in outgassed solution. Little interest has centred upon metalloporphyrins with paramagnetic central metal ions, such as CuTPP, since the excited state lifetimes of these compounds are often extremely short. For example, ClFeTPP has a reported lifetime for the lowest energy excited state of only ca. 30 ps in solution. In this paper, we consider the photophysical properties of CuTPP and related compounds and show that the triplet manifold consists of several thermally-equilibrating excited states.

CuTPP and its close analogues show no fluorescence from the first excited singlet state ($\Phi_F < 10^{-5}$) whilst the radiative rate constant (k_F) has a value of ca. 10^7 s^{-1} . Thus, the lifetime of the first excited singlet state must be less than 1 ps. These values are unaffected by the presence of electron donating or withdrawing substituents attached to the porphyrin ring.

Room temperature luminescence cannot be observed but

relatively intense phosphorescence is seen in frozen glasses. For CuTPP in methylcyclohexane at 80K, the observed phosphorescence spectrum is quite broad with a maximum around 750 nm. Close examination of the ground state absorption spectrum shows that there is a weak S_0-T_1 transition around 710 nm so that the luminescence seems to arise from the triplet manifold. The total luminescence quantum yield at 80K is 0.06. Time resolved studies show that at least two emitting states contribute towards the observed luminescence; the derived lifetimes being 0.6 and 0.1 ms at 80K.

The maximum of the phosphorescence emission was found to be strongly dependent upon the nature of any substituent groups attached to the porphyrin ring. Electron donating groups pushed the maximum towards 730 nm whilst withdrawing groups gave a maximum around 800 nm. In all cases, the emission spectrum could be resolved into two peaks. One peak, centred at 740 nm, was independent of substituent and had an excited state lifetime of ca. 0.1 ms. This is assigned to emission from the tripquartet state. The second peak was dependent upon the type of substituent and had the longer lifetime. This luminescence is assigned to a charge transfer state.

At room temperature in outgassed benzene solution, the triplet excited state absorption spectra of the various copper porphyrins are so broad that intimate spectral details cannot be resolved. Kinetic studies show that the excited state lifetimes are around 35 ns. Presumably, the tripquartet and charge transfer states are in thermal equilibrium at 300K.

WEDNESDAY 16 JULY 1986

SESSION D: ELECTRON/PROTON/ENERGY TRANSFER PROCESSES

Chairman: F. WILKINSON

- 09.30-10.00 **Keynote Lecture** G. WILSE ROBINSON: Molecular aspects of ionic hydration reactions
- 10.00-10.15 G.S. BEDDARD: Photoinduced electron transfer in capped porphyrins
- 10.15-10.30 S.M.B. COSTA: Fluorescence quenching kinetics in reversed micelles
- 10.30-10.45 L.K. PATTERSON: Effects of molecular organisation on photophysical behaviour. Kinetics of pyrene labelled lipids in spread monolayers
- 10.45-11.00 **COFFEE**
- 11.00-11.30 **Keynote Lecture** M. KASHA: Proton-transfer spectroscopy. The tautomeric potential and its perturbation
- 11.30-11.45 R.S. DAVIDSON: Triplet production and quenching in the reactions between aromatic hydrocarbons and tertiary amines
- 11.45-12.00 D. CREED: Intramolecular and intermolecular processes in the photochemistry of tertiary-amino substituted thiazine dyes
- 12.00-12.15 K. KALYANASUNDARAM: Luminescence, absorption and redox reactions of MLCT excited state of tricarbonylchloro(polypyridyl)rhenium(I) complexes
- 12.15-12.30 M.I. SAVADATTI: Energy transfer dye lasers
- 12.30 **LUNCH**

POSTERS ASSOCIATED WITH SESSION D:

P. DOUGLAS: Photochemistry of 1H-pyrazolo (3,2-c)-s-triazole azamethine dyes

Molecular Aspects of Ionic Hydration Reactions

G. W. Robinson

Texas Tech University

Lubbock, Texas 79409

Photokinetic experiments [1-5] on ultrafast timescales have suggested that the integrity of the quasi-tetrahedral oxygen structure of liquid water sets the stage for both electron and proton hydration in aqueous media [6]. Acid dissociation, and the attendant proton hydration, produces the much discussed H_9O_4^+ ion [7] as a direct kinetic product. The parallel electron process gives rise to a similarly constituted ion, H_8O_4^- . This may be the hydration product of a distorted water anion H_2O^- , such as an $\text{OH}^- \cdots \text{H}_3\text{O}$ semi-ionic pair, and bears on the solvated electron problem [8,9] in radiation chemistry. In Eigen's rate measurements [10,11] of acid/base neutralization, the reactions were diffusion controlled. Using newly developed mixed solvent methods [12], the reverse dissociation process has been found to span the gap between a "diffusion controlled" regime --

translation of water molecules to satisfy the local concentration requirement, and a "reaction controlled" ("hydration controlled") regime -- rotational diffusion of water molecules to satisfy the local structural requirement. Hydration rates of these "elementary ions" in the hydration controlled regime parallel dielectric and spin-lattice relaxation, shear viscosity and other physical phenomena in water where large amplitude rotations of water molecules play a dominant role. The necessary hydrogen reorientational motions in elementary ion hydration at threshold energies thus limit the rates of electron and proton hydration processes to $\leq \tau_D^{-1}$, where τ_D is the Debye relaxation time. The role of the longitudinal relaxation time τ_L ($\ll \tau_D$) in ion hydration is also discussed. A new semi-empirical parameter [13,14], which correlates thermodynamic and transport properties and the hydration rates with molecular rotations in pure liquid water (-30°C to $+100^\circ\text{C}$), is introduced. Comparisons between photon-initiated acids, such as the excited states of 1- and 2-naphthol [15], and normal weak acids are made. These proton precursors are further compared with electron precursors. Free energy diagrams are introduced to help understand these correlations, with emphasis on the entropic contribution, which often dominates enthalpy terms. Equilibrium populations of states in the transition region quantitatively explain the rate phenomena. New absolute rate expressions for acid dissociation/

recombination processes, which incorporate τ_D^{-1} and thermodynamic data, directly follow. A hydrogen:deuterium isotope rate factor of approximately 2.5:1 arises from purely entropic effects because of the stiffly structured nature of the hydrated proton or electron.

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Photoinduced Electron Transfer in Capped Porphyrins

R. Harrison, G.S. Beddard
Dept. of Chemistry,
University of Manchester
J. Cowan, J.K.M. Sanders
Dept. of Chemistry,
University of Cambridge

Photoinduced electron transfer from porphyrins to several capping groups, such as quinone or pyromellitide, has been demonstrated to occur on the picosecond time scale. Both charge separation and recombination were observed. The rates of these processes depend upon reaction free energy and good agreement with theory is obtained. Temperature dependent measurements show the electron transfer rate falling as the temperature is lowered, reaching a steady value where tunneling limits the rate.

FLUORESCENCE QUENCHING KINETICS IN REVERSED MICELLES

SÍLVIA M. B. COSTA

CENTRO DE QUÍMICA ESTRUTURAL, COMPLEXO I
INSTITUTO SUPERIOR TÉCNICO
AV. ROVISCO PAIS, 1096 LISBOA CODEX, PORTUGAL

Reversed micelles have been used to mimic membrane functions since they offer the possibility of binding substrates in charged microscopic interfaces as well as that of solubilizing ionic molecules in water pools. Studies of absorption and emission of zinc tetraphenylporphyrin (ZnTPP) in reversed micelles of benzyldimethyl-n-hexadecylammonium chloride (BHDC) showed an equilibrium between two spectroscopically different porphyrin species formed by varying the water content $w_o = [H_2O]/[Surf]$ in these micelles(1). Similar findings were observed with the water soluble derivatives, zinc tetramethyl pyridilporphyrin (ZnTMPyP⁴⁺) and zinc tetrasulphonate phenylporphyrin (ZnTSPP⁴⁻).

Fluorescence quenching kinetics studied by steady-state and time-resolved fluorescence spectroscopy were used to assess the probe location. The results obtained are summarized as follows:

- 1) The quencher located at the organic phase (duroquinone) interacts dynamically with the singlet-state of the porphyrin (ZnTPP or ZnTSPP⁴⁻) but at higher quencher concentrations the distribution at the micellar interface has to be considered. The rate constant for the quenching process can be evaluated from (1) and (2).

$$\frac{I_f^o}{I_f} = (1 + k_q \tau_o [Q_t]) \exp (K [Q_t]) \quad (1)$$

$$\frac{\tau_f^o}{\tau_f} = 1 + k_q \tau_o [Q_t] \quad (2)$$

where K is the equilibrium constant between quencher molecules (Q_e) in the organic phase and quencher molecules in the micellar interface (Q_i), and Q_t is the total quencher concentration. Fluorescence intensities at intermediate w_o would have to be corrected for the distribution function of aggregates of porphyrin.

- 2) The quencher bound at the interface (anthraquinone sulphonate) in the water pool interacts statically with porphyrin molecules at the interface but does not quench porphyrin molecules in the organic phase. Steady-state data is in rather good agreement with data obtained from a time correlated single photon counting study of the system ZnTPP/AQS/BHDC/Benzene ($w_o = 0$) (2). By contrast, if porphyrin molecules are in the water pools, the quenching is dynamic and its efficiency increases with the size of the water pool.
- 3) The quencher located in the water pool (methyl viologen) not bound at the interface interacts only with porphyrin molecules also in the water pool. At high water content a statistical homogeneous distribution is observed but the quenching efficiency is much greater than in the aqueous solution, whereas at low water content the water pool is rigid, the interaction is static and a Poisson distribution of the quencher is observed.

The occurrence of efficient fluorescence quenching in these organizes will be discussed in the context of photoelectron transfer in reversed micelles⁽³⁾ supported by laser flash photolysis studies in these systems.

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Effects of Molecular Organization on Photophysical Behavior.

Kinetics of Pyrene Labeled Lipids in Spread Monolayers.

Maria Bohorquez and L.K. Patterson

Radiation Laboratory and Department of Chemistry

University of Notre Dame, Notre Dame, Indiana 46556 USA

Because the environment of a pyrene molecule may markedly influence its behavior in a variety of photophysical processes (e.g. monomer quenching, excimer formation and decay, exciplex formation) this molecule is an excellent probe for examining the effects of molecular organization on excited state behavior. The spread monolayer at the air-water interface provides a unique model system in which to study such effects, providing as it does the means for continuously controlling the degree of organization in the system and a thermodynamic means for monitoring that organization. Using both steady state and time resolved fluorescence techniques, one may then attempt to correlate the behavior of a probe, such as pyrene, at the molecular level with thermodynamic data gathered from surface pressure-area measurements. Such correlation should reveal useful information concerning the interplay of influences exerted by molecules in organized arrays and behavior of excited states. The kinetics of singlet pyrene monomer and excimer have been examined in monolayers of dioleoylphosphatidylcholine containing the lipid probe, 6-(pyrenylhexanoyl)-2-palmitoyl-sn-glycero-3-phosphorylcholine. Steady state and time resolved measurements were carried out as a function of probe concentration and surface pressure. The data have been interpreted in terms of the Birks' treatment of monomer-excimer equilibria at high probe concentration to obtain diffusion coefficients for the probe.

PROTON-TRANSFER SPECTROSCOPY. THE TAUTOMERIC POTENTIAL AND ITS PERTURBATION.

Michael Kasha

Department of Chemistry and Institute of Molecular Biophysics

The Florida State University, Tallahassee, Florida 32306

Proton-transfer electronic spectroscopy is currently under intensive investigation in many laboratories. The reasons for this accelerated interest include: (a) picosecond laser spectroscopy permits detailed analysis of the mechanism of phototautomerization [1, 2]; (b) new laser development can derive from some of the molecular species which are found to phototautomerize [3]; (c) detailed quantitative mechanistic models on the fundamental nature of ground-state tautomerism are being developed; (d) the phenomena involved in phototautomerism are spectroscopically novel, and finally (e) (photo-) proton pump mechanisms are of great current interest in biology.

In experimental studies, intramolecular proton transfer can be classified by distinct cases: (1) intrinsic; (2) dependent on cyclic (H-bonded) mono-solvate formation or dimerization, or (3) requiring two or more solvent molecules cyclically bound to the solute. The general result is that Case (1) molecules (e.g., 3-hydroxychromone, 3-hydroxyflavone [3-6]) can exhibit excited-state proton transfer only in the absence of external H-bonding perturbation; Case (2) molecule monosolvates [7] and dimers [8] (e.g., 7-azaindole) can exhibit excited-state proton transfer tautomer fluorescence in competition with normal fluorescence; Case (3) molecules (e.g., 7-hydroxyquinoline [9, 10]) require, we propose, a 2-molecule hydrogen-bonded solvent cycle for a proton transfer bridge. All intramolecular cases lose excited-state proton transfer tautomerization with discrete chain H-bonding perturbation at the solute proton-donor and proton-acceptor sites [5].

Competition is offered to the above processes by other intermolecular phenomena, e.g., anion formation by proton transfer to

solvent molecules [5] (3-hydroxyflavone); exciplex formation with solvent molecules [11] (7-azaindole); and more complex internal conversion quenching mechanisms through excited state interaction perturbed by solvation [12] (5-hydroxyflavone).

Spectroscopic study of excited-state intramolecular proton-transfer focuses attention on the nature of the multiple-minimum potential function appropriate to each case, and the consequences of its effect on proton tunneling, or barrier activation. In general, the potential functions for intramolecular proton transfer are found to be subject to inter-molecular solvent-cage perturbations, or specific solute-solvent site perturbations. The Somorjai-Hornig [13] double-minimum potential with its quartic repulsion and quadratic barrier can serve as one starting point; in contrast, the Goldanskii double-minimum potential based on Morse functions [14], may prove to be more physically realistic. To these intramolecular potentials one can adduce the influence of inter-molecular perturbations by the Dellinger-Kasha solvent cage perturbation model [15, 16] based either on a Gaussian viscous-flow potential barrier, or the analytical Lennard-Jones potential barrier [17].

In classical chemistry, tautomerization has been defined in terms of the equilibrium ratio between two tautomeric forms. Now with laser pumping in the four state system, the ground state and excited states of the unstable tautomer can be studied, in particular those cases in which the "odd" tautomer is little populated at normal molecule ground state equilibrium. Thus, the dynamics of "odd" tautomer formation and disappearance, as well as pulsed Raman spectroscopy of vibrational frequencies of "odd" tautomers become accessible. Another aspect previously overlooked is the role of triplet potentials in singlet state tautomerization, a topic now under study in our laboratory with picosecond spectroscopy.

A survey of the above phenomena will be given, with extensions to photobiological molecular cases (lumichrome and DNA bases) [18]. The detailed molecular mechanisms for the cases studied offer a pathway to the development of proton-pump mechanisms currently under discussion in membrane transport [19, 20].

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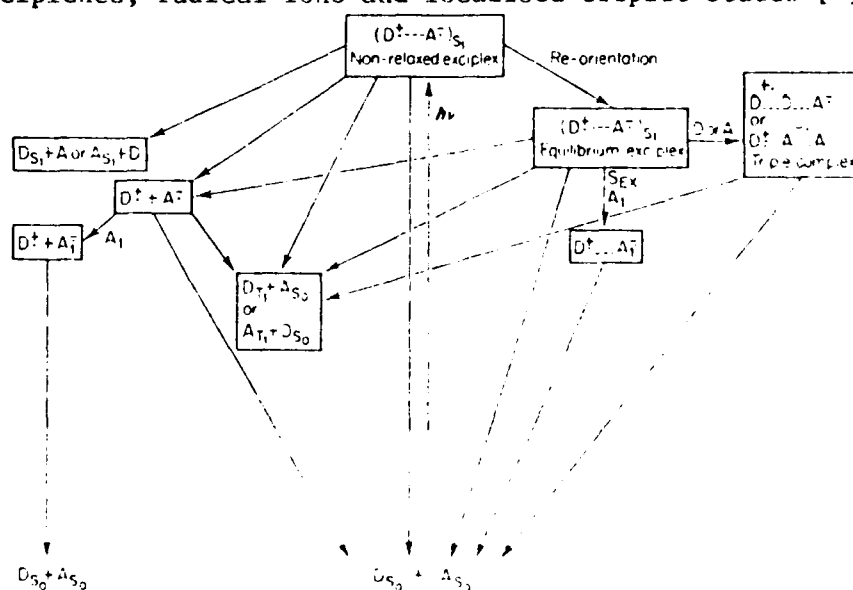
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TRIPLET PRODUCTION AND QUENCHING IN THE REACTIONS BETWEEN AROMATIC HYDROCARBONS AND TERTIARY AMINES

R.A. Beecroft, R.S. Davidson and D. Goodwin

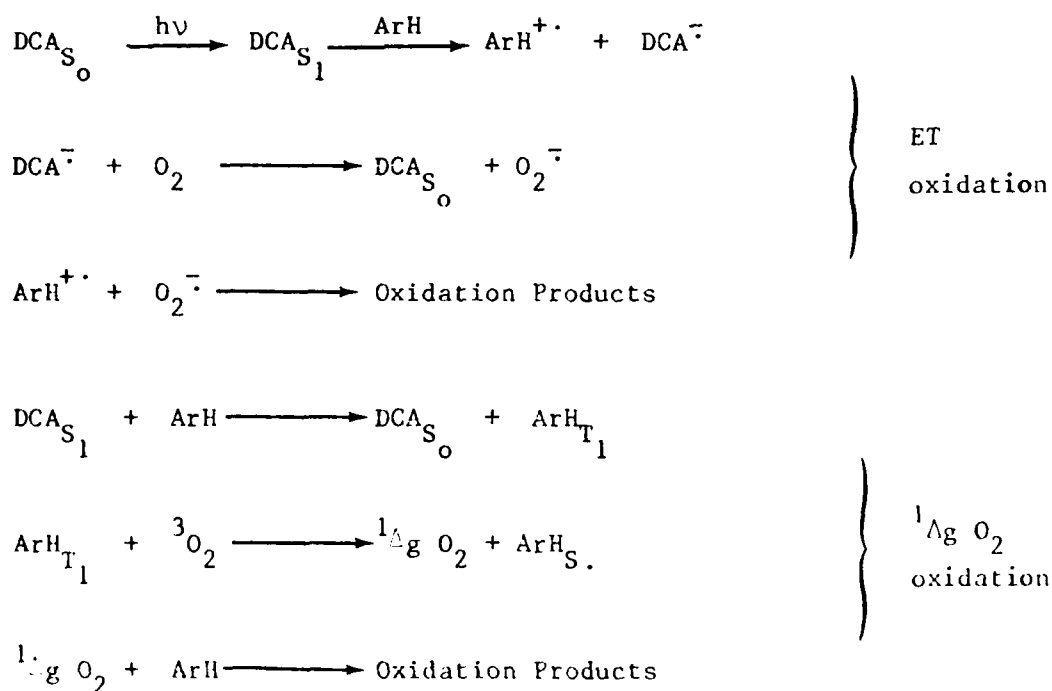
Department of Chemistry, The City University,
Northampton Square, London EC1V 0HB, U.K.

Microsecond [1], nanosecond [2] and picosecond [3] flash photolysis have played an important part in unravelling the complex and intertwining pathways of the photophysical processes associated with photoinduced electron transfer reactions. The decay pathways of the initial encounter complex between a molecule in its excited singlet state and a potential electron donor or acceptor can lead to exciplexes, radical ions and localised triplet states [4].



Boxes indicate species which may lead to chemical reaction. In this scheme it is assumed that D_{T1} or A_{T1} are of lower energy than $D^+ + A^-$. D_{S0} , A_{S0} represent the donor and acceptor molecules in their singlet ground state.

The production of triplet states [5] via electron transfer processes and their decay routes appears to be the 'Cinderella' of the system. That triplet states are produced by such systems has been demonstrated using microsecond and nanosecond flash photolysis [5]. The influence of magnetic field effects upon the intersystem crossing processes has been particularly useful for obtaining the rate constants for triplet production by the recombination of radical ions [6]. Which route predominates for triplet production is solvent dependent with the processes involving radical ions being favoured by the use of highly polar solvents. These results are not without consequence for chemistry. For example, the production of localised triplet states in oxygenated solution can lead, via energy transfer to singlet oxygen production. Studies of the kinetic solvent isotope effects exhibited by photooxidation reactions in which exciplexes and excimers are the source of triplet states confirm the correctness of this proposal [7]. In a recent very detailed study of the photooxidation of stilbene sensitised by 9,10-dicyanoanthracene it has been shown that electron transfer and singlet oxygen pathways compete and which process predominates is highly solvent dependent [8].



That electron transfer between aromatic hydrocarbons and cyanoanthracenes takes place has been confirmed by laser flash photolysis [9].

In accord with other workers we have found that the quenching of the excited singlet state of aromatic hydrocarbons by tertiary amines leads to production of the triplet aromatic hydrocarbon. Studies of the decay of the triplet species showed that they are quenched by tertiary amines [10]. In order to enhance this process we have used a variety of α,ω -diaminoalkanes as quenchers. Since acetonitrile was employed as solvent for these reactions we expected, on the basis of earlier work [11], to see a small effect of chain length (the number of methylene groups interposed between the amino groups). The only trend to be observed was a small increase in rate constant as the chain length increased. We believe that the quenching of the triplet aromatic hydrocarbons by tertiary amines is an electron transfer process with the quenching process occurring in the encounter complex.

Financial Support for the project was given by the SERC and The City University, for which we are extremely grateful. In addition, RSD should also like to express his gratitude to Sir George Porter FRS, for introducing him to the technique of laser flash photolysis by allowing him to have driving lessons at the Royal Institution.

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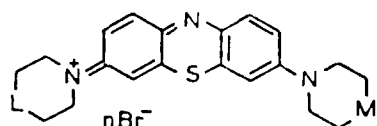
INTRAMOLECULAR AND INTERMOLECULAR PROCESSES IN THE PHOTOCHEMISTRY OF TERTIARY-AMINO SUBSTITUTED THIAZINE DYES

David Creed

Dept. of Chemistry, University of Southern Mississippi

Southern Station, Hattiesburg, MS 39406-5043, USA

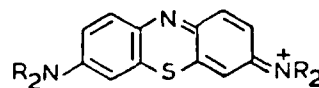
The singlet and triplet state properties of tertiary amino-substituted thiazine dyes such as 1 and 2 differ markedly from those of analogous dyes such as 3 and 4 that lack easily oxidizable side chain groups. A combination of steady-state



1, L = M = NCH₃, n = 1

2, L = O, M = NCH₃, n = 1

3, L = M = N⁺(CH₃)₂, n = 3



4, R = CH₂CH₂OH

and transient spectroscopic methods is being used to investigate the photophysics and photochemistry of these compounds. Lifetimes, τ_s , of the weak dye fluorescence have been measured using the ca. 20ps, 532nm output of a mode-locked Nd-YAG laser with streak camera detection. Values of τ_s for 3 and 4 at pH 2 or 9 are in the range of 160-250ps and τ_s for 1 at pH 2 is 190ps. However, at pH 9 where the tertiary amino groups are unprotonated τ_s for 1 drops to ca. 40ps. For the unsymmetrically substituted dye, 2, the effects of pH are less dramatic: τ_s values are 100ps and 60ps at pH 2 and 9, respectively. The short singlet lifetimes preclude any diffusional quenching process and we are currently seeking evidence from flash photolysis experiments for intramolecular electron transfer from the side-chain to the ring as a possible quenching mechanism for the singlet state. The intermolecular photoreduction of excited thiazine dyes by amines

is already well-known¹. Indeed the triplet state of 1 is self-quenched at pH 10 with $k_{SQ} = 1.1 \times 10^9 M^{-1} s^{-1}$, an order of magnitude greater than typical k_{SQ} values for N-alkyl substituted thiazine dyes.² Significant effects of pH on the triplet lifetimes, τ_T of these dyes, can also be observed although complicated by triplet state protonation in addition to the ground state protonation of the amino side-chains. For example, τ_T is 5 μs for 1 in 0.1N H_2SO_4 but only 0.7 μs at pH 10. This effect is the opposite to that observed for thiazine dyes such as 4 or methylene blue that generally have unprotonated triplet states much longer lived than the protonated states.

The relevance of these photophysical observations to the photochemistry of dyes such as 1 will be further discussed.

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Acknowledgements. Picosecond time scale experiments were conducted at the Center for Fast Kinetics Research (CFKR) at the University of Texas. Work done at the CFKR is supported by the Biotechnology Branch of the Division of Research Resources of NIH and by the University of Texas. Nanosecond flash photolysis equipment at the University of Southern Mississippi was purchased through a generous grant from the National Science Foundation.

LUMINESCENCE, ABSORPTION AND REDOX REACTIONS OF MLCT EXCITED STATE
OF TRICARBONYLCHLORO(POLYPYRIDYL)RHENIUM(I) COMPLEXES

K. Kalyanasundaram

Institute of Physical Chemistry,
Swiss Federal Institute of Technology (EPFL),
1015 Lausanne, Switzerland

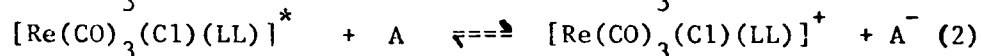
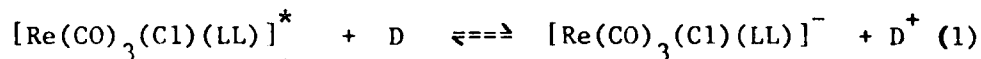
Amongst mononuclear metal carbonyl derivatives, polypyridyl-rhenium(I) complexes are interesting candidates for detailed studies of photochemistry and photophysics[1,2] Novel excited state reactions such as sensitized photoreduction of extreneous ligands, photosubstitution and catalytic reduction of CO_2 have been reported to occur[3-6]. In this paper we describe some of our laser flash photolysis results on three aspects of the photophysics and photoredox chemistry of MLCT excited state of tricarbonylchloro-(polypyridyl)Re(I) complexes, $[\text{Re}(\text{CO})_3(\text{Cl})(\text{LL})]$, ($\text{LL}=\text{bpy}, \text{Me}_2\text{-bpy}, \text{phen}$ and 5-Cl phen): a) medium sensitivity of the luminescence, b) absorption spectral features and c) reversible and irreversible reductive quenching of the MLCT excited state and their relevance to the problem of photoinduced catalytic reduction of CO_2 .

The absorption spectra of these complexes in the near UV-Visible region are dominated by intense MLCT $[\text{Re}(\text{I})(d\pi) - \pi^*(\text{LL})]$ transitions. The complexes exhibit weak red luminescence in fluid solutions ($\phi > 10^{-3}$). The MLCT absorption, emission spectra are rather broad, asymmetric arising presumably from several different electronic transitions. Both the absorption, emission are extremely sensitive to the nature of the solvent medium. Table 1 presents some representative data for the phen, bpy complexes. In general, the change of solvent from polar to non-polar in character is accompanied by a red shift in the CT absorption, enhanced emission yields and longer lifetimes. The emission maxima of 'bpy' complexes hardly show any spectral shift while those of 'phen' exhibit small blue shifts. The MLCT excited state lifetimes are typically in the range of 40-70 nsec for bpy and 150-340 nsec. for phen as the diimine ligand. More

extensive data on the solvent effects and a discussion on the origin of these solvents will be presented.

The absorption spectra of the MLCT excited state of these polypyridylRe(I) complexes have been recorded using a nsec. laser flash photolysis set up. Fig. 1A presents a representative difference spectrum (for the 'phen' complex) in degassed acetonitrile. The spectra are characterised by two maxima, one around 480-500 nm (estimation of the exact maximum rendered difficult by the emission) and the other around 300 nm (phen) or 350 nm (bpy-type). The minima observed around 380 nm are very close to the maxima in the gr.state absorption. Extinction coefficients at the maxima have been determined via intensity saturation methods.

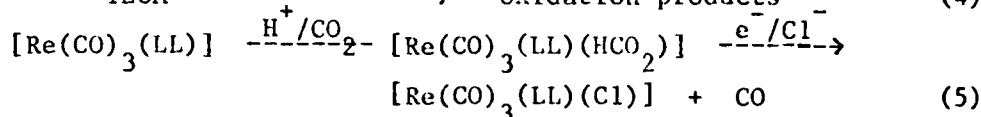
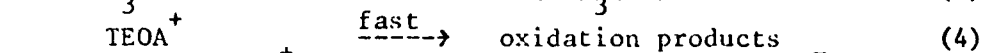
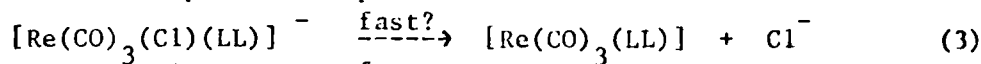
As with the other transition metal polypyridyl complexes with a low lying MLCT excited state, the tricarbonylhalo(polypyridyl)Re complexes also undergo efficient excited state electron transfer reactions, oxidatively and reductively:



Determination of the excited state absorption spectrum allows a quantitative study of the nature, efficiency of such photoredox processes. The reductive quenching in particular has received some attention recently as a potential route for photoinduced catalytic reduction of CO_2 to CO, a topic of much interest in the photochemical conversion of solar energy. The cage escape yields of photoredox products and nature of reverse electron transfer have been examined in detail for several reversible, irreversible quenchers. Fig. 1B presents some representative spectra of the redox intermediates obtained during the reductive quenching of $[\text{Re}(\text{CO})_3(\text{Cl})(\text{phen})]$ by various amines. The spectra are characterised by absorptions from the amine cations (D^+) and the reduced Re complex.

Quantitative studies of the transients formed via eq.(1) have shown that the cage escape yield of products are indeed quite high ($\phi > 0.7$). With aromatic amines as donors (dimethylaniline(DMA) or diphenylamine(DPA) for example), at high laser pulse intensities the reverse electron transfer occurs very efficiently (over 90%, II order equal concentration kinetics) at diffusion controlled rates. For aliphatic amines such as triethanolamine(TEOA) or triethylamine(TEA), the transients decay very slowly in a complex manner over several milliseconds. As the decay kinetics are not the same over the entire spectral range and small growths observed at 550-600 nm, it is inferred that either or both of the redox products disintegrate rapidly in competition with the reverse electron transfer. The formation and decay behaviour of the redox products are very similar in Ar-bubbled and CO_2 -bubbled solutions, suggesting the

intervention of CO_2 to occur at some later stages after the disintegration of the photoredox products. Details on the kinetic behaviour



of the redox products at several wavelengths, evolution of the absorption spectra of the transients and possible mechanisms for the catalytic reduction of CO_2 will be elaborated.

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Table 1 Absorption, emission characteristics of MLCT excited state of $[\text{Re}(\text{CO})_3(\text{Cl})(\text{LL})]$ in various solvents at room temperature

Solvent	LL = 2,2-bpy			LL = 1,10-phen		
	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	τ_{ns}	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	τ_{ns}
CH_3CN	370	612	48	364	602	178
DMF	373	610	45	366	604	155
EtOH	372	604	36	369	590	216
CH_2Cl_2	384	612	50	374	592	288
THF	388	614	65	382	612	335
Dioxane	390	614		384	610	
Benzene	400	612	70	388	596	320

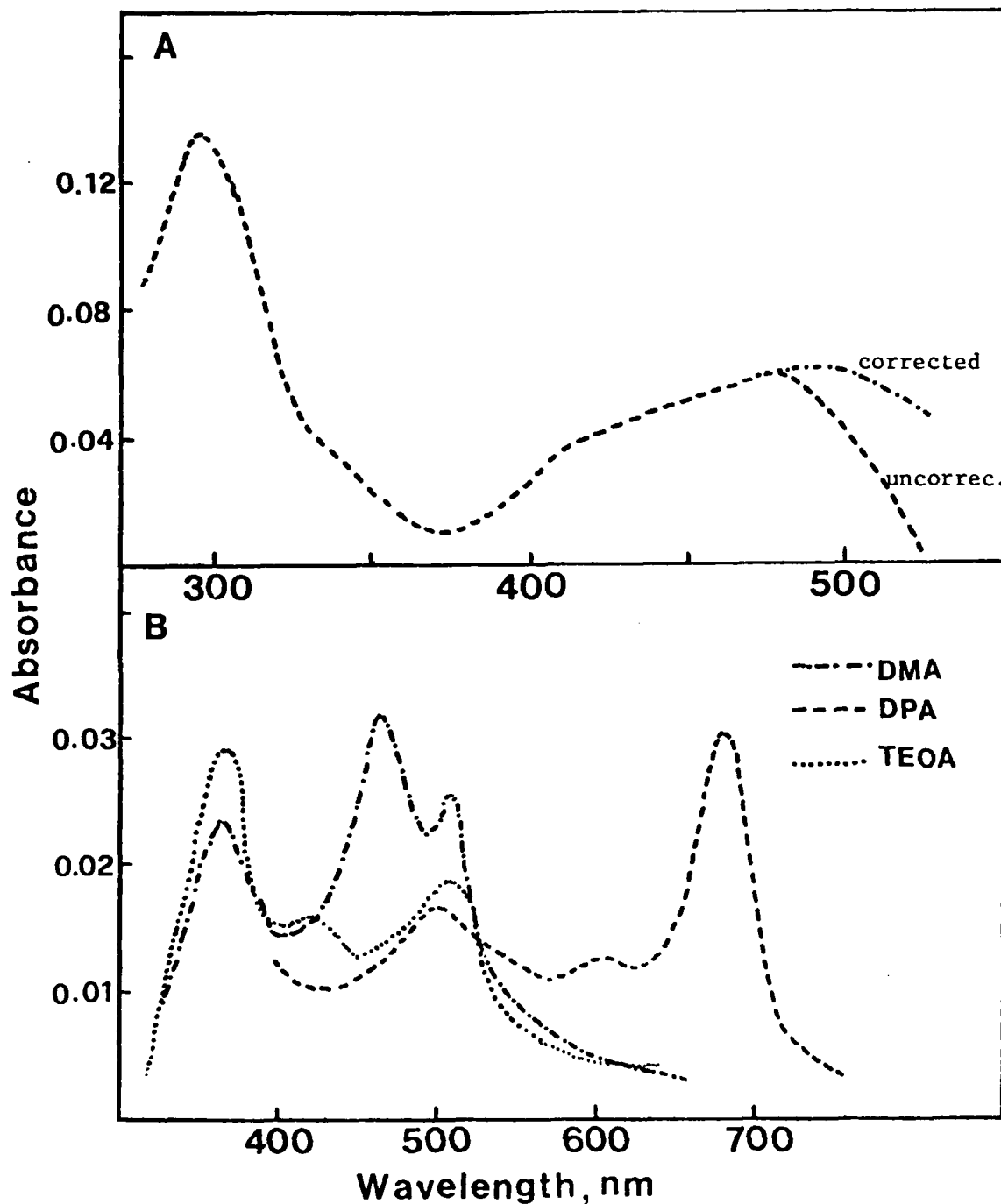


Fig. 1A Transient difference absorption spectrum for the MLCT excited state of $[\text{Re}(\text{CO})_3(\text{Cl})(\text{phen})]$ in CH_3CN .

Fig. 1B Transient difference absorption spectra of redox intermediates formed during the reductive quenching of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{Cl})]$ by amines in acetonitrile solutions.

ENERGY TRANSFER DYE LASERS.

M. I. Savadatti

Department of Physics, Karnatak University,

Dharwad 580.003, India.

Energy Transfer Dye Lasers (ETDL) have increased the number of dyes that lase, extended the tunability and range of dye lasers, enhanced the power out-put and produced dye lasers lasing simultaneously at different wavelengths. ETDL are particularly advantageous when pumping is done at a single wavelength, say, with nitrogen or excimer laser. The dyes that have been used in ETDL are evaluated in terms of observations on parameters like: wavelength shifts, lifetime changes, concentration effects and mechanisms of energy transfer.

Our experiments on energy transfer lasers with some new dyes are described and discussed in relation to the reported generalities and inferences.

Photochemistry of 1H-Pyrazolo [3,2-c]-s-Triazole Azomethine Dyes

P. Douglas*

Research Division, Kodak Ltd

Harrow, Middlesex, England

The photodegradation of colour print materials has been an active area of research in the photographic industry since the nineteen forties. Over the ensuing four decades the image stability of photographic prints has improved by a factor of ~ 75 (1), and present day image dyes fade with quantum yields of $\sim 10^{-6}$ under normal illumination.

The majority of colour print materials use azomethine dyes as colourants, and it has been found that the magenta image, obtained with a pyrazolone azomethine dye, is limiting for light stability. In addition to their 'relatively' poor light stability, the magenta pyrazolone dyes present a problem for colour reproduction in that they have an undesirable secondary absorption band in the blue.

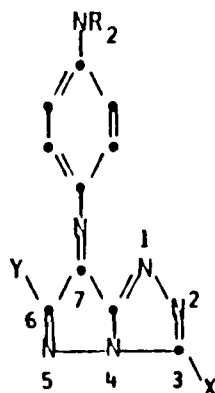
The magenta pyrazolo-triazole azomethine dyes (Structure 1), do not suffer from this secondary absorption band, and are potential replacements for the current pyrazolone azomethine dyes (2). However, it is clear that any replacement must have adequate light stability, and in this presentation details are given of the photochemical characteristics of these compounds, with emphasis on information obtained using flash photolysis techniques.

i) Absorption : Characteristics of the absorption spectra are an intense ($\epsilon_{\text{max}} \sim 5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) band in the visible and weaker absorptions in the ultra-violet. In polar solvents the visible band is broad and structureless but non-polar solvents or low temperatures resolve this into a vibrational progression of 3 or 4 bands.

ii) Emission : Room temperature fluorescence is extremely weak ($\Phi_F \sim 1 \times 10^{-4}$), but increases dramatically ($\Phi_F \sim 0.8$) at 77 K in rigid organic glasses. The room temperature emission is extremely broad and unstructured with a Stokes shift of $\sim 1000 \text{ cm}^{-1}$. At 77 K structural features 'mirror image' those seen in absorption with a Stokes shift of $\sim 250 \text{ cm}^{-1}$.

iii) Isomerisation : The dyes undergo direct and triplet sensitised syn-anti isomerisation, which can be readily studied by flash photolysis. ns flash photolysis shows that the isomerisation is essentially complete within the excitation pulse. Oxygen quenching of isomerisation indicates that at least 5-10% of the isomerisation originates from the triplet state, and this suggests the possibility of a relatively efficient photodegradation via a $^1\text{O}_2$ mechanism. The rate constant for the first-order thermal back isomerisation is substituent dependent with activation energies in the $\sim 35\text{-}70 \text{ kJ mol}^{-1}$ range, and log Arrhenius factors of $\sim 9 - 13$.

iv) Triplet state characteristics : Attempts to detect the dye triplet using flash photolysis, phosphorescence, and heavy-atom solvent absorption techniques were all unsuccessful, and characterisation of the triplet-state has relied on indirect methods. A comparison of direct and triplet sensitized isomerisation yields suggests that $\Phi_T \leq 0.04$, the observation of oxygen quenching of isomerisation with $\sim 5\text{-}10\%$ efficiency implies a triplet lifetime of at least $\sim 10 \text{ ns}$, and energy transfer measurements give triplet energies of $\sim 100\text{-}118 \text{ kJ mol}^{-1}$.



(1)

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*Present address; Chemistry Department, University College of Swansea, Singleton Park, Swansea SA2 8PP.

SESSION E: THEORETICAL ASPECTS

Chairman: R.N. DIXON

- 14.00-14.30 **Keynote Lecture** S.A. RICE: A conceptual extension of flash photolysis: coherent pulse sequence induced control of selectivity of reactions
- 14.30-14.45 S.H. LIN: Theoretical and experimental study of the quenching of singlet oxygen by solvent
- 14.45-15.00 B. STEVENS: IMO-LCMO description of photoinduced charge separation in a 4-centre unit
- 15.00 **Closing Remarks and Review** : SIR GEORGE PORTER, P.R.S.
- 15.30 **TEA**

POSTERS associated with Session E:

- J.A. ALTMANN: An ab initio SCFMO study of the relative stability of carbonyl imines
- S.J. FORMOSINHO: Extrathermodynamic relationships in chemical kinetics: a general intersecting state model

END OF SYMPOSIUM

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A Conceptual Extension of Flash Photolysis: Coherent Pulse
Sequence Induced Control of Selectivity of Reactions

Stuart A. Rice

The James Franck Institute and Department of Chemistry

University of Chicago, Chicago, Illinois 60637, U.S.A.

We present a novel approach to the control of selectivity of photochemical reaction products. The central idea is that in a two-photon or multiphoton process that is resonant with an excited electronic state, the resonant excited state potential energy surface can be used to assist chemistry on the ground state potential energy surface. By controlling the delay between a pair of ultrashort (femtosecond) laser pulses, it is possible to control the propagation time on the excited state potential energy surface. Different propagation times, in turn, can be used to generate different photochemical products. There are many cases for which selectivity of product formation should be possible using this scheme. Our examples show a variety of behaviors ranging from virtually 100% selectivity to poor selectivity, depending on the nature of the excited state potential energy surface. Branching ratios obtained using a swarm of classical trajectories are in good qualitative agreement with full quantum mechanical calculations.

Theoretical and Experimental Study of the Quenching
of Singlet Oxygen by Solvent

Y.Y. Lin, Z.T. Chu and S. H. Lin

Department of Chemistry

Arizona State University
Tempe, Az 85287

A theory has been developed to account for the quenching of siglet ($^1\Delta_g$) oxygen by the solvent in terms of intermolecular electronic-vibrational energy transfer. According to this theory, the bimolecular rate constant can be quantitatively related to the electronic transition moment and the Franck-Condon factors of $^1\Delta_g(v) \rightarrow ^3\Sigma_g(v')$ transitions, the infrared absorption intensities of solvent in the energy regions of $^1\Delta_g(v) \rightarrow ^3\Sigma_g(v')$ transitions and the Franck-Condon factors of local modes.

The lifetimes of singlet oxygen in a number of sensitized solutions have been determined by measuring the time-resolved decay of singlet oxygen luminescence at $1.27 \mu\text{m}$. The excitation source is laser light which has a pulse width of 15 ns with a maximum power of 6 mJ at 592 nm. The lifetimes of singlet oxygen in n-iodoalkane, n-bromoalkane and n-chloroalkane systems have shown good linear relationships between the bimolecular rate constants and the number of methylene groups in the carbon skeleton. The heavy atom effect of the iodine atom on the quenching rate constant has been determined.

IMO-LCMO DESCRIPTION OF PHOTOINDUCED CHARGE SEPARATION IN A 4-CENTRE UNIT

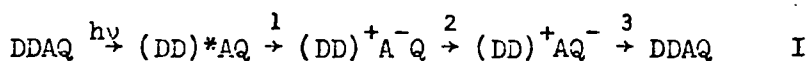
Brian Stevens

University of South Florida

Tampa, Florida 33620, USA.

The design and synthesis of electron-donor-acceptor units, which combine efficient photoinduced charge separation with slow charge recombination, is fundamental to the development of artificial photosynthetic systems. We examine here the 4-centre unit DDAQ where DD is an electron donor pair and A and Q are respectively primary and secondary electron acceptors, with a view to describing the consequences of its electronic excitation in terms of inter-molecular orbitals (IMO) of the unit.

Generally the desired sequence of events leading to charge separation is represented in 'valence bond' terminology by



where the asterisk denotes electronic excitation of a locally-excited donor dimer state of the unit, processes 1 and 2 are extremely fast on the scale of radiative relaxation times (ns) and 3 is relatively slow on the same scale. These properties are translated into the following requirements:-

- if processes 1 and 2 are accompanied by small free energy changes (to minimise photon energy loss) they should be diabatic; process 3 involving a large energy loss will be slow if it is also diabatic;¹
- the relative orientation of molecular subunits should be fixed to prevent orbital correlation switching² which may open up adiabatic channels for processes 1-3.
- The exergonic PCS sequence I in the uncoupled system requires that electron affinities (EA) of the molecular components decrease in order $\text{EA}(\text{Q}) > \text{EA}(\text{A}) > \text{EA}(\text{DD})$ consistent with the

antibonding of MO energy ordering

- d) Singlet excitation energies of the molecular components increase in order $E(^1DD^*) < E(^1A^*) < E(^1Q^*)$ to avoid the energy transfer sequence



(in the uncoupled system) which would otherwise compete with PCS sequence I. This (with condition C) establishes the bonding MO energy ordering $\phi_{DD} > \phi_A > \phi_Q$ and permits the reverse energy transfer sequence



- e) in which the donor pair acts as an energy trap;
the MO energy ordering

$$\phi_{DD}^* > \phi_A^* > \phi_Q^* > \phi_{DD} > \phi_A > \phi_Q$$

should be preserved in the PCS unit, ie.

$$\psi_{DD}^* > \psi_A^* > \psi_Q^* > \psi_{DD} > \psi_A > \psi_Q$$

where ψ denotes a 4-centre IMO of the unit with predominately x character^x. This is assured by weak coupling between dimer and acceptor orbitals.

Unit IMO (ψ_1) are constructed as linear combinations of MO belonging to the same symmetry species of the DDAQ point group which is unspecified. However dimer orbitals necessarily originate in syn correlation³ of identical MO ie.

$$\phi_D^* \pm \phi_D^* \rightarrow \psi_{DD}^*(\pm) ; \phi_D \pm \phi_D \rightarrow \psi_{DD}(\pm)$$

and it is assumed that the MO of acceptors A and Q exhibit anti-correlation, ie.

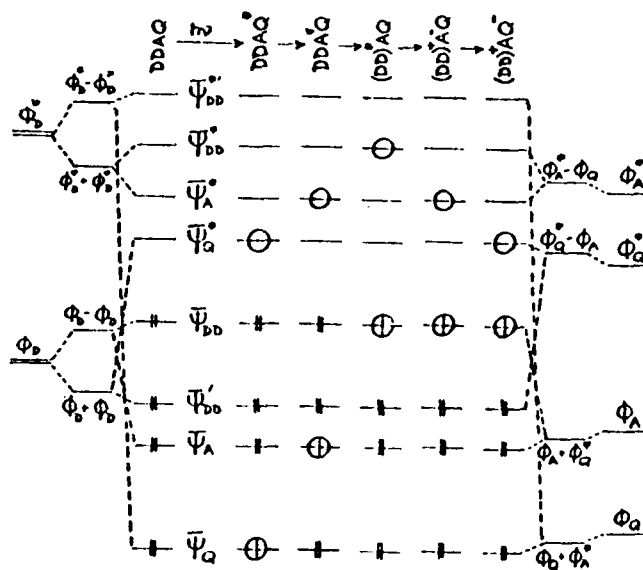
$$\phi_A^* \pm \phi_Q \rightarrow \psi_{A^*Q}(\pm) ; \phi_Q^* \pm \phi_A \rightarrow \psi_{Q^*A}(\pm)$$

a complete description of the unit IMO is now afforded by dual (syn and anti) correlation of dimer (ψ_{DD}) and acceptor (ψ_{AQ}) composite orbitals belonging to the same (unspecified) symmetry species as shown for example in the figure where

$$\psi_{DD}^1 = c_1(\phi_D^* - \phi_D^*) - (a_1\phi_Q + b_1\phi_A^*) \quad (c_1^2 \gg a_1^2 + b_1^2)$$

$$\psi_Q = c_2(\phi_D^* - \phi_D^*) + (a_2\phi_Q + b_2\phi_{A^*}) \quad (a_2^2 \gg b_2^2 + c_2^2)$$

It is perhaps useful in a mechanistic sense to regard the ψ and ψ^* unit orbitals as valence and conduction orbitals respectively, and to describe single occupancy of a valence orbital as a hole $+$ and of a conduction orbital as an electron $-$. In this terminology the figure illustrates the sequence of events following local excitation of 'acceptor' or 'donor' state as a simultaneous translation of hole and electron (energy transfer) until the hole is localised in the highest energy valence (dimer) orbital, followed by a series of rapid one-electron relaxations between conduction orbitals which corresponds to diabatic charge separation. It is not immediately obvious from this description why the charge neutralization step is slow unless the vibrational overlap integral $\langle \chi_{DD} + \chi_{DD} \rangle \langle \chi_Q - \chi_Q \rangle$ involves the nuclear component χ_{DD} of a dissociated dimer ground state function which has little amplitude at the equilibrium configuration of the cation $(DD)^+$. In this case the role of the dimer (special pair) in the PCS unit is three-fold in that it acts as an excitation energy trap, localises the positive hole and exhibits minimal vibrational overlap between the (unbound) ground and cationic states.



- ¹ G.W.Robinson and R.P.Frosch, J.Chem.Phys.
- ² B.Stevens, J.Phys.Chem., 88 (1984) 669
- ³ B.Stevens, Chem.Phys., 100 (1985) 193
- ⁴ B.Stevens, Mol.Phys., 55 (1985) 589

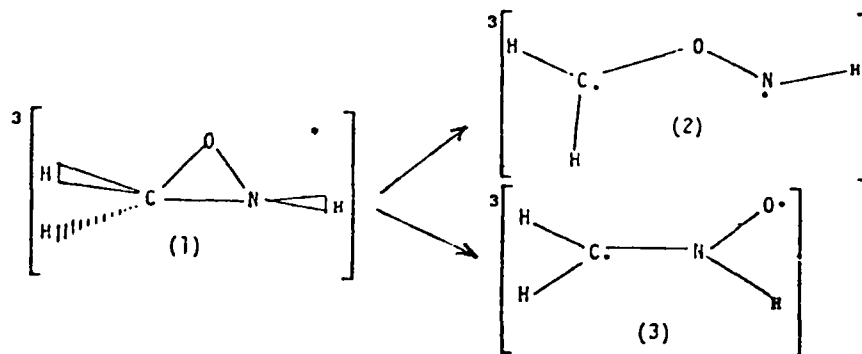
An ab initio investigation of the relative stability of carbonyl imines.

Julianna A. Altmann

University of London Computer Centre

20 Guilford Street, London WC1N 1DZ

The structures of the excited triplet species 1 - 3 have been determined by complete geometry optimisation using ab initio open shell gradient methods and a high quality (6-31G*) basis set. All three species appear to have undergone significant structural changes upon excitation.



The relative stability of the various species is in the order $3 \gg 2 \gg 1$. The energy difference between species 3 and 2, however, is relatively small (23 KJ/mole) as compared to the difference of 230 KJ/mole obtained for the ground state molecules. This suggests that triplet carbonyl imine may be observable experimentally.

An investigation of the mechanism of the formation of carbonyl imine (2) is in progress. A preliminary work that involved computation of one of the possible pathways, the electrocyclic ring opening of oxaziridine (1), gave a barrier of 86.2 KJ/mole.

Extrathermodynamics Relationships in Chemical Kinetics.

A General Intersecting-State Model

Sebastião J. Formosinho

Departamento de Química, Universidade de Coimbra

3049 Coimbra, Portugal

A new classical model for the estimation of energy barriers of chemical reactions is presented (1). It is shown that the potential energy along a reaction coordinate can be calculated in terms of the reaction energy, the force constants and the equilibrium bond lengths of the reactive bonds, the bond order of the transition state and the configuration entropy. The model is applied to the study of hydride, methyl transfer and unimolecular reactions in the vapour phase and electron transfer, solvent exchange, nucleophilic substitution and sigmatropic shift reactions in liquid solutions.

The intersecting-state model encompasses several of the more important simple theoretical models of chemical reactivity and provides a unifying view of many of the thermodynamic, geometric and electronic factors which have been used in the past.

- (1) A.J.C. Varandas and S.J. Formosinho, J. Chem. Soc., Chem. Commun. (1986), 163; J. Chem. Soc. Faraday Trans. 2, in press.

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