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**NON-RADIATIVE ELECTRONIC ENERGY TRANSFER IN
ORGANIC LIQUIDS AT HIGH "DONOR" CONCENTRATIONS**

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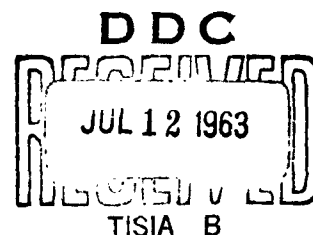
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I. Abstract

The efficiency of electronic energy transfer from the liquids benzene, toluene, p-xylene and mesitylene to p-terphenyl have been determined both for ultraviolet excitation in the first absorption band and for Cs^{137} gamma excitation. In addition, the efficiency with which oxygen quenches the transport process has been determined for both modes of excitation. Both energy transfer and oxygen quenching constants are larger than would be predicted on the basis of a diffusion limited rate. Dilution of the aromatic liquids with hexane is found to significantly reduce the rate of energy transfer. In previous reports a similar effect on the quenching rate was noted. The participation of the bulk solvent in these processes seems to be implicated. Mechanisms of energy transfer utilizing the states of the bulk solvent are briefly reviewed.

The relative scintillation efficiencies have been determined for solutions of p-terphenyl in benzene, toluene, p-xylene and mesitylene and compared with values approximately calculated from the optical transition probabilities and the efficiencies of internal conversion from upper electronic states to the transferring state - the first excited singlet.

The construction of the fluorimeter is described and the emission spectrum of pure liquid benzene presented.

II. Scintillation Properties of Liquids¹

INTRODUCTION

A fraction of the energy dissipated by a high energy charged particle in its passage through a condensed phase may, under proper conditions, ultimately appear (in ca 10^{-8} - 10^{-9} sec) as a scintillation pulse with spectral distribution characteristic of the absorbing material. This phenomenon has stimulated considerable research activity in view of its application as a device for detection of nuclear particles. However, at the same time, research effort has been directed towards elucidating the mechanism responsible for the observed scintillation pulse. Both aspects of the field have been the subject of numerous reviews during the past ten years (1-5).

In pure liquids, the energy efficiency of the conversion is very low. In the most favorable cases (e.g., p-xylene) the efficiency is less than 0.1%. In the least favorable cases, such as water and the simple aliphatic alcohols, it is a factor of 50-100 lower² (6-7). For the "better" liquids, the efficiency can be improved by almost two orders of magnitude by dissolving in them small quantities of p-terphenyl, anthracene, diphenyloxazole or indeed most any substance with a high fluorescence efficiency and an absorption band red shifted with respect to the emission band of the solvent (4). A typical case is a 10^{-2} M solution of p-terphenyl in benzene. If one excites this solution with Cs¹³⁷ γ - rays, one observes a luminescence with a spectral distribution almost completely characteristic of the

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²This is after correction for the contribution made by Čerenkov radiation.

emission spectrum of p-terphenyl. The energy efficiency of this scintillation pulse has not yet been reliably measured. However, in a well degassed solution, the efficiency may be estimated to be about equal to that of a thin anthracene crystal for which values between 4-6% are currently quoted (8, 9, 10). Reducing the terphenyl concentration by a factor of ten, reduces the energy efficiency by about a factor of 1.5. Although the efficiency of the scintillation process is not high, it is clearly greater than could be expected from the probability of having the primary charged particle, or any of the electrons produced in its degradation, directly interact with p-terphenyl. Since, then, the initial energy absorption is predominately by the solvent, one must postulate a mechanism for the transfer of some of this energy from the solvent to the solute.

In the following sections of this paper we consider and discuss some of the evidence bearing both on the mechanism of this energy transfer and on the relationship between scintillation efficiency and nature of the solvent.

THE DEPENDENCE OF THE SCINTILLATION PULSE ON SOLUTE CONCENTRATION

The energy ultimately transferred to the solvent by a fast electron of initial energy E may be considered to lead eventually to the production of a number M_E of solvent molecules capable of transferring electronic energy to the solute. The number of photons N_E emitted by the solute in such a system may then be written

$$N_E = M_E \phi_t \phi_f \quad (1)$$

where ϕ_t refers to the fraction of solvent molecules that transfer their energy to the solute and ϕ_f refers to the fraction of solute molecules that radiate this energy. It is, of course, implicitly assumed here that all M_E molecules are equivalent, at least to the extent of possessing the same probability for transferring their energy to the solute. This assumption, as will be shown later, seems to be

valid for the systems we consider, namely, aromatic solvents.

In most scintillation experiments one normally measures a quantity I_E proportional to N_E . For most experiments the proportionality constant is, unfortunately, not determined. However, for constant experimental conditions and for the same solute this "constant" is independent of solvent. Thus a comparison may be made of the scintillation efficiencies of a series of solvents all containing the same solute. This will be done in the last section of this paper.

The dependence of I_E on solute concentration is contained implicitly in both ϕ_t and ϕ_f . A possible method for separation of the observed concentration dependence of I_E into each of its two parts was first suggested by Kallmann and Furst on the basis of studies made with a large variety of solvent-solute combinations (11). The concentration dependence of ϕ_f obtained in this fashion is identical to that obtained when the solute is directly excited optically in its first absorption band. It is given by

$$\phi_f = \frac{\phi_f^0}{1 + Kc} \quad (2)$$

where c is solute concentration, K is a constant characteristically known as a self-quenching constant and ϕ_f^0 is to be identified, at least in the optical experiments, with the emission quantum yield at infinite dilution. In the cases of p-terphenyl and diphenyloxazole, as solutes, K is less than 3 liter/mole. Therefore, for studies involving these solutes at concentrations less than 10^{-2} M, ϕ_f may be regarded as constant and the concentration dependence of ϕ_t obtained directly from measurements of I_E .

The dependence of I_E on solute concentration has been investigated for many aromatic hydrocarbon solutions and shown to be consistent with a transfer efficiency, ϕ_t , proportional to

$$\phi_t \sim \frac{c}{1 + ac} \quad (3)$$

where c is solute concentration and a a transfer constant characteristic of the particular solute-solvent pair chosen (11, 12).

The proportionality constant cannot, of course, be specified since M_E is not known. The solvents that we have most extensively studied are benzene, toluene, p-xylene and mesitylene with p-terphenyl as solute. In all cases, unless otherwise specified, the solvents are spectroscopically clean and carefully degassed. In Table I are listed the transfer constants recently obtained for p-terphenyl in these solvents using Cs^{137} excitation (13). Values of the same magnitude (*i.e.*, 1500-1800 liter/mole) have been reported for diphenyloxazole in toluene and p-xylene solutions (15, 16).

Similar information pertinent to the mechanism of energy transport can be determined by studying the time dependence of the scintillation pulse (17). Making the same assumptions required for the validity of equation (1), we would expect that the decay of the pulse should be determined by two processes, the rate of energy transfer to solute and the rate at which the solute emits. Simple analysis of this leads to a decay law involving the sum of two exponentials. For the case of aromatic hydrocarbon solutions, this is experimentally verified at least within the precision of present day apparatus (18). However, again one must somehow determine which decay constant belongs to which physical process. This problem has been solved using methods analogous to those used in the similar problem that occurred in intensity measurements. For the case of p-terphenyl in benzene, the solute emission decay time is identified as 2.5×10^{-9} s (18) and the decay time

τ corresponding to the lifetime of the transferring solvent species can be expressed as

$$\tau = \frac{\tau_0}{1 + ac} \quad (4)$$

where a has the same significance and experimentally the same magnitude as before (15-20). The quantity τ_0 in equation (4) is the decay time extrapolated to

zero solute concentration and has been experimentally identified reasonably well with the decay time of the emission from the pure solvent (16).

It is also possible to sensitize a solute emission by exciting the solvent optically in its first absorption band. Furthermore, a comparison of the intensity of the sensitized emission to the intensity obtained by directly exciting the solute in its own first absorption band permits one to obtain a value for the transfer efficiency ϕ_t . The dependence of this efficiency on solute concentration has been determined for a number of aromatic systems and shown to be consistent with the form:

$$\phi_t = \frac{a c}{1 + a c} \quad (5)$$

where a is the transfer constant and c the solute concentration (13, 21, 22). Within experimental error, a is identical to the value obtained using Cs^{137} as an excitation source (see Table I.) It is important to note that equation (5) predicts unit transfer efficiency at infinite solute concentration. Consequently there must be no "instantaneous" quenching of these aromatic molecules in their first electronic singlet states, at least not at the low excitation densities employed in the usual optical experiments. Electronic energy transfer to p-terphenyl is, therefore, competitive with all other possible fates for the excited solvent.

For optical excitation throughout the first solvent absorption band, equation (5) adequately describes the concentration dependence of ϕ_t with a retaining a constant value. For excitation in the second and third optical absorption bands, the transfer efficiency is reduced and its functional dependence on solute concentration altered to the form

$$\phi_t = \frac{\beta a c}{1 + a c} \quad (6)$$

where β is a function only of exciting wavelength with the value 1, of course, for any wavelength within the first band and ≤ 1 at all other wavelengths (13). Evidence for the form of equation (6) derives from the fact that $1/\phi_t$ depends

linearly on $1/c$ with intercept and slope strongly dependent on exciting wavelength but ratio of intercept to slope, a , approximately constant³ at the value obtained for first band excitation. The emission yields of the pure solvents have also been studied as a function of exciting wavelength and found to decrease with decreasing wavelength (23). Indeed, the solvent emission yield when normalized to unity for excitation in the first band, reproduces almost exactly the values, β , obtained in the sensitized emission experiments. The following interpretation is suggested. Most, if not all, of the sensitization occurs via the lowest excited singlet state of the solvent. Furthermore, the transfer efficiency, ϕ_t , in equation (6) is a product of two efficiencies, β - an internal conversion efficiency from an upper electronic state of the solvent to the sensitizing state, and $\frac{ac}{1+ac}$ - an efficiency of energy transfer to *p*-terphenyl from this latter state.

In view of the demonstrated invariance of a to mode of excitation (see Table I) and the absence of evidence for any appreciable transfer from upper electronic states,⁴ we shall assume that the same mechanism of energy transport obtains in both the scintillation process (induced by Cs^{137} γ -rays) and the process induced by optical absorption in the first solvent band.

QUENCHING EFFECTS

Oxygen, bromobenzene or carbon tetrachloride, when present in small amounts in these two-component aromatic systems, quench the luminescence. In general, most of this quenching cannot be attributed to an interaction between the excited solute and the quencher. The major contribution seems to derive from

³There seems to be some tendency for a to decrease with decreasing wavelength. For example in the case of benzene - *p*-terphenyl solutions a decreases from 1350 l/m at 2600Å to about 1100 l/m at 1610Å. However, for the same wavelength variation, β changes from 1.0 to 0.3.

⁴Measurements have only been reliably extended to the short wavelength side of the third absorption band of the alkylbenzenes (i. e., 1610Å) (23).

the interference of the quencher with the rate of energy transfer to the solute (12, 14, 24, 25). Quencher and solute act competitively for solvent energy and with comparable efficiencies. In the case of bromobenzene quenching of the scintillation process, N_E may be expressed as

$$N_E = M_E \phi_t' \phi_f \quad (7)$$

with

$$\phi_t' \sim \frac{c}{1 + ac + \gamma d} \quad (8)$$

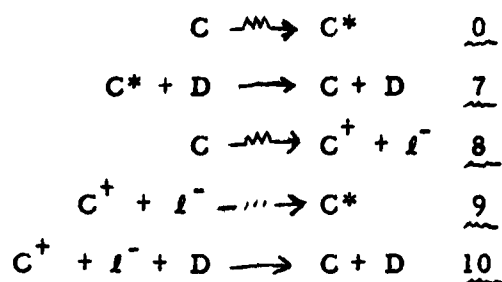
where a , and c are as previously defined, d is the concentration of quencher and γ is a quenching constant independent of both solute and solvent concentration.

In the case of optical excitation, a similar relationship between transfer efficiency ϕ_t' and bromobenzene concentration is obtained with the same value for a but a somewhat lower value for γ (12, 24). Using Cs^{137} excitation

$\gamma = 500 \pm 60 \text{ l/m}$ for bromobenzene quenching of p-terphenyl-benzene solutions. Using $2137\text{\AA}$ excitation $\gamma = 350 \pm 120 \text{ l/m}$ for the same system (24). A similar disparity has been noted for carbon tetrachloride quenching of p-terphenyl - toluene solutions (14) with again the higher quenching efficiency for the scintillation process. In the case of oxygen, the luminescence from degassed and air-equilibrated solutions of $2 \times 10^{-3} \text{ M}$ p-terphenyl in benzene, toluene, p-xylene and mesitylene have been compared (13). This has been done both for UV excitation in the first band of the solvent and for Cs^{137} excitation. The results are presented in Table II. The values for γ have been corrected for the measured effect of O_2 on the fluorescence yield of terphenyl (ϕ_f). This contributes uniformly in all solvents about 10% to the reduced intensity. With this correction, γ was then calculated assuming the validity of equation (8). This, however, has not yet been reliably demonstrated for oxygen quenching.

In view of our assumption that the energy transport process is independent of mode of excitation, differences in quenching efficiency must seek explanation in

processes of the type:⁵



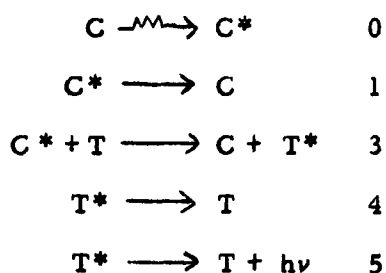
where C, C* and D refer respectively to solvent in ground state, solvent in first excited state (transferring state), and quencher. It is suggested, therefore, that in the scintillation process the quencher may interfere not only by interaction (process 7) with the transferring state of the solvent (which it may do also in the optical process) but, in addition, by partially inhibiting the formation of such transferring states (process 10).

MECHANISMS OF ENERGY TRANSPORT

The fluorescence quantum yields of the pure liquid alkyl benzenes are not known accurately but are probably less than 0.10. Values of 0.01 and 0.03 have been reported for toluene and o-xylene (26) and from relative measurements that we have made, even in the most favorable case of p-xylene the yield should not exceed 0.05. However, the energy transfer efficiencies at 2×10^{-3} M p-terphenyl are 0.72 (for toluene), 0.81 for p-xylene and extrapolate to unity at infinite terphenyl concentration. Clearly, the mechanism for energy transfer cannot involve radiative processes to any important extent for terphenyl concentrations above about 10^{-4} M. Further evidence for this point of view is obtained from the observation that the decay time of solvent emission is reduced by the addition of

⁵Not shown in this scheme is the transport process whereby C* transfers energy ultimately to the solute.

solute to the same extent as the intensity of solute emission is increased (18, 20). The transfer process we are considering, therefore, is predominantly nonradiative. One possible mechanism for such a process in a liquid is as follows. By optical absorption or ultimately from the energy dissipated by a fast electron, a specific solvent molecule is electronically excited. The molecule diffuses to within some distance R of the solute and then in a process which may involve perhaps an exchange interaction or some interaction of longer range, transfers energy to the solute. In terms of a conventional kinetic sequence we could write:



where C and T refer to solvent and solute respectively. With this scheme it is simple to show that the transfer efficiency, the transfer decay time and the quenching efficiency (if reaction 7 is involved) will all have the proper dependence on solute concentration. Furthermore, α , γ and τ_0 (see equation 4) can now be identified as

$$\begin{aligned}
 \alpha &= k_3/k_1 \\
 \gamma &= k_7/k_1 \\
 \tau_0 &= 1/k_1
 \end{aligned} \tag{9}$$

To go one step further, if this model is correct, we should be able to estimate a lower limit for the encounter distance R using measured values of α , and τ_0 and the appropriate solution to the diffusion equation (27). For values of τ_0 of the order of 10^{-8} sec, and reaction probability not too small at R nor diffusive displacements too large compared to R ,⁶ the transient term appearing in the solution

⁶All of these conditions are reasonable for our problem.

to the diffusion equation may be neglected. Thus one obtains for the specific rate of reaction, k ,

$$k = \frac{4\pi NDR}{1000} \quad (10)$$

where N is Avogadro's number and D the mutual diffusion coefficient. The self diffusion constant of benzene and the diffusion constant of oxygen have been determined as $2.15 \times 10^{-5} \text{ cm}^2/\text{sec}$ (28) and $5.7 \times 10^{-5} \text{ cm}^2/\text{sec}$ (29) respectively. In the absence of similar information for the other solvents, a value of $D = 4.30 \times 10^{-5} \text{ cm}^2/\text{sec}$ was used in all cases for calculation of the encounter distance for the energy transfer reaction (R_a) and a value of $D = 7.8 \times 10^{-5} \text{ cm}^2/\text{sec}$ used for the calculation of the encounter distance (R_γ) for the quenching reaction. In Table III, experimental values of τ_0 (16) and calculated values of R_a and R_γ are presented. It will be noted that for both reactions, the values for R are somewhat larger than would be expected for geometrical encounter distances (29). It is perhaps not unexpected that the energy transfer process would have associated with it a larger cross-section. However, it is much more difficult to explain a similarly high value for oxygen quenching since "resonance" processes presumably cannot occur in this case.

Attempts to determine experimentally the role of diffusion in these processes have taken two directions - one, a study of the effect of viscosity, the other a study of related processes in rigid plastic solutions. In the case of viscosity variation, there is evidence that the transfer efficiency is lowered as the viscosity increases (15, 31). For example, the transfer efficiency is 0.48 for a solution of 2.26×10^{-3} M diphenyloxazole containing ten parts paraffin oil to one part toluene (viscosity 10 cp) whereas a value of 0.78 has been obtained for the same solution with cyclohexane used in place of the paraffin oil (viscosity ≈ 1 cp). It should be noted that in the absence of diphenyloxazole the decay time of toluene remained the same in the two systems. Thus diffusional processes seem to be implicated. However, the variation of transfer efficiency with change in viscosity is somewhat smaller

than one would predict for diffusion controlled processes. Furthermore, one obtains at viscosities at which all diffusional processes should be stopped, transfer efficiencies much higher than can be accounted for by radiative processes (31).

Measurements made in rigid plastic systems are also difficult to interpret in terms of their pertinence to the question of diffusional processes in liquid systems. In addition to this, there are experimental disagreements. Knau (32) finds the transfer process from benzene to anthracene to be similar to that from polystyrene to anthracene. A similar absence of effect of solidification on transfer efficiency was reported earlier by Hardwick for transfer from naphthalene to anthracene (33). However, measurements from many other laboratories seem to indicate much lower transfer efficiencies in rigid plastics at solute concentrations comparable to those used in the liquid (19, 22, 34-37). Since in both plastic and liquid systems, ϕ_t seems to exhibit the same type of dependence on solute concentration (see equation (3)), the difference in behavior can be expressed more quantitatively in terms of transfer constants. Comparing benzene $\longrightarrow$ terphenyl transfer with polystyrene $\longrightarrow$ terphenyl transfer, the ratio α (solution)/ α (plastic) = 30 (19, 35).

A long range "resonance" energy transfer of the Förster type (38) from some one initially excited solvent molecule to the solute can be shown, in the absence of diffusion, to be too inefficient to explain the observed values of ϕ_t . In the case of transfer from p-xylene to p-terphenyl a value for R_0 of about 20 Å can be calculated⁷ (for random orientation) assuming a p-xylene emission quantum yield of 0.05. By suitably averaging the pair wise transfer probability over a random distribution of solute molecules about the excited energy donor molecule, Förster

⁷ R_0 is the distance between excited p-xylene and p-terphenyl for which the transfer probability is unity within the lifetime of the p-xylene ($\tau_0 = 20$ n sec.).

has derived an expression for the transfer efficiency

$$\phi_t = \frac{\pi}{2} \times e^{\pi/4 x^2} \left[1 - \operatorname{erf} \left(\frac{\sqrt{\pi}}{2} x \right) \right] \quad (11)$$

where $x = 2.51 \times 10^{-3} c R_0^3$ with c in mole/liter and R_0 in Angstroms, and $\operatorname{erf} \left(\frac{\sqrt{\pi}}{2} x \right)$ is the error function (39). For $R_0 = 20 \text{ \AA}$, and a solute concentration $c = 10^{-2} \text{ M}$, equation (11) predicts $\phi_t = 0.26$. Experimentally one obtains $\phi_t = 0.96$. Similar discrepancies exist for the other solvents.

In both previous models, material diffusion and long range transfer, electronic states of the bulk solvent are assumed not to participate directly in the transfer process. Alternatively we may consider a model in which energy moves from its initial absorption site to the solute (or quencher) exclusively via excited states of the bulk solvent. Two limiting cases (weak and strong coupling) are usually considered theoretically (40,41). Their distinction depends, approximately, upon the relative strengths of two electrostatic interactions - one, an interaction between an electronically excited configuration of one solvent molecule "A" with a ground state configuration of a neighboring solvent molecule, the other an interaction between electronic and nuclear motions within the molecule "A". For the case in which the intermolecular coupling is relatively weak, an initial excitation of the solvent via photon or electron impact leads to an excited electronic state which may be considered as localized on a single solvent molecule. The subsequent motion of this excitation is diffusive with a diffusion length of the order of a molecular diameter. For energy transport in the alkyl benzenes, the weak coupling approximation predicts transfer efficiencies at least an order of magnitude too small (12,13). This conclusion is based on a calculation of the excitation diffusion coefficient using the procedure suggested by Forster (39).

In the intermediate cases of relatively stronger intermolecular coupling, the initially excited state may be considered as delocalized over a region of the solvent

large compared to the dimension of^a single molecule. The description of the initial state is now best presented as a wave packet (or exciton state) and it is in terms of the motion of this packet that the energy transport process is to be envisioned. In a liquid, interactions of the exciton with nuclear motions tend to deflect it from the more rectilinear path characteristic of the stronger coupling cases that obtain in a low temperature solid. In the absence of any correlation between successive scattering events, the motion of the exciton may again be considered as diffusive but now with a diffusion length larger than a molecular diameter. Similar considerations have been applied to the description of energy transport processes in molecular crystals (42, 43).

The efficiency of optically initiated energy transfer from toluene to anthracene has been studied as a function of degree of dilution of toluene in cyclohexane (21, 44). The concentration of solute was kept constant. No variation in transfer efficiency was found for experiments carried to dilutions of 1:80 in degassed solutions and 1:400 in aerated solutions. The conclusion drawn was that transport via the bulk solvent need not be invoked to explain results in the pure liquid.

We have recently performed similar experiments involving p-xylene with hexane as diluent and anthracene as solute (13). The results are shown in Table IV together with recently reported values of the emission decay times of p-xylene in hexane solutions (30). About an 8% decrease in ϕ_t may be noted over the entire range. This corresponds to a decrease of about 17% in the kinetically more significant parameter α . However, since the time, τ_0 , available for transfer increases with dilution, there must be a decrease in rate of transfer (k_3) by a factor of about 1.7. If transfer were exclusively by material diffusion, both the increase in τ_0 and the decrease in viscosity⁸ on dilution would have predicted an increase in α about a factor of 3. Similar effects have been noted for p-xylene and benzene transfer to p-terphenyl (13).

⁸ $\eta(\text{p-xylene})/\eta(\text{hexane}) = 2$

It appears, therefore, that in the pure liquid, processes other than material diffusion and long range transfer contribute to the observed energy transport. How much is contributed cannot be determined at the present time. However, regardless of the exact magnitude of this contribution by the bulk solvent, it cannot be derived from the concept of excitations initially localized on single molecular sites.

RELATIVE SCINTILLATION EFFICIENCY

For high speed electrons or gamma rays, the energy efficiencies of the aromatic solutions at about 10^{-2} M p-terphenyl concentration are probably between 4-6%. Since energy transfer efficiencies are essentially unity at high p-terphenyl concentrations and the terphenyl emission quantum yield is about 0.5⁹ (4), these efficiencies are equivalent to the requirement of about 40 ev for the production of one excited solvent state capable of transferring energy.

Values for W (energy/ion pr) are not known for the aromatic liquids. For molecular gases, $W \approx 25$ ev (45). Assuming this value applies to the liquid, and further assuming an aromatic average ionization potential ≈ 9 ev and an aromatic average excitation potential ≈ 7 ev, one derives that about 3.5 primary excitations are produced per 40 ev absorbed. Therefore, approximately 70% of the primary excitations do not ultimately appear as states of the solvent capable of transferring energy. Discussions of the possible source for this inefficiency have appeared repeatedly in the literature (1, 2, 4, 46), and generally involve postulating some form of rapid quenching reactions involving excited solvent states in regions of high LET.

⁹The literature value refers to a p-terphenyl crystal. However, 0.5 is also obtained from the measured emission decay time of p-terphenyl in solution and its integrated absorption spectrum (13).

Internal conversion efficiencies (β) from the second and third electronic states of pure alkyl benzene liquids to their lowest excited singlet states have recently been determined (23). It was decided, therefore, to investigate the role this might play in explaining relative scintillation efficiencies in these liquids. The dependence of I_E (equation (1)) on p-terphenyl concentration was determined for Cs¹³⁷ excitation. By extrapolating to infinite concentration, relative values¹⁰ of $M_E \phi_f$ were determined (13). Relative values of ϕ_f were obtained optically. The results are presented in columns 2 and 3 of Table V. In column 4 are presented relative values, f , of the integrated optical transition probabilities ($f \sim \int \frac{\epsilon(\nu)}{2} d\nu$).¹¹ These numbers are presumed to be approximately related to the total cross-section for excitations (47). In column 5 are presented relative values g of the integrated optical transition probabilities weighted by the measured internal conversion efficiencies to the first excited singlet ($g \sim \int \frac{\epsilon(\nu)}{2} \beta(\nu) d\nu$).¹¹ These numbers are presumed to be approximately related to the probability of producing first excited states via the electron impact induced excitations and are therefore to be compared with their experimental counterpart M_E .

It will be noted that both the relative ordering of M_E as well as the gap between the value of M_E for benzene and values for the other solvents are predicted by g . These trends are not apparent in the optical transition probabilities. However, the spread in the experimentally determined values for M_E is much less than predicted by g . Assuming there is some validity to these calculations, one possible explanation is that many of the transferring states arise from processes not involving the conversion of excitations. Recombination of electrons with positive ions might provide such a mechanism for the direct production of a transferring state and has already been suggested by the disparity between scintillation and

¹⁰Corrected for differences in gamma-ray attenuation.

¹¹All integrals were terminated at about 7.5 ev. Values for β are not yet determined above this energy. Values for the extinction coefficients $\epsilon(2)$ were determined from dilute solution absorption spectra.

optically induced quenching processes.

III. Description of the Fluorimeter

A schematic of the fluorimeter is shown in Figure 1. The source of illumination is a 900 watt Xe arc lamp, A. The light is collected by lens system B and made incident on a Bausch and Lomb 250 mm grating monochromator. The monochromator is normally operated at a spectral half width of about $60\text{-}100\text{\AA}$. The subsequent optical system comprised of lenses B and C and front surface mirrors D and E direct the monochromatic beam onto a 1 cm cylindrical quartz cell F. A concave front surface mirror G is used to collect the emission and focus it onto the entrance slit of a Beckman DU monochromator. Although not shown in Figure 1, the optical system is symmetrical about an axis passing through the entrance slit of the DU and the exit slit of the Bausch and Lomb monochromator. Thus a cell F' not shown but placed symmetrically with respect to F may alternatively be illuminated via D' and E' (not shown). By rotating the platform containing D, D' and G, either cell F or F' may be illuminated and its emission collected and analyzed. After dispersion by the DU the fluorescence is made incident on the cathode of a 6256B EMI photomultiplier K, via a front surface mirror H and lens J. The output of the photomultiplier may either be monitored by a DC μA ammeter or alternatively, pulse amplified and displayed on a scaler. In either mode of operation the photomultiplier is normally cooled to dry ice temperatures. The resulting noise level at a tube gain of about 10^6 is of the order of 3 counts/min.

All solutions are carefully degassed by successive freeze-thaw cycles on a high vacuum manifold and then connected to the fluorescence cell via a break seal. After evacuation of the fluorescence cell to ca. 10^{-6} mm, the first solution is admitted to the cell and retained therein by means of a solenoid operated ground glass float valve. At the conclusion of an experi-

ment this valve is opened and the solution drained into a reservoir. This procedure is similar to that previously employed and reported in an earlier publication (24).

The equipment is sufficiently sensitive to measure accurately the emission from pure liquid benzene with quantum yield estimated at about 0.01. The spectral distribution of this emission excited at $2500\text{\AA}$ for a 1 M benzene solution in cyclohexane and pure liquid benzene is shown in the upper and lower halves of Figure 2 respectively. The appearance of a long wavelength component in the emission apparent in the pure liquid spectrum has been previously reported (30). Its assignment is uncertain although an excimer origin has been suggested. Measurements to determine whether a difference exists in the O_2 quenching efficiency of the long and short wavelength components of the emission are currently being made.

IV. Personnel and Publications

Sanford Lipsky, Assistant Professor

William P. Helman, Research Assistant

- a) S. Lipsky, W. P. Helman and J. F. Merklin, Quenching of Electronic Energy Transfer in Organic Liquids, In Luminescence of Organic and Inorganic Materials, p. 83-99 (H. P. Kallmann and G. M. Spruch, Editors) John Wiley and Sons, New York, 1962.
- b) S. Lipsky, Evidence for Triplet-Triplet Transfer from Benzene to Biacetyl in Cyclohexane Solution. J. Chem. Phys. (accepted for publication, June, 1963).
- c) S. Lipsky, Scintillation Properties of Liquids, presented at International Symposium on Physical Processes in Radiation Biology and to be published as supplement in Advances in Radiation Biology, 1963.
- d) S. Lipsky, Propagation of a One-Dimensional Exciton, Quarterly Status Report No. 6 to Air Force Command and Control Development Division, 1962 (to be submitted for publication).

TABLE I

Values of the Transfer Constant, α ,
in Units of liter/mole for Degassed p-Terphenyl Solutions^a

Solvent	Cs ¹³⁷ Excitation	UV Excitation in first solvent absorption band
Benzene	1400 $\pm$ 75	1350 $\pm$ 75
Toluene	1250 $\pm$ 75 ^b	1350 $\pm$ 75 ^b
p-Xylene	2170 $\pm$ 75	2150 $\pm$ 75
Mesitylene	580 $\pm$ 15	560 $\pm$ 15

^aMeasurements were made at terphenyl concentrations ranging from 0.5×10^{-3} to 2×10^{-3} M.

^bA value of 1290 l/mole can be obtained from data reported by Kilin, Kovyrzina and Rozman (14).

TABLE II

Values of the O_2 Quenching Constant, γ ,
in Units of liter/mole for p-Terphenyl Solutions^a

Solvent	$[O_2] \frac{\text{mole}}{\text{liter}} (13)$	Cs^{137} Excitation	UV Excitation in first solvent absorption band
Benzene	$1.38 \pm .04 \times 10^{-3}$	1800 ± 150	2000 ± 150
Toluene	$1.52 \pm .05 \times 10^{-3}$	1650 ± 100	1200 ± 100
p-Xylene	$1.32 \pm .10 \times 10^{-3}$	2900 ± 200	
Mesitylene	$1.13 \pm .07 \times 10^{-3}$	1150 ± 100	900 ± 100

^aDetermined from measurements at 2×10^{-3} M p-terphenyl.

TABLE III

Specific Rates and Diffusion Encounter Distances for Reactions
Involving Energy Transfer to p-Terphenyl and Quenching by Oxygen

Solvent ^a	τ_0^b (n sec)(16)	k_3^c (l/mole sec)	$R_a(\text{\AA})$	k_7^d (l/mole sec)	$R_\gamma(\text{\AA})$
Benzene	17.7	7.8×10^{10}	24	11×10^{10}	19
Toluene	19.0	6.8×10^{10}	21	6.3×10^{10}	11
p-Xylene	20.2	11×10^{10}	34	14×10^{10}	24

^aThere is no literature value currently available for the mesitylene decay time.

^bValues of 22 ns, 23ns and 20 ns have recently been reported for benzene, toluene and p-xylene respectively (30).

^cValues of a from columns 2 and 3 of Table I were averaged to calculate k_3 .

^dValue of γ taken from column 4 of Table II, for benzene and toluene and from column 3 of Table II for p-xylene.

TABLE IV

Effect of Dilution on Transfer Efficiency
from p-Xylene to Anthracene (1.12×10^{-3} M).

[p-xylene] (mole/liter)	ϕ_t	α (liter/mole)	τ_0 (n sec) (30)
8.1	0.63	1500	20
0.81	0.62	1450	26
0.081	0.60	1350	28
0.0081	0.58	1250	28

TABLE V

Comparison of Scintillation Efficiency
and Internal Conversion Efficiency in Alkyl Benzene Liquids

Solvent	ϕ_f (relative)	M_E	f	g
Benzene	1.00	1.00	1.00	1.00
Toluene		1.36 ^a	1.46	1.83
p-Xylene	0.97	1.48	1.58	2.69
Mesitylene	0.94	1.55	1.29	3.12

^a ϕ_f for toluene assumed to be 0.98.

Figure 1. Fluorimeter Schematic

Figure 2. Emission Spectrum of Liquid Benzene

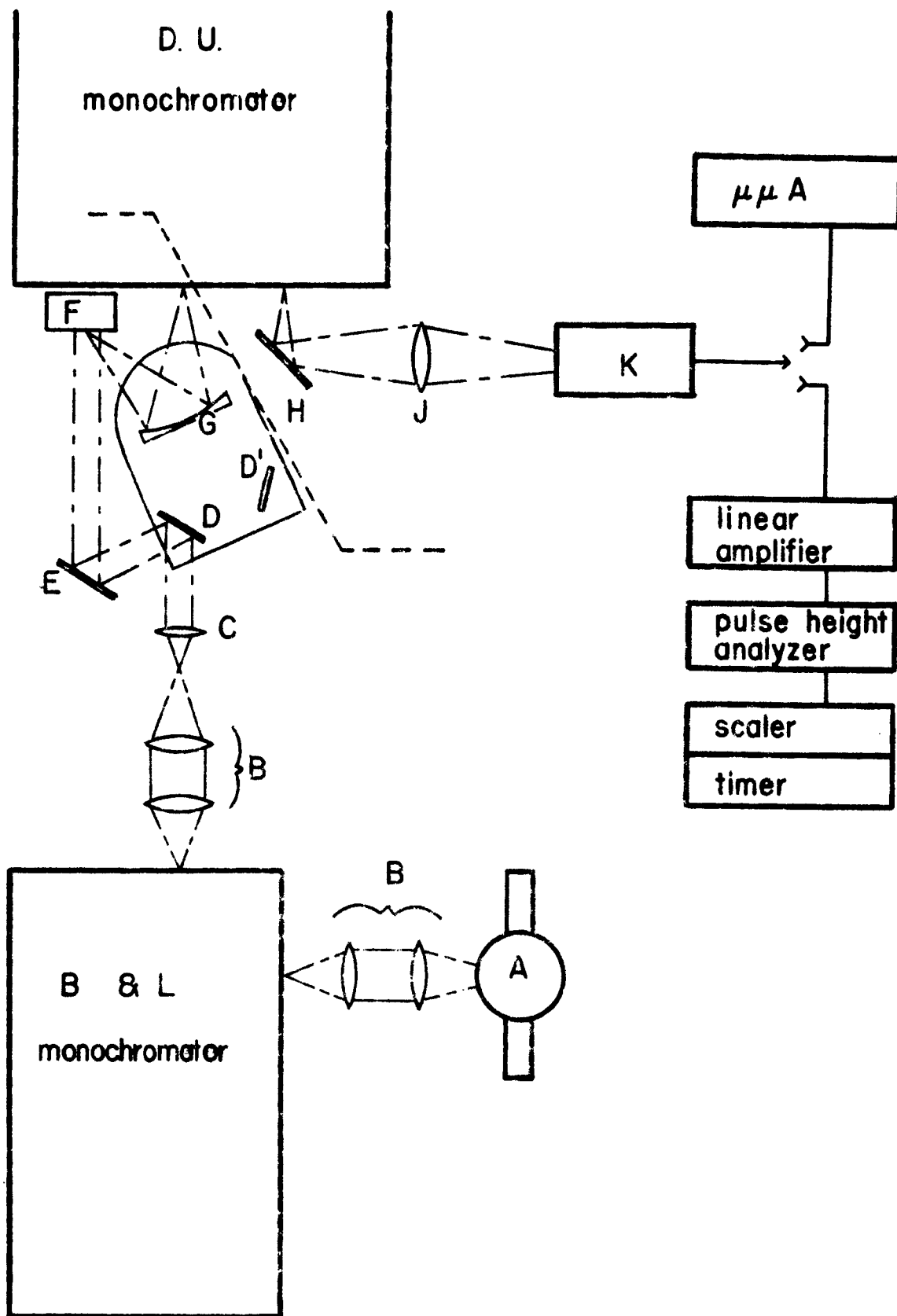


FIGURE 1

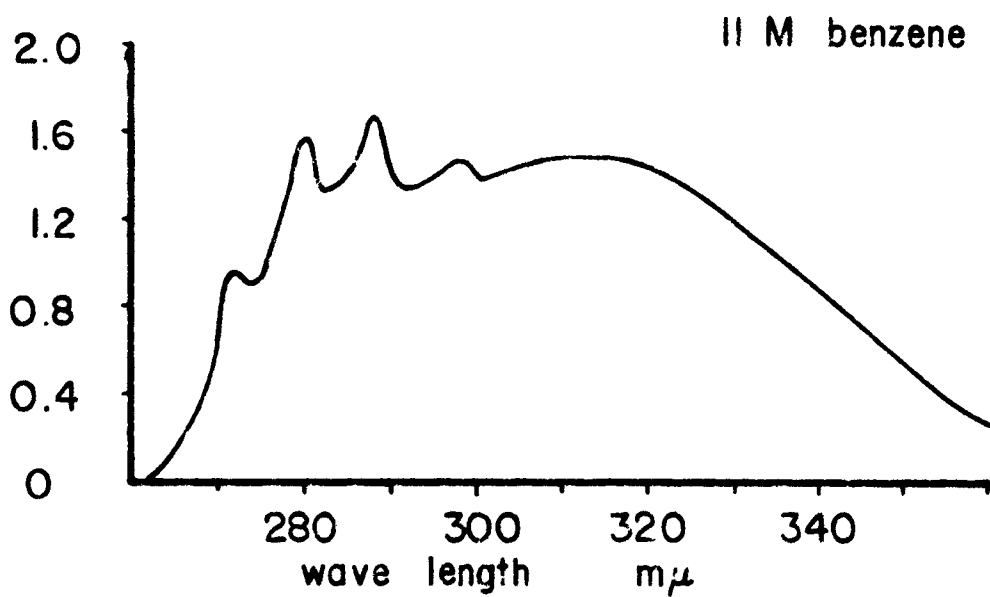
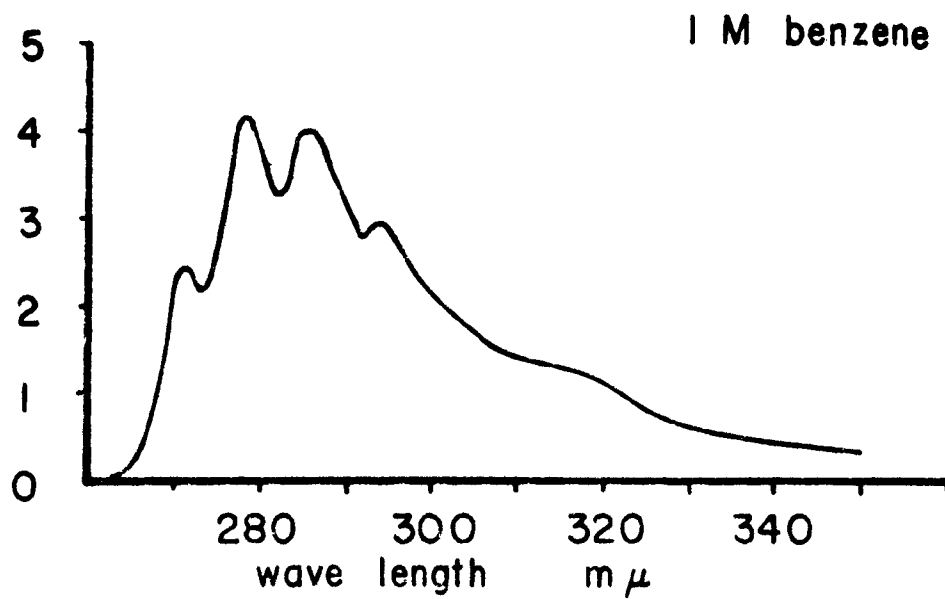


FIGURE 2

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p-terphenyl have been determined both for UV excitation in the first absorption band and for Cs 137 γ excitation. The efficiency with which oxygen quenches the transport process has also been determined. Dilution of the aromatic liquids with hexane is found to reduce the rate of energy transfer. Mechanisms of energy transfer utilizing the states of the bulk solvent are briefly reviewed. Relative scintillation efficiencies have been determined and compared with approximately calculated values.	UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED
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