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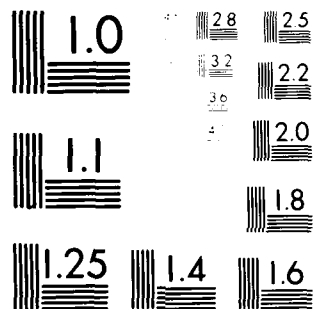
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Chemiluminescence of Organic Compounds,

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Gary B. Schuster and Steven P. Schmidt

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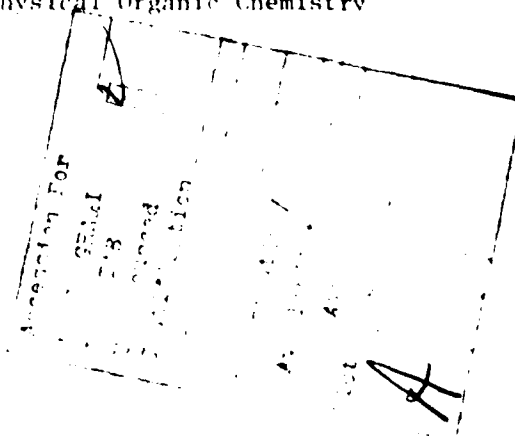
Chemiluminescence of Organic Compounds

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I. INTRODUCTION

The emission of visible light from a chemical reaction or by a living organism is a striking phenomenon and a rather remarkable occurrence. Perhaps stimulated initially by the mere peculiarity and uniqueness of such events, interest in bioluminescent and chemiluminescent reactions has grown and diversified significantly over the past several decades. Today the reasons for interest in chemiluminescent and bioluminescent systems are remarkably varied, and the field is quite interdisciplinary.

Identification of the varying biological functions, classification of the bioluminescent relationships between different organisms, elucidation of the detailed reaction pathway, and the possibility of convenient study of the effect of enzyme or substrate modification have all been prime motivations for the study of bioluminescence (McCapra, 1976 ; Henry and Michelson, 1978 ; Hastings and Wilson, 1976 ; Cormier et al., 1975). Interest in chemiluminescence has been stimulated by its remarkable sensitivity and often selectivity as an analytical tool. As a result, chemiluminescence has found extensive application in the detection of trace metals in solution (Montano and Ingle, 1979 ; Marino et al., 1979) and of metabolites and hosts of other substrates (Mendenhall, 1977 ; Williams and Seite, 1976). Still other interest in chemiluminescent reactions has been directed toward the development of a commercial, portable, "cold" light source (Rauhut, 1969).

Of most relevance to the present work, however, is the interest in chemiluminescent reactions generated by their relation to fundamental molecular transformations and dynamics. Study of these reactions promises to yield important information concerning these molecular processes. To this end, attention has focused on the really extraordinary step of the chemiluminescence process, the chemiexcitation step, the key nonadiabatic process in which a

ground state reactant is transformed into an electronically excited state product. It is within this step that most of the mystery and intrigue in chemiluminescence remains.

The field of chemiluminescence has experienced tremendous growth and witnessed significant advancements in the past decade. To a large extent, the recent progress toward the understanding of chemiluminescent processes can be attributed to achievements and advancements in three general areas.

The first area of achievement was the discovery and subsequent intensive investigation of the chemiluminescent reaction of 1,2-dioxetanes. The discovery of this reaction, a simple unimolecular rearrangement, has allowed experimentalists to focus on the study of the key step of chemiexcitation. Previously studied chemiluminescent reactions often involved complicated reaction systems and sequences, required several reagents, and often afforded multiple products via transient intermediates. While some such systems have yielded to intensive investigation, the most revealing probes of chemiexcitation have been studies of simple unimolecular rearrangements such as that of the 1,2-dioxetanes.

A second area of recent advancement has come in the general field of electron-transfer chemiluminescence. While electron-transfer reactions constituted some of the earliest examples of chemiluminescent reactions in solution (Dufford et al., 1923), the reaction systems were often complex. This, compounded with low yields of light made interpretation of results difficult. More recently, electron-transfer chemiluminescence has been investigated extensively as electrogenerated chemiluminescence (ECL). In this technique, radical ions ultimately capable of chemiexcitation by electron-transfer are produced by electrochemical means. Such systems are

more easily controlled than other chemically oxidative systems, and hence the results of such electrochemical experiments are more readily interpreted. Thus, through ECL studies significant progress has been made in recent years toward the understanding of chemiexcitation by electron transfer.

A third general area of recent advancement which has served to stimulate interest and has offered new insights into the processes of chemiluminescence has been the identification of chemically initiated electron-exchange luminescence (CIEEL) as a general mechanism for the chemical formation of light (Schuster, 1979 ; Schuster et al., 1979). This mechanism links what had been two very separate domains: the chemiluminescent rearrangement of high-energy-content organic molecules and electron-transfer chemiluminescence.

The recent studies of 1,2-dioxetane chemiluminescence, ECL, and CIEEL have brought significant advancement to the field of chemiluminescence. The relatively simple nature of these processes has allowed attention to be focused on the nature of chemiexcitation and much has been learned. In addition, these relatively simple systems subsequently have been advanced as key intermediates, key steps or key sequences in many more complicated chemi- and bioluminescent systems.

A vast amount of experimental data on chemiluminescent reactions in solution has been reported during the last decade. This, and the height of general interest in the field are evidenced by the large number of review articles published in that period. These include general reviews of organic reaction chemiluminescence (Rauhut, 1979 ; Hastings and Wilson, 1976 ; Gundermann, 1974 ; White et al., 1974 ; McCapra, 1973 ; Goto, 1979 ; Brandl, 1979 ; Kamiya, 1980) and bioluminescence (McCapra, 1976;

Henry and Michelson, 1978 ; Hastings and Wilson, 1976 ; Cormier et al., 1975) as well as reviews of more narrowly defined scope on the chemiluminescence of 1,2-dioxetanes (Bartlett and Landis, 1979 ; Horn et al., 1978-79 ; Adam, 1977; Wilson, T., 1976; Turro et al., 1974a; Mumford, 1975), the chemiluminescence

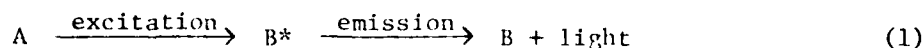
of hydrazides (Roswell and White, 1978 ; White and Roswell, 1970), electron-transfer chemiluminescence (Faulkner, 1978 ; Hercules, 1969), electrogenerated chemiluminescence (Faulkner, 1976), and the electron-exchange chemiluminescence of organic peroxides (Schuster, 1979 ; Schuster et al., 1979).

In this work we shall examine the general requirements for a reaction to be chemiluminescent, present in more detail the three important generalized mechanisms of chemiluminescence in solution, and finally discuss specific chemiluminescent systems.

II General Requirements for Chemiluminescence

Why should any chemical reaction generate electronically excited-state products when it could generate the same species in their ground state? Despite the seeming plethora of available data, this question, the fundamental question concerning chemiluminescence in solution, remains largely unanswered. Yet certain general requirements which must be met for a reaction to be chemiluminescent are readily identified. In this discussion we shall present these requirements, and then look at additional factors and components which are thought to influence the efficiency of a chemiluminescent reaction.

Ultimately, all chemiluminescent reaction sequences can be reduced to two key steps, the chemical excitation step (which may, of course, be unimolecular or bimolecular) and the emission step (equation 1). The overall quantum efficiency of a chemiluminescent reaction, ϕ_{CL} , defined as the number



of einsteins of light (Avagadro's number of photons) produced per mole of reactant, is the product of the efficiencies of the individual steps (equation 2), where ϕ_{CE} is the efficiency of chemical excitation and ϕ_{EM} is the

$$\phi_{CL} = \phi_{CE} \times \phi_{EM} \quad (2)$$

efficiency of emission.

An obvious requirement of a chemiluminescent reaction is that a product molecule be capable of receiving the chemical excitation energy and forming an excited state. Typically, for chemiluminescent reactions of organic molecules in solution, the energetically accessible excited states are of aromatic

hydrocarbons and of carbonyl compounds. For chemiluminescence to be observed it is also necessary that the electronically excited product be capable of luminescing under the reaction conditions. If ϕ_{EM} is low, as is typically the case for the carbonyl chromophore and for virtually all triplet excited states, then the overall efficiency, ϕ_{CL} , will be low even if the chemiexcitation efficiency, ϕ_{CE} , is high (Borkman and Kearns, 1966 ; Calvert and Pitts, 1966). In such cases this difficulty can be circumvented by the addition of a suitable acceptor molecule which is excited by energy transfer and subsequently emits light. An additional term for the efficiency of energy transfer, ϕ_{ET} must then enter the overall efficiency calculation.

Fortunately, the factors which affect ϕ_{EM} and ϕ_{ET} are fairly well understood. Through careful application of the rules derived from photochemical studies of energy transfer reactions it is possible in most cases to efficiently convert the chemically generated excited state to a photon of light (Wilson and Schaap, 1971; Belyakov and Vassil'ev, 1970). Thus one is able to focus attention on the much less well understood factors which affect ϕ_{CE} . These factors are the subject of our remaining discussion on general requirements for chemiluminescent reactions.

Certainly the most stringent requirement for efficient chemiexcitation is one of energetics. Organic chromophores have excited state energies, ΔE^* , in the range of 50 to 100 kcal/mol, and the energy required to populate the excited state chemically must be supplied by the reaction. Moreover, in a multistep reaction, the necessary energy must be released in a single step, due to the essentially instantaneous nature of the chemical excitation. In a multistep reaction in which the individual steps are unable to provide the necessary energy for excitation, energy released in an early step will be dissipated in solution by vibrational

relaxation and hence will not be available to supplement the energy released by a subsequent step (Rauhut *et al.*, 1965b; Rauhut, 1979).

The major source of the energy required for excitation is the reaction enthalpy, ΔH_r . There are numerous examples, however, of chemiluminescent reactions in which the energy of the observed photon is greater than ΔH_r (Bartlett and Landis, 1979 ; Horn *et al.*, 1978-79 ; Adam, 1977 ; Wilson, 1976 ; Turro *et al.*, 1974b; Mumford, 1975 ; McCapra, 1966 ; Lechtken *et al.*, 1973). In these cases, where the reaction enthalpy alone does not provide sufficient energy for excitation, i.e. $-\Delta H_r < \Delta E^*$, additional energy may be provided by the activation enthalpy of the reaction, $\Delta H^\ddagger$. Thus, the first law of thermodynamics is satisfied by the requirements of equation 3. An objection to the inclusion of $\Delta H^\ddagger$ for satisfaction of the energy requirement had been made on thermodynamic grounds (Perrin, 1975) but was later shown to be incorrect (Lissi, 1976 ; Wilson, E. B., 1976).

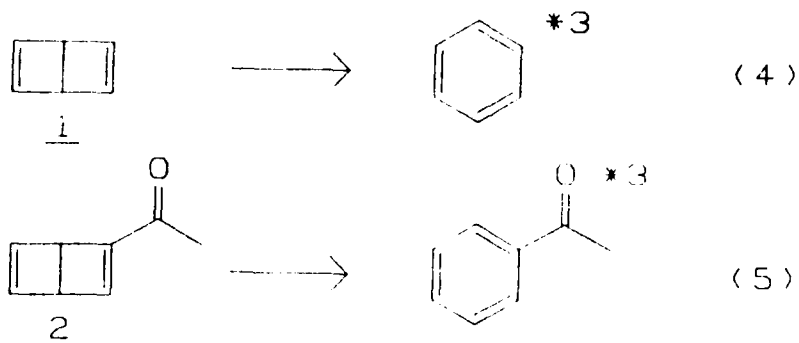
$$-\Delta H_r + \Delta H^\ddagger \geq \Delta E^* \quad (3)$$

The energy requirement of equation 3 is a necessary but not a sufficient condition for a reaction to be chemiluminescent (Richardson, 1980). While few organic reactions meet this requirement, and this accounts mainly for the rarity of chemiluminescence, there are other important factors which influence first whether a reaction will be chemiluminescent and thereafter the efficiency of chemiexcitation. Provided the energy requirement is met, there still must be a reason for the rather amazing non-equilibrium formation of excited state products. In this section we will discuss those factors which are thought to favor the selection of an excited state over a ground state product.

Qualitative reasoning rests on the Franck-Condon Principle (Birks, 1970) as a basis for identifying the kinetic factors which favor a path leading to excited state products. In short, this principle holds that conversion between electronic states occurs without a change in molecular geometry. Nuclear positions and momenta can change only over a long time relative to state changes (and electron transfers) which occur instantaneously.

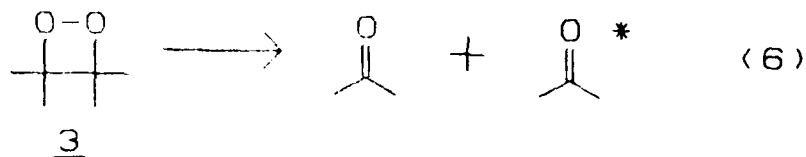
This principle has important implications for requirements on molecular geometry which will affect the efficiency of a chemiluminescent reaction. Since the state transformation from ground to excited occurs without a change in geometry, it will be most facile when the geometry of the transition state of the reaction is similar to the geometry of the excited state of the incipient chromophore. If the transition state geometry and the geometry of the excited state of the product are similar, formation of the excited state may be preferred over formation of the ground state since less mechanical restructuring will be required. Typically in a rearrangement reaction, bonds which are being broken and those which are being formed are longer at the transition state than in the ground state of the reactant or product. Significantly, the bonds of an organic chromophore are typically longer in the excited state than in the ground state (Moule and Walsh, 1975). Thus it seems best suited to chemiexcitation that the bonds of the target chromophore be involved directly in the rearrangement.

Possible examples of the importance of the coincidence of transition-state and excited-state geometries and also the importance of the location of the essential reaction or localization of reaction energy are the chemiluminescent rearrangements of Dewar benzene (1) and Dewar acetophenone (2) to benzene and acetophenone, respectively (Lechtken *et al.*, 1973 ; Turro *et al.*, 1974c; Turro *et al.*, 1975). The efficiency of excited state production though quite low is approximately



the same for both systems. Yet the triplet of acetophenone is more accessible energetically than that of benzene by about 10 kcal/mol and one might have expected, had energy considerations been of prime importance, that the yield of excited states from 2 would be substantially higher than from 1. A possible explanation for the observed results lies in the geometric requirements imposed by the Franck-Condon Principle. In 2 the key bond-breaking and making processes occur in the benzene ring, remote from the final localization of excitation energy in the carbonyl region. The geometry of the lowest excited state of acetophenone, which is $n\pi^*$ in character, is characterized by an elongated carbonyl bond. The geometry of the transition state for reaction 5, however, is probably characterized by an elongated para carbon-carbon bond and a carbon-oxygen bond of normal length. Thus, reasonable coincidence between the transition state geometry and excited state product geometry is not expected for reaction 5.

Another example of the idea of transition state and excited state geometry congruencies can be found in the chemiluminescent reaction of 1,2-dioxetanes, equation 6. The excited state of formaldehyde is known to be bent, with the oxygen ca. 20° above the plane formed by the carbon and its two



hydrogens (Moule and Walsh, 1975; Raynes, 1966), and other simple carbonyl compounds are usually assumed to adopt a similar structure. 1,2-Dioxetanes such as 3 generate excited state carbonyl products with high efficiency, and it has been noted that their geometry approaches that expected for the excited state of the carbonyl products (Numan *et al.*, 1977).

The geometric requirements imposed by Franck-Condon factors necessitate a re-evaluation of the energy requirement of equation 3. The requirement must somehow account for any non-congruence between the transition state geometry and the geometry of the excited state. In equation 3, ΔE^* is the energy of the excited state at a relaxed geometry. If there is geometric non-congruence, that is the excited state at the relaxed geometry is not accessible, then the crossing between the ground and excited state must occur at a non-relaxed geometry, one of higher energy. Thus a geometry factor, $\Delta E'$ must be added to the energy requirement:

$$-\Delta H_r + \text{---}^\ddagger \geq \Delta E^* + \Delta E' \quad (7)$$

While the magnitude of $\Delta E'$ is very difficult to evaluate due to the inherent difficulty in predicting the shapes of the potential energy surfaces, it may well be significant and thus should not be neglected.

An alternative (yet equivalent) statement of the Franck-Condon Principle is that a molecule cannot accept a large amount of kinetic energy instantaneously and

thus become mechanically excited. Thus speed in a reaction, meaning energy is released in period of time on the order of or less than the time of a vibration, combined with high exoergicity, favors formation of an electronically excited state over formation of a highly vibrationally excited ground state. Electron-transfer reactions have an inherent advantage for the formation of excited states in this respect. The electron transfer occurs fast, without a change in geometry, and the relatively slower process of energy dissipation through bond vibration is not effectively competitive with electronic excitation.

For rearrangement and fragmentation reactions, this kinetic competition between mechanical excitation and electronic excitation suggests that limiting the number of vibrational modes of the product will limit the capability of the reaction to dissipate energy vibrationally. It has been suggested, therefore, that the formation of small molecules favors selection of the excited state (Rauhut, 1969 ; Rauhut, 1979). Numerous examples of efficient chemiluminescent reactions which do not involve the formation of small products, however, force one to question the importance of such a requirement (Schuster *et al.*, 1975 ; Zaklika *et al.*, 1978a; Dixon, 1981).

A theoretical treatment of chemiluminescent reactions has been presented by Marcus (1965 , 1970). Although developed for electron-transfer reactions, this treatment appears to be applicable to other chemiluminescent reactions when appropriately modified. The importance of Marcus theory is that it demonstrates that other factors besides energetics, which might loosely be termed geometry, are also important in determining whether a reaction will be chemiluminescent. A useful description and discussion of Marcus's treatment has been given by Hercules (1969).

Marcus considers the relative probabilities for an electron-transfer reaction leading to excited state products vs. ground state products in terms of the accessibility of crossing points of the free energy surfaces. Most

importantly, the accessibility, or activation free energy, ΔG^* , is related to the free energy of the reaction, ΔG^0 . For a reaction proceeding to a given electronic state, the barrier ΔG^* , initially decreases as ΔG^0 becomes increasingly negative and then, most significantly, actually increases as ΔG^0 continues to become increasingly negative. Thus, for highly exoergic reactions, the barrier to formation of the ground state may actually be higher than the barrier to formation of the excited state. The situation, however, may be complicated if there are large configurational differences between the ground and excited state of the product, which would result in a decrease in the accessibility of the excited state and hence an overall reduction in the chemiexcitation efficiency. While difficulty in evaluating the various parameters of Marcus theory, especially as influenced by configurational differences, is a shortcoming, this treatment does provide a useful picture with a theoretical basis.

Still other factors may be important in influencing first whether a reaction will be chemiluminescent and second the efficiency of chemiexcitation. Spin orbit coupling factors could play a significant role in determining the efficiency of triplet state generation (Turro and Lechtken, 1973) and thus could be especially important for reactions in which only the triplet state and not the first excited singlet state, was energetically accessible. Finally, the possible influence of orbital symmetry constraints, which is of considerable historical interest at least, has not been fully evaluated. It has been suggested that orbital symmetry forbiddance is a prerequisite for a reaction to be efficiently chemiluminescent (McCapra, 1968), a concept which was endorsed and expanded by others (Kearns, 1969). For concerted pericyclic reactions, "forbiddance" does provide a low energy crossing of ground and

excited state surfaces and consequently direct formation of electronically excited products would be predicted (Dewar et al, 1974 ; Turro and Devaquet, 1978). However, there have been no experimental verifications of the concertedness of what would be a "forbidden" pericyclic chemiluminescent reaction, nor has a direct comparison of orbital symmetry "allowed" and "forbidden" processes which are potentially chemiluminescent, been made.

III Generalized Mechanisms for Chemiluminescence of Organic Compounds in Solution

Until a few years ago, just two general schemes had been proposed to explain the chemiluminescence of organic compounds.

In the first sequence (Figure 1), a high-energy reactant molecule undergoes an exergonic reaction, typically a rearrangement or fragmentation, to generate a product molecule in an electronically excited state. If the initially formed excited state is emissive, direct chemiluminescence results. Alternatively, the initially formed excited state can transfer its energy to a suitable acceptor molecule. Subsequent emission from this species results in indirect chemiluminescence. Examples of chemiluminescent reactions which are included in this general scheme are the unimolecular fragmentation of 1,2-dioxetanes, the rearrangement of bewar benzenes, and the classical chemiluminescent reactions of luminol.

The second general mechanism for chemical light formation is one-electron transfer (Faulkner, 1976 ; Faulkner, 1978 ; Hercules, 1969). The simplest of bimolecular reactions, energetic electron-transfer reactions possess several additional characteristics which make them perhaps the most intuitively reasonable choice for a general mechanistic class of chemiluminescent reactions.

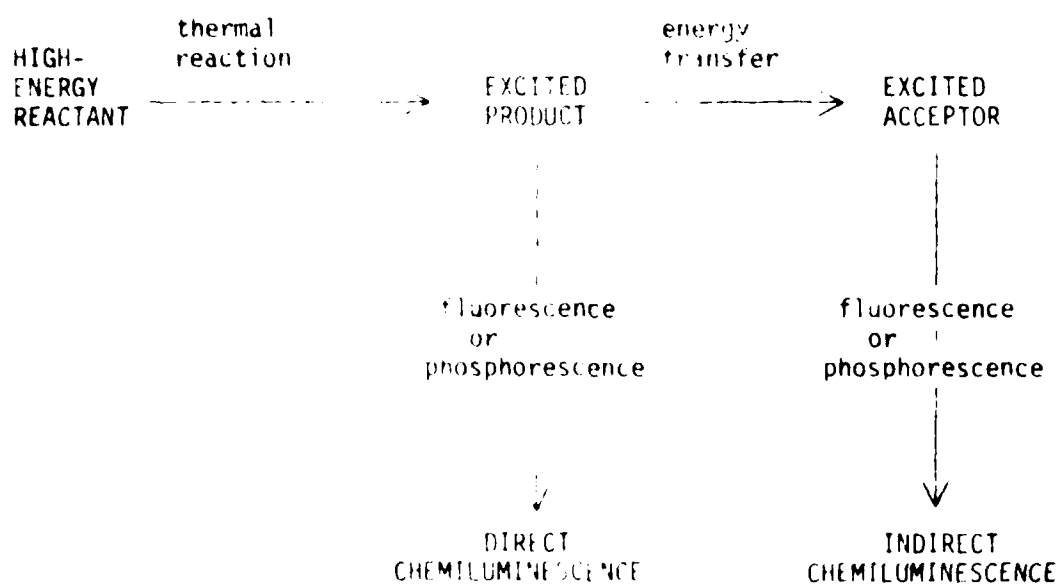
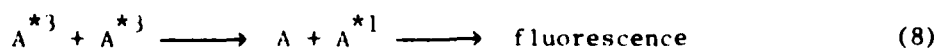


Figure 1. Excited states of luminescent molecules generated directly and indirectly from exothermic reaction.

The electron transfer chemiexcitation is shown schematically in molecular orbital terms in Figure 2. Although other electron transfer reactions are potentially chemiluminescent (Tokel-Takvoryan *et al.*, 1973), the charge annihilation reaction of oppositely charged aromatic radical ions is the prototypical case and has been most extensively studied. This is due to the convenient preparation of the radical ions by electrochemical means, the large range of redox potentials which are available, and the high fluorescence efficiency of the product aromatic hydrocarbons (Faulkner, 1978). This technique for light formation has become known as electrogenerated chemiluminescence (ECL).

Transfer of an electron from the radical anion ($D^{\cdot -}$) to the radical cation ($A^{\cdot +}$) results in chemiexcitation. Subsequent emission from the directly formed excited state, or one derived therefrom, results in chemiluminescence. As depicted in Figure 2, the donor (D) has received the excitation energy. In fact, depending on the system and the relative energetics, either ion precursor may become excited and subsequently emit. Figure 2 also depicts formation of an excited state of singlet multiplicity. The triplet state may, of course, be formed as well. In fact, in many systems the excited singlet is energetically inaccessible and the triplet is the exclusive excited state product. In such a case, the ultimate fluorescence which is observed comes from a singlet state which arises from annihilation of two triplets formed directly by two distinct redox events (equation 8).



A third generalized mechanism for chemiluminescence of organic molecules in solution has been identified recently as chemically initiated electron-exchange luminescence (CIEEL) (Schuster, 1979 ; Schuster *et al.*, 1979). In essential features it is a combination of the two previously described mechanisms for excited state generation. A schematic representation is given in Figure 3.

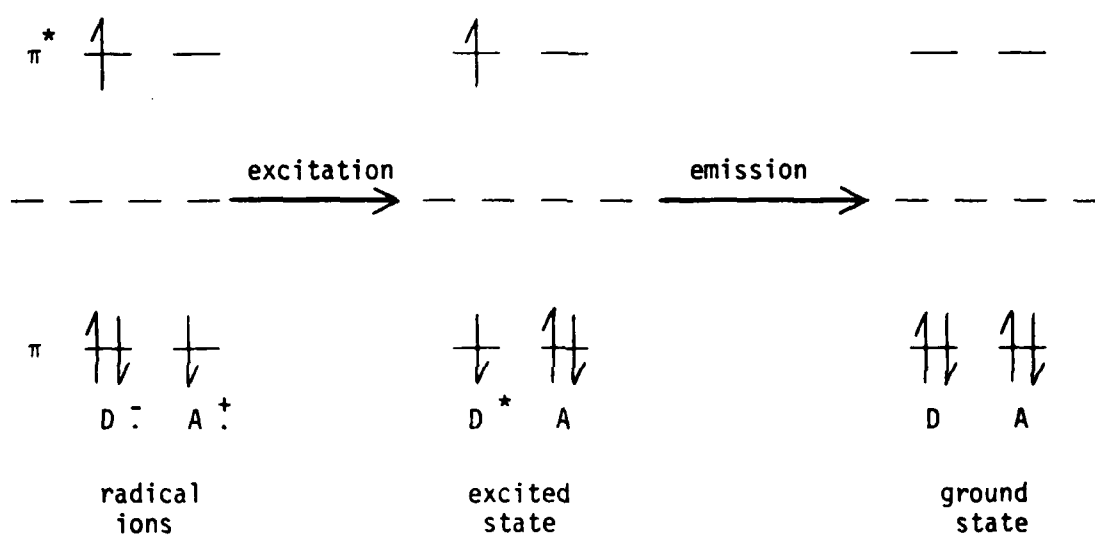


Figure 2. Electron-transfer chemiluminescence.
Radical ion annihilation is depicted.

In short, the sequence is initiated by one-electron transfer from a suitable donor molecule (activator, ACT) to a high energy content organic molecule (a peroxide for all systems described thus far). Subsequent rearrangement or loss of a neutral fragment (carbon dioxide for example) transforms the reduced peroxide into a highly reducing species, in the form of a radical anion. Charge annihilation then generates an electronically excited state of ACT and the final step of the sequence is emission from ACT. Such a sequence, in which the emission of light is from an excited state formed directly from a bimolecular reaction between substrate and catalyst, has been termed activated chemiluminescence (Dixon and Schuster, 1979).

The net transformation in the CIEEL sequence involves conversion of a high energy content molecule to products of much lower energy. This transformation ultimately is the source of the large amount of energy required for chemiluminescence, and in this respect CIEEL is related to the first generalized mechanism. Bond energy is converted to excitation energy. The actual mechanism of chemiexcitation, however, is the radical ion annihilation case of the more general electron-transfer chemiluminescence. CIEEL differs distinctly from ECL, however, in that the radical ions are produced chemically rather than electrochemically. Moreover, CIEEL has an advantage over ECL in the strive to achieve maximum efficiency in chemiluminescence in that the highly reactive radical ions which ultimately annihilate are born within the same solvent cage.

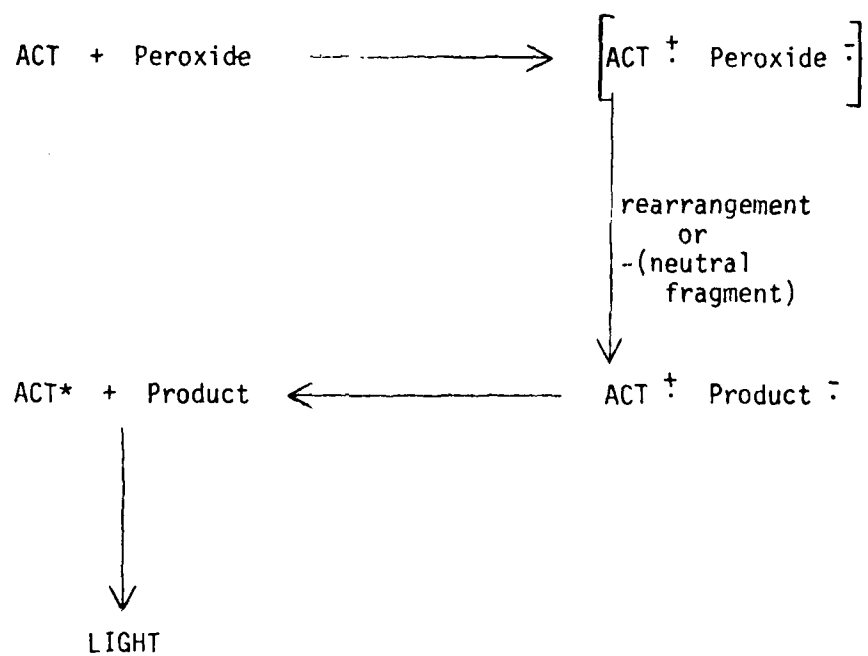


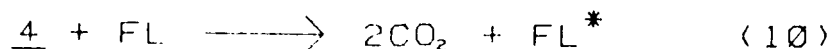
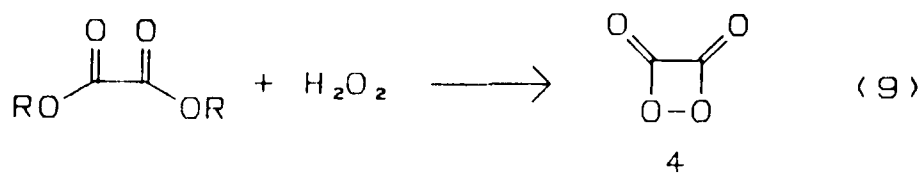
Figure 3. Chemically Initiated Electron-Exchange Luminescence

IV Chemiluminescence of Molecular Systems

A. Peroxyoxalate Chemiluminescence.

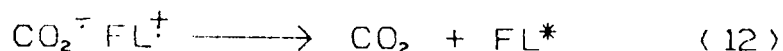
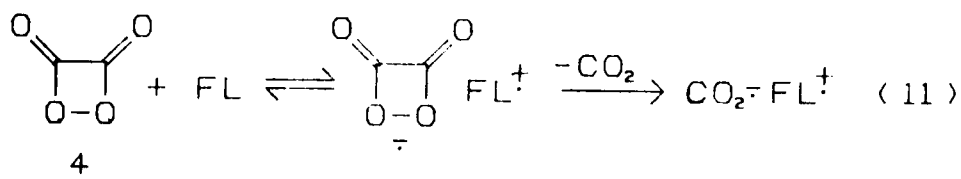
The reaction of certain derivatives of oxalic acid with hydrogen peroxide in the presence of a suitable fluorescer represents an early demonstration of a relatively efficient, non-enzymatic chemiluminescent system (Rauhut, 1969). Work in this area was initiated by the report of Chandross on the chemiluminescent reaction of oxalyl chloride and hydrogen peroxide in the presence of anthracene (Chandross, 1963). While in subsequent work Rauhut was able to maximize the quantum efficiency of this reaction at 5% (Rauhut et al., 1966), the major advancement in this area came with the discovery, also by Rauhut and co-workers, of the even higher quantum efficiencies which were obtainable from the reaction of certain electronegatively substituted aryl oxalates with hydrogen peroxide and fluorescent compounds (Rauhut et al., 1967).

A remarkably wide range of oxalates has been investigated, and it is clear that a high quantum efficiency requires a good leaving group. Bis(2,4,6-trichlorophenyl)oxalate and bis(2,4-dinitrophenyl)oxalate are popular examples and have enjoyed use in delightful demonstrations (Mohan and Turro, 1974). Efficiencies as high as 22-27% have been reported with these esters and fluorsceners such as rubrene. The high yield of light is the result of a high efficiency of singlet excitation of the fluorescer which can be achieved by careful choice of reaction conditions, and the high fluorescence efficiency of the fluorsceners which are employed. The mechanism for this reaction, although still tentative, features 1,2-dioxetanedione (4) as the key intermediate. Unfortunately 4 has continued to elude direct detection (Cordes et al., 1969 ; DeCorpo et al., 1972 ; Stauff et al., 1972 , 1976), and some early evidence for the metastability of the key intermediate toward unimolecular decomposition has been questioned (White et al., 1973).



The intimate role of the fluorescer in this chemiluminescent system was appreciated early. While the fluorescer is independent of the key intermediate (thus allowing a choice of emission wavelength by the choice of a suitable fluorescer) (Rauhut *et al.*, 1975), the fluorescer appears to catalyze the release of the energy stored in the intermediate and direct it toward the formation of excited states. Rauhut (1969) suggested that this catalysis was due to an initially formed charge-transfer complex between the fluorescer and the intermediate. The intimate role of the fluorescer was further demonstrated by Lechtken and Turro (1974) and Sherman *et al.* (1978) who showed a dependency of the chemiluminescence efficiency on the nature of the fluorescer. In particular, the intensity was found to fall off slowly with increasing singlet energy of the fluorescer. Such behavior is not typical of conventional energy transfer and suggests that the fluorescer is excited in the chemiexcitation step.

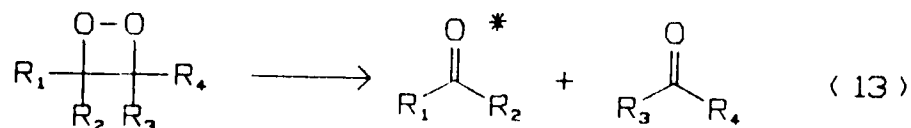
McCapra (1973) expanded the ideas of Rauhut and suggested, as an interesting possibility, an excitation mechanism which had certain features in common with electron-transfer chemiluminescence. Electron transfer from the fluorescer to the presumed dioxetanedione, followed by decarboxylation, generates carbon dioxide radical anion and the fluorescer radical cation. Chemiexcitation occurs by annihilation of these radical ions.



This sequence, although highly speculative at the time of its proposal, has gained support in recent years (McCapra, 1977) with the experimental establishment of the involvement of a CIEEL mechanism in the chemiluminescence of other peroxides (Schuster, 1979; Schuster *et al.*, 1979). Nevertheless, final verification of the CIEEL type mechanism in this system awaits the presentation of further evidence for the intermediacy of 4.

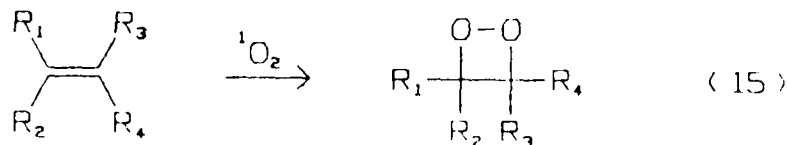
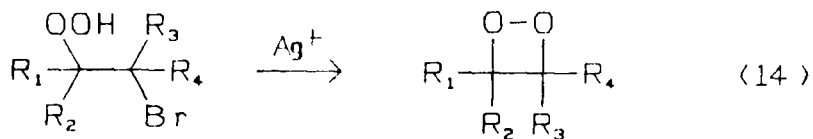
B. Dioxetane Chemiluminescence

By far the chemiluminescent reaction which has been most extensively investigated over the past decade is the unimolecular transformation of the 1,2-dioxetanes to two carbonyl-containing products, one of which may be formed in an electronically excited state (equation 13). Before the preparation, isolation and characterization of a stable dioxetane was first reported



by Kopecky and Mumford (1969), dioxetanes had received considerable attention as potential intermediates in many chemi- and bioluminescent reactions. This early suggestion, made by White and Harding (1964, 1965) rationalized the apparently ubiquitous role of oxygen, as well as the common appearance of carbonyl-containing products, in these reactions. Moreover, the expected great exoergicity of this reaction, due in part to the weak oxygen-oxygen bond and the strain energy of the four-membered ring, appeared to meet the energetic requirements for an efficient chemiluminescent reaction. Finally, orbital symmetry ideas, which were quite fashionable at the time, predicted a symmetry allowed transformation, if concerted, to excited state products (McCapra, 1968).

Kopecky's synthesis of trimethyldioxetane employed the base mediated dehydrohalogenation of 2-methyl-2-hydroperoxy-3-bromobutane. Subsequently, this type of eliminative cyclization (equation 14) has been applied to the preparation of scores of dioxetanes. Additionally, many dioxetanes have been prepared by the addition of singlet oxygen to the electron-rich olefins which do not possess allylic hydrogens (equation 15) a method discovered first by



Bartlett and Schaap (1970). More recently this procedure has been expanded to include some trisubstituted olefins (Asveld and Kellog, 1980). The wide applicability of these procedures to the preparation of dioxetanes of diverse structure, and what proved to many workers to be a surprising stability of most alkyl and alkoxy substituted dioxetanes, have facilitated their study and contributed to the tremendous amount of activity in the field. To date well over 100 dioxetanes have been prepared and scrutinized with the objective of elucidating the mechanistic details of their remarkable transformation to excited state carbonyl-containing products.

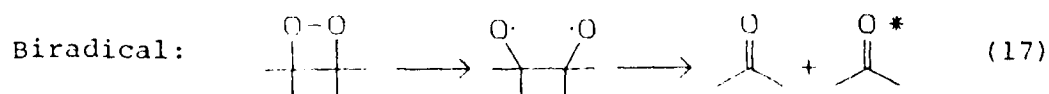
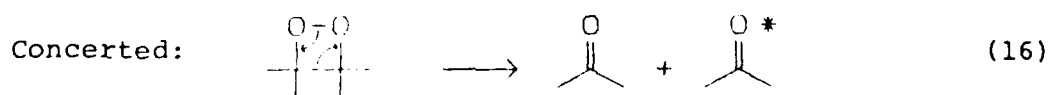
1,2-Dioxetanes have been the subject of several specialized reviews in recent years (Bartlett and Landis, 1979 ; Horn *et al.*, 1978-79 ; Adam, 1977; Wilson, T., 1976; Turro *et al.*, 1974a; Mumford, 1975). These articles cover with depth which is not possible here such dioxetane topics as 1) preparation, 2) physical and spectroscopic characterization, 3) experimental techniques, especially for the study of chemiluminescence, 4) mechanisms of decomposition and chemiexcitation, 5) ground state transformations, and 6) reactions involving dioxetanes as postulated intermediates. The interested reader is referred to these articles for details on these specialized topics, and for some historically interesting perspectives.

In this treatment we will limit ourselves to a discussion of work which deals directly with the mechanism of the decomposition of 1,2-dioxetanes and with the mechanism of chemiexcitation, paying particular attention to the efficiency and selectivity of this process. Emphasis will be placed on the most recent results and developments in this area.

In the past few years two rather distinct classes of chemiluminescent dioxetanes have become evident. Alkyl, alkoxy, and simple aryl substituted dioxetanes, which includes the earliest dioxetanes prepared, are characterized by reasonable stability ($E_a = 23-30$ kcal/mol), excitation efficiencies in the range of 5-30%, and a high ratio of triplet to singlet excited state products,

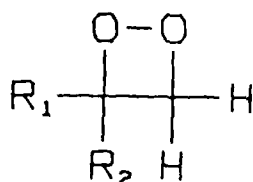
typically more than 50 to 1. Dioxetanes with aminoaryl and other easily oxidized substituents differ markedly from the first class of dioxetanes. They are characterized by much lower activation energies for reaction, different solvent effects on the decomposition reaction, a high yield of singlet excited states, and, apparently, a different mechanism for reaction and chemiexcitation.

A mechanism postulated for dioxetane decomposition by McCapra (1968) hypothesized simultaneous cleavage of the oxygen-oxygen and the carbon-carbon bonds in a concerted manner leading, as predicted by orbital correlation, directly to excited state products (equation 16). While this mechanism was able to account for the experimentally observed high yield of excited state products, it did not in this simple form account for the high ratio of triplet to singlet excited state products. Turro, therefore, later expanded this picture by suggesting that the spin multiplicity change occurred simultaneously with bond cleavage through a spin-orbit coupling mechanism enhanced by a rotation of the electronic charge on one oxygen atom by 90° about the C-O axis (Turro and Lechtken, 1973).



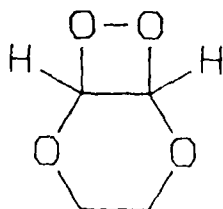
The other mechanistic extreme is the two-step mechanism, first considered by White and Harding (1964, 1965) and examined experimentally first /by Richardson (O'Neal and Richardson, 1970 ; Richardson et al., 1972). Cleavage of the weak oxygen-oxygen bond generates a short-lived biradical intermediate which cleaves rapidly in a second step to carbonyl-containing products. The initially formed singlet biradical is postulated to partition between singlet ground and excited state carbonyl products, and the triplet biradical. Singlet and triplet states of the biradical should approach each other in energy with sufficient spatial separation of the oxygen atoms. Hence intersystem crossing to the triplet via spin-orbit coupling will be facilitated in the biradical. Cleavage of the triplet biradical should lead to formation of a triplet excited state product.

To date, no piece of experimental evidence requires a concerted mechanism. On the other hand, considerable data, although often circumstantial or indirect, support the intermediacy of a biradical. The initial postulation of a biradical mechanism was supported by activation parameters determined for a series of variously substituted dioxetanes (5) (Richardson et al., 1974 ; 1975, 1978) and by thermochemical calculations (O'Neal and Richardson, 1970 ; Richardson et al., 1974). The relative insensitivity of the dioxetane decomposition rate to substitution, particularly in comparing the phenyl, anisyl, and benzyl substituted dioxetanes (5c,d,e) supports cleavage of the oxygen-oxygen bond, which is one bond removed from the position of substitution, in the rate-determining step. One would expect in a concerted mechanism that the reactivity of the dioxetane would be enhanced by substituents which would conjugate with the developing carbonyl bond. Similarly, a study by Wilson et al. (1976) supports the suggestion that there is very little carbon-carbon bond elongation in the transition state of the rate-determining step of the cleavage reaction. Activation

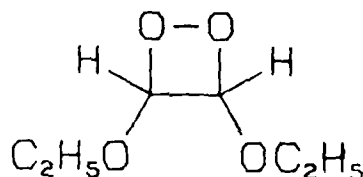


- 5
- a. $R_1 = R_2 = \text{CH}_3$
 - b. $R_1 = \text{CH}_3$; $R_2 = \text{C}_6\text{H}_5$
 - c. $R_1 = R_2 = \text{C}_6\text{H}_5$
 - d. $R_1 = R_2 = \text{C}_6\text{H}_5\text{CH}_2$
 - e. $R_1 = R_2 = \text{CH}_3\text{OC}_6\text{H}_4$

parameters for the decomposition of dioxetanes 6 and 7 are identical within experimental error. Apparently the added 3-4 kcal/mol of ring strain of the bicyclic dioxetane 6 is not released until after the transition state has been passed.



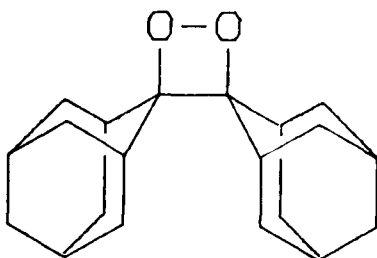
6



7

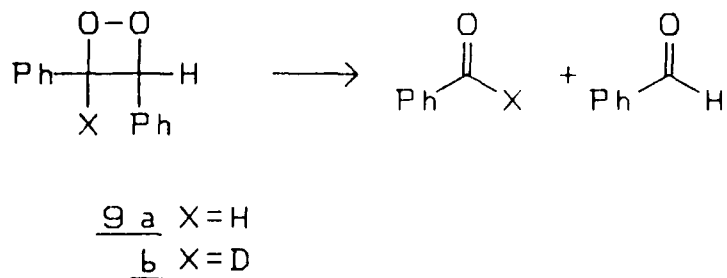
In fact, the largest effects of substituents on the activation parameters of dioxetanes belonging to the first class for decomposition/are attributable to steric effects within the framework of a biradical mechanism. The extraordinary stability of the sterically crowded adamantylideneadamantane-1,2-dioxetane (8) ($E_a = 35$ kcal/mol) (Schuster *et al.*, 1975) and of the norbornylidenenorbornane-1,2-dioxetane (Bartlett and Ho, 1974) suggest a transition state of the rate-determining

step characterized by extensive elongation of the oxygen-oxygen bond and hence further compression of the bulky substituents. Significant carbon-carbon bond elongation in the transition state and the concomitant relief of steric strain among the substituents would have been expected to manifest itself in a lowering of the activation energy for decomposition.



8

A sensitive probe of the mechanism of dioxetane decomposition is the effect of deuterium substitution on the rate of reaction. Koo and Schuster (1977a) investigated the reaction of dioxetanes 9a and 9b and found no kinetic or product isotope effect. This was considered consistent only with a biradical



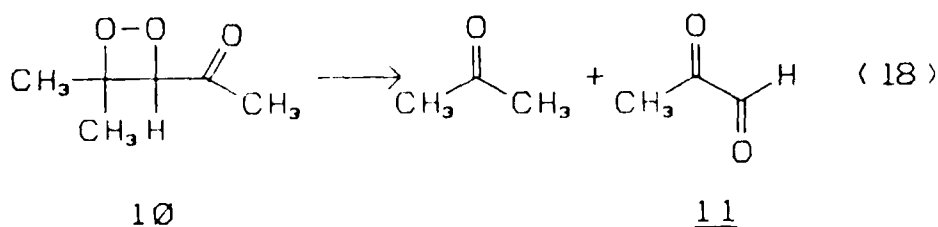
mechanism. A concerted mechanism, in which the hybridization of the ring carbons change from sp^3 toward sp^2 as the reaction approaches the transition state, predicts, in contrast to the experimental result, an inverse deuterium isotope effect.

In sum, a good deal of experimental evidence has been gathered which supports, although indirectly, the intermediacy of a 1,4-biradical in the chemiluminescent reaction of simple dioxetanes. Yet there is no direct evidence that such biradicals exist with finite lifetimes. An attempted independent generation of a 1,4-biradical by decomposition of a dinitrite proved inconclusive (Suzuki, 1979). The influence of quenchers, radical scavengers, and external heavy atoms on the chemiluminescent reaction of trimethyldioxetane (Simo and Stauff, 1975) and adamantylideneadamantane-1,2-dioxetane (8) (Neidl and Stauff, 1978) was studied. While the authors interpret their results in terms of a relatively long-lived precursor to the excited-state product, namely the 1,4-biradical, the results are open to alternative explanations (Horn *et al.*, 1978-79).

The extensive experimental interest in the chemiluminescence of dioxetanes and the relative simplicity of the dioxetane structure have led to a number of theoretical studies. Early semi-empirical calculations appear to be of little value, their results depending on the details of the procedure used (Dewar and Kirschner, 1974 ; Aoyama *et al.*, 1976 ; Eaker and Hinze, 1975). The most reliable computational study reported to date is the *ab initio* GVB calculations of Harding and Goddard (1977), who conclude that the reaction proceeds through a biradical intermediate which is located about 14 kcal/mol above the ground state of dioxetane. Moreover, they conclude that the eight states of the biradical (singlet and triplet $4\pi, 2\sigma$; two $3\pi, 3\sigma$; and $2\pi, 4\sigma$) are separated by only 3 kcal/mol, thus suggesting that the spin multiplicity of the product

carbonyl compounds may depend in part upon the energy of the excited states relative to these biradicals.

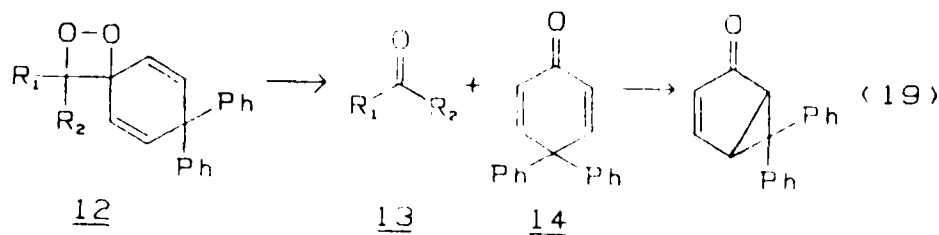
Some experimental support for the idea that the excited state spin selectivity is dependent on the relative energetics of the excited states and the biradical intermediate is derived from the study of 3-acetyl-4,4-dimethyldioxetane (10) by Horn and Schuster (1973). The relatively low ratio of triplet to singlet excited state methylglyoxal (11) which was observed (9 ± 3)



is interpreted as a result of a nearly statistical partitioning of the suspected biradical intermediates among the available spin states of the low energy dicarbonyl compound. Unlike biradicals derived from dioxetanes which dissociate to simple ketones and aldehydes ($E_s = 84-88$ kcal/mol, $E_t = 78-80$ kcal/mol) the biradical derived from 10 is expected to lie well above both the singlet and triplet excited states of methylglyoxal (64 and 55 kcal/mol respectively).

Several recent studies have addressed the interesting issue of electronic excitation energy partitioning in dissymmetric dioxetane thermolysis. The first quantitative determination of energy partitioning was reported by Horn and Schuster (1978). Dioxetane 10 generated not only the excited singlet and triplet of methylglyoxal with moderate efficiencies (1.6% and 15% respectively) but also generated a substantial amount of triplet acetone (0.5%). Yet the triplet state of acetone lies approximately 14 kcal/mol above the triplet of methylglyoxal.

Zimmerman *et al.* (1975, 1976) studied the series of dioxetanes 12. One of the primary products is the cyclohexadienone 14 which, if formed in an

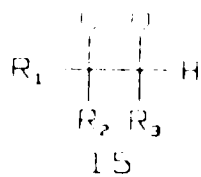


- | | |
|-------------------------------|----------------------------------|
| a, $\text{R}_1 = \text{Me}$ | $\text{R}_2 = \text{Ph}$ |
| b, $\text{R}_1 = \text{Me}$ | $\text{R}_2 = m\text{-MeOPh}$ |
| c, $\text{R}_1 = \text{Me}$ | $\text{R}_2 = 2\text{-Naphthyl}$ |
| d, $\text{R}_1 = \text{N-Bu}$ | $\text{R}_2 = \text{Ph}$ |

excited state, undergoes the well studied "Type A" rearrangement. The yield of excited 14 was found to vary only slightly with the nature of the other fragment (13) despite the fact that the excitation energies of 13a-d bracket that of the triplet of 14. The yield of excited 14 from dioxetane 12c, is especially interesting, for the lowest triplet of 13c (a $\pi\pi^*$ state, 59 kcal/mol) lies well below the triplet of 14 (an $n\pi^*$ state, 68.5 kcal/mol). The authors suggest that there is a large kinetic factor favoring the formation of $n\pi^*$ triplets. However, no direct search for excited 13c was reported, so little can be said about excitation energy distribution. Also, the geometry of 13c in its lowest, $\pi\pi^*$ triplet may not be similar to that of the reaction transition state (Franck-Condon geometry factors). Formation of $n\pi^*$ 13c would remove the apparent energetic advantage of 13c over $n\pi^*$ 14.

Finally, Richardson and his students have recently reported a study of excited state energy distribution between dissimilar carbonyl molecules produced from 1,2-dioxetanes 15 (Richardson *et al.*, 1979). The location of the

excitation energy on one or the other of the carbonyl products, as determined by trapping with olefins, appears to approach a Boltzmann like distribution determined by the carbonyl triplet energies.

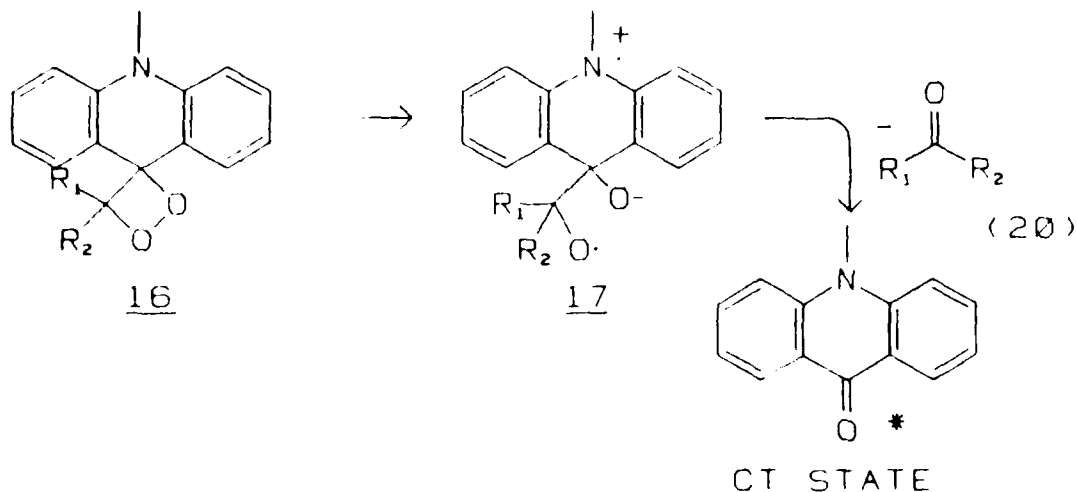


- a, $\text{R}_1 = \text{R}_2 = \text{CH}_3$ $\text{R}_3 = \text{H}$
 b, $\text{R}_1 = \text{Ph}$ $\text{R}_2 = \text{CH}_3$ $\text{R}_3 = \text{H}$
 c, $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{Ph}$

Several years ago it was noted that the behavior of dioxetanes substituted with large resonance groups (for example the dioxetanes postulated as intermediates in many bioluminescent reactions) is quite distinct from that of alkyl, alkoxy, or simple aryl-substituted dioxetanes (Wilson, T., 1976). The decomposition products of these dioxetanes are often highly fluorescent, possessing *** lowest excited states, the yields of excited singlet states are often remarkably high, and the dioxetane stability is apparently low. It was suggested at that time that an alternative mechanism, perhaps a truly concerted mechanism, was operative.

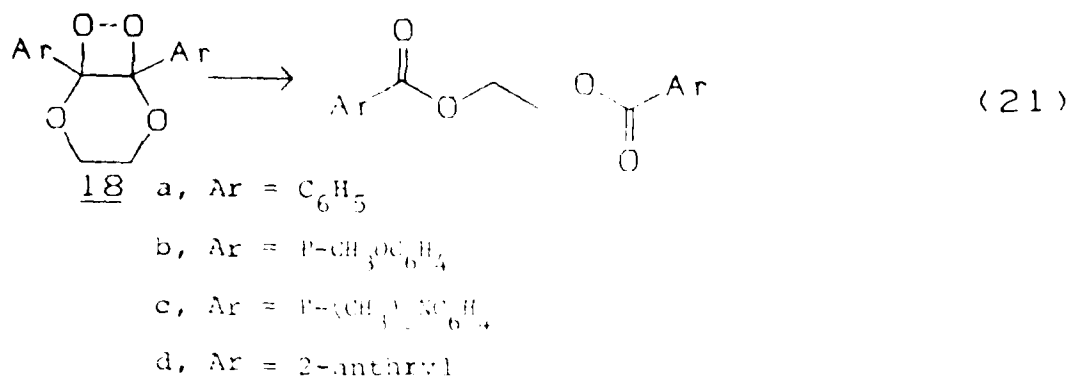
In recent years several new dioxetanes substituted with easily oxidized groups, notably various aminoaryl groups, have been prepared and studied. Also in recent years, the chemically initiated electron-exchange luminescence (CIEEL) pathway has been shown to be capable of generating high yields of chemiluminescence from certain peroxides (Schuster, 1979; Schuster et al., 1979). CIEEL offers an explanation for the unusual properties of these dioxetanes.

McCapra (1977) and Singer (Lee and Singer, 1980, Lee et al., 1976) have studied the N-methylacridan dioxetanes 16. These compounds are characterized by relatively low activation energies for reaction (15-25 kcal/mol) and by a high efficiency of singlet excited state N-methylacridone generation (4-25%). The proposed mechanism involved intramolecular electron-transfer (nitrogen to peroxide bond) induced decomposition leading to a charge polarized intermediate (17). Cleavage of this intermediate directly generates a charge



transfer resonance structural form of the excited state of N-methylacridone. It is interesting, as well as supportive of the proposed mechanism, that the chemiluminescence of 16 can be reversibly quenched by addition of acetic acid, presumably the result of reversible protonation of the nitrogen lone pair.

Schaap and co-workers have studied the chemiluminescent reaction of the series of aryl-substituted dioxetanes 18a (Zaklika et al., 1978a; Zaklika et al., 1978b; Zaklika et al., 1979a, b) and 18b in which the substituents are aryl groups. The reaction of these dioxetanes with alkyl-substituted



1,2-dioxetanes in stability, and similarly generate moderate yields of triplet excited states. Dioxetane 13c, however, possessing the easily oxidized dimethylaminophenyl substituent, is destabilized relative to 18a and b, and gives excited singlet states in high yield. Moreover, there is a substantial solvent effect on the decomposition of 13c, the rate constant increasing markedly with increasing solvent polarity. A thermally activated electron-transfer mechanism has been proposed for 13c. The chemiluminescence of 18d on which there is a remarkable effect of solvent is particularly intriguing. Polarity effects are negligible by comparison to the unique effect of 2,2,2-trifluoroethanol, in which both the rate of reaction and the yield of light are increased by approximately 10% over that in methylene chloride. The singlet excitation efficiency in this solvent is reported to be a remarkable 67%. Silica gel chromatography of 18d was used to increase the yield of light. Apparently the effect of the trifluoroethanol, 2,2,2-trifluoroethanol is to make the peroxide bond of the dioxetane more redox labile to protonation or hydrogen bonding, thus facilitating either homolysis or electron transfer from the peroxide bond.

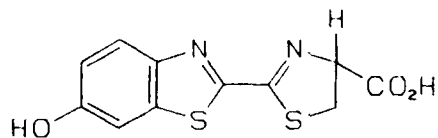
It is interesting to note that the decomposition of 18d is an intramolecular electron transfer reaction, and that the products are excited state products

are the N-methyl-indolyl substituted dioxetanes studied by Goto et al. (Goto and Nakamura, 1978; Nakamura and Goto, 1979a; 1979b). These dioxetanes are of additional interest because of the high-energy uv chemiluminescence (320nm) which is observed in some cases and the observation of intramolecular exciplex emission in other instances.

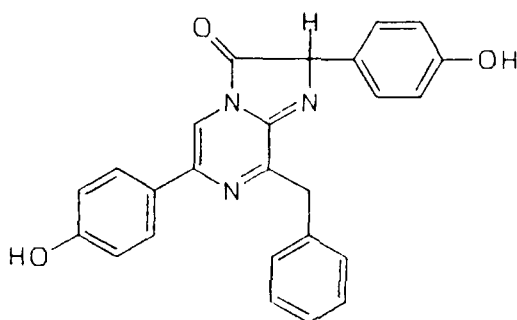
Despite the clear implication of the involvement of intramolecular electron transfer in the chemiluminescence of certain dioxetanes, there have been no clear examples of intermolecular electron exchange luminescence processes with dioxetanes. In a recent note, however, Wilson (1979) reports the observation of catalysis of the chemiluminescence of tetramethoxy-1,2-dioxetane by rubrene and, most surprisingly, by 9,10-dicyanoanthracene. While catalysis by the added fluorescers was not kinetically discernible, a lowering of the activation energy for chemiluminescence was observed. These results were interpreted not in terms of an actual electron transfer with the formation of radical ions, but rather in terms of charge transfer interactions between fluorescer and dioxetane in the collision complex. In any event, these results certainly emphasize the caution required in considering the fluorescer as a passive energy acceptor in dioxetane chemiluminescence.

C. Dioxetanone Chemiluminescence

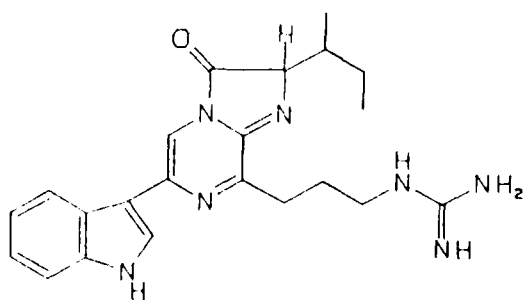
The chemiluminescence of dioxetanones is of particular interest due to their postulated intermediates in several bioluminescence reactions, including that of the firefly, the sea pansy *Renilla*, and the ostracod crustacean *Pypridina* (Figure 1). The generalized mechanism for these bioluminescence reactions (Equation 2) involving oxidation of a substrate (luciferin) and luminescent decomposition of an intermediate, accounts for the established requirement of molecular oxygen, the production of carbon dioxide, and emission from the oxyluciferin.



firefly

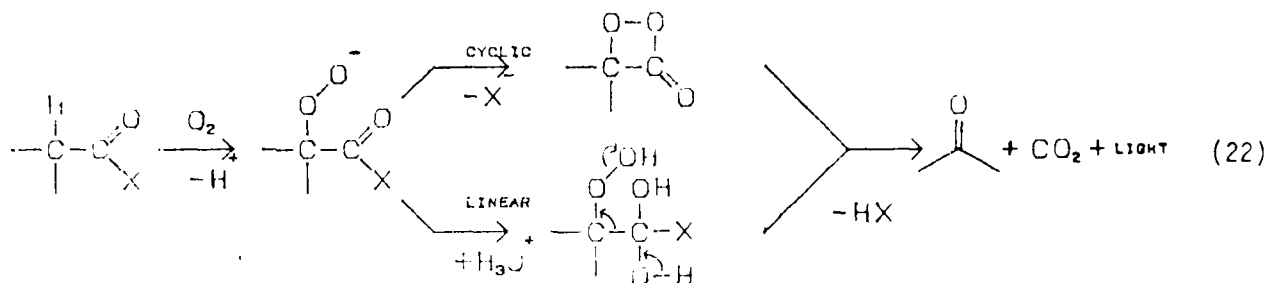


Renilla



Cypridina

Figure 4. Luciferins.

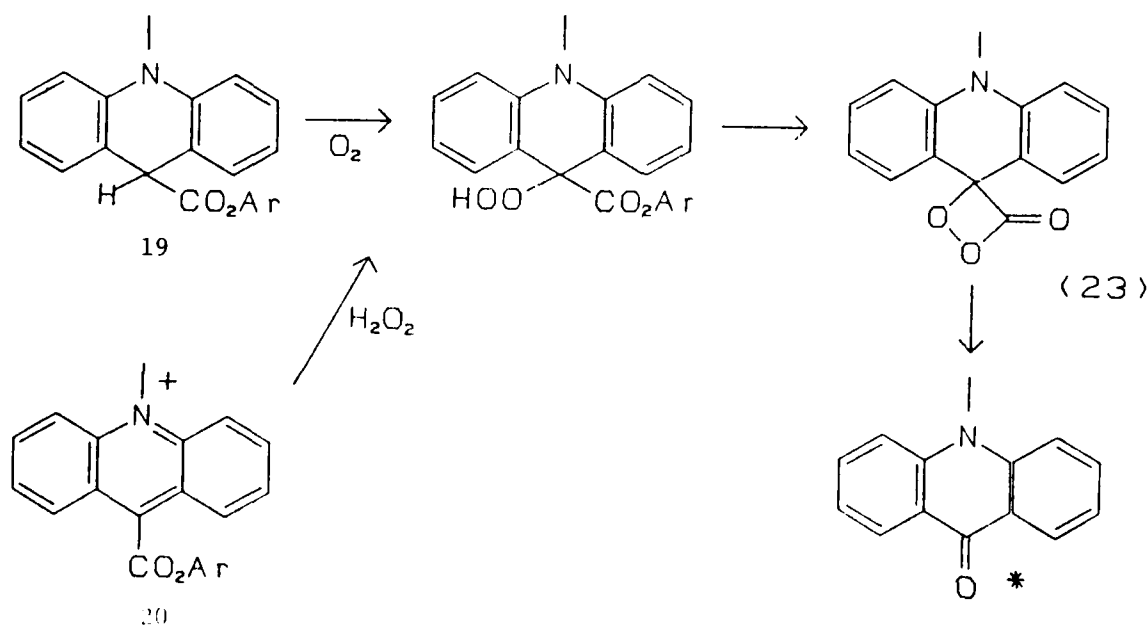


In principle, the cyclic route is distinguishable from the alternative, linear route, by labeling experiments. The dioxetanone route predicts that one oxygen in the CO_2 is derived from the molecular oxygen; the linear route predicts that one oxygen in the CO_2 is derived from the aqueous medium. In practice, experimental attempts to distinguish between the two possibilities have been the source of considerable controversy, as will be illustrated for the case of the firefly, but which now has been settled in favor of the dioxetanone route.

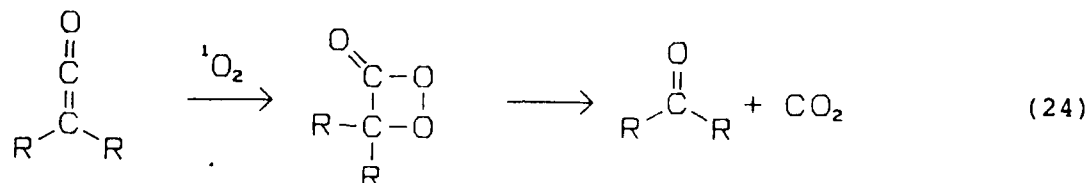
Early labeling studies employing $^{18}\text{O}_2$ (Deluca and Dempsey, 1970) and even more recent studies by the same group employing $^{17}\text{O}_2$ and H_2^{18}O (Tsuji et al., 1977) cast doubt on the dioxetanone mechanism for the firefly by purporting to show that CO_2 formed was not labeled. However, the recognition of the danger of complete isotopic exchange of labeled carbon dioxide in aqueous media (Shimomura and Johnson, 1971) in turn cast doubt on these results. Later studies by two independent groups demonstrated, in fact, that ^{18}O (from $^{18}\text{O}_2$) is incorporated into CO_2 in the chemiluminescent (non-enzymatic) reaction of firefly luciferin in dry dimethyl sulfoxide with potassium tert-butoxide (White et al., 1975; White et al., 1980) as well as in the bioluminescent reaction (Shimomura et al., 1977; Shimomura and Johnson, 1979). A recently reported study of the reaction of ^{14}C -carboxyl-labeled luciferin in

the presence of $^{17}\text{O}_2$ and H_2O^{18} by the group originally opposed to the cyclic route, is in fact fully consistent with the dioxetanone mechanism (Wannland *et al.*, 1978), and its intermediacy now appears secure. Similar labeling studies support dioxetanone intermediates in the bioluminescent reactions of *Cypridina* (Shimomura and Johnson, 1971, 1975, 1979) *Renilla* (Hart *et al.*, 1978), and the related *Oplophorus* (Shimomura *et al.*, 1978).

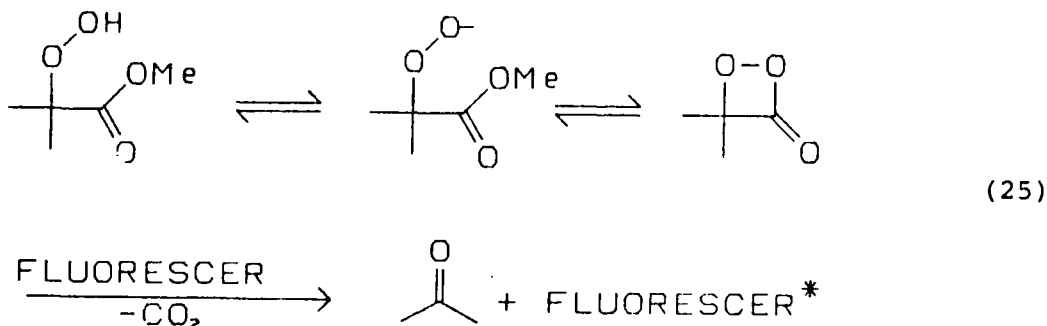
In addition to their implication as reactive intermediates in bioluminescence, dioxetanones have been proposed as key intermediates in several chemiluminescent systems. Most notable are the chemiluminescent oxidation reaction of acridan esters (19) and the chemiluminescent reaction of the related acridinium salts (20) (Rauhut *et al.*, 1965a; McCapra *et al.*, 1979). Both reactions are quite efficient in singlet excited state generation ($\phi_{\text{CE}} = 10\%$ and 2% respectively) and, owing to the elegant work of McCapra and others, are among the best understood complex chemiluminescent reaction mechanisms.



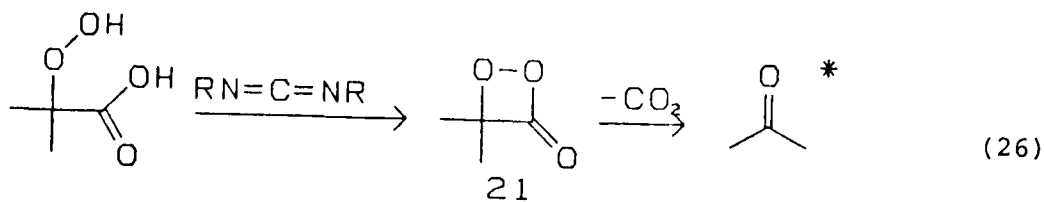
Early in the investigation of chemiluminescent phenomena, dioxetanones were proposed as the key intermediate in the chemiluminescent reaction of diphenylketene and singlet oxygen in the presence of fluoresters (Bollyky, 1970), a suggestion later substantiated by the preparation of stable dioxetanones by the addition of singlet oxygen, generated by triphenylphosphite ozonide decomposition, to several ketenes (Turro *et al.*, 1977 ; Turro and Chow, 1980). Direct chemiluminescence has also been observed from the gas phase reaction of ketene with singlet oxygen, affording the first evidence for unsubstituted dioxetanone (Bogan *et al.*, 1979).



Recently, the chemiluminescence from the base-catalyzed decomposition of an α -hydroperoxy ester was described in terms of a dioxetanone intermediate (equation 25) (Sawaki and Ogata, 1977).



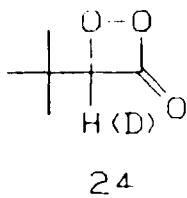
Eight years ago Adam (Adam and Liu, 1972; Adam and Steinmetzer, 1972) reported the first synthesis and characterization of authentic dioxetanones, prepared by dehydrative cyclization of the corresponding α -hydroperoxy acids, equation 26. They were shown to thermolyze as anticipated to carbon dioxide and the corresponding ketone with the concomitant emission of light.



Thermolysis of dimethyldioxetanone (21) produces both excited singlet and triplet states of acetone, identified by their characteristic fluorescence and phosphorescence spectra and by their behavior toward oxygen quenching in FreonTM-113 solution. The spectra are superimposable with those from tetramethyl-1,2-dioxetane (3) under comparable conditions. The yields of excited singlet and triplet acetone produced from the thermolysis of 21 were determined relative to the yields of excited singlet and triplet acetone from thermolysis of 3 by direct comparison of chemiluminescence intensities under identical reaction conditions. The yields from 3 are fairly well established at 0.2 and 30%, respectively, and the excited state yields thus determined from 21 are 0.1 and 1.5% for the singlet and the triplet, respectively (Schmidt and Schuster 1978b, 1980a). Similar excitation efficiencies for 21 have been reported by Adam *et al* (1974, 1979) and by Turro and Chow (1980). Thus dimethyldioxetanone is qualitatively similar to alkyl-substituted dioxetanes in the unimolecular chemiluminescent thermolysis in that the formation of triplet excited states is favored over the formation of singlet excited states. The total yield of excited states from 21 is, however, twenty times lower than from 3, despite

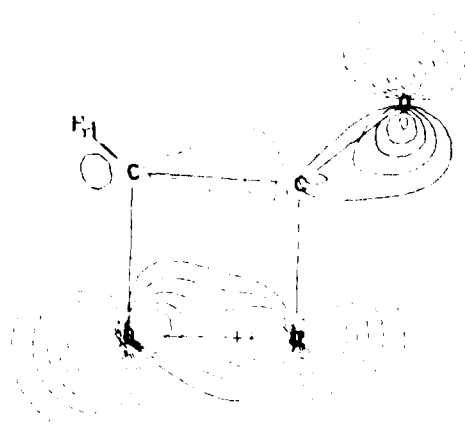
the fact that the thermolysis of 21 is approximately 20 kcal/mol more exothermic than thermolysis of 3.

The kinetic activation energy for the decomposition of 21, E_a , is 22 kcal/mol in several solvents. Significantly, the activation energy for excited singlet acetone formation, E_{chl} , was determined to be 25 kcal/mol, (Schmidt and Schuster, 1978b, 1980a) suggesting that two competitive parallel pathways for decomposition of 21 are operative. The more highly activated pathway leads to excited states, while the lower leads to "dark" decomposition. Activation parameters recently reported by Turro and Chow conflict with these results, however (Turro and Chow, 1980). Both E_a and E_{chl} were measured to be 22 kcal/mol and their data thus do not differentiate paths leading to ground and excited-state acetone. The only apparent difference between the two measurements of E_{chl} is the temperature range employed, but this difference alone does not accommodate the discrepancy. The qualitatively similar reaction and chemiexcitation parameters for dioxetanones and the closely analogous alkyl-substituted dioxetanes suggests that similar reaction mechanisms are operative. For the dioxetanes a good deal of experimental evidence favors the biradical path (see above). Experimental evidence for the dioxetanones is lacking. An attempt to distinguish between the two mechanistic extremes by a study of deuterium kinetic isotope effects, analogous to the study on dioxetanes by Koo and Schuster (1977a), was reported recently by Adam and Yany (1980). tert-Butyldioxetanone with deuterium substitution on the ring carbon was investigated. While virtually no kinetic isotope effect was reported ($k_H/k_D = 1.06$), and this was interpreted by the authors as being consistent with the biradical mechanism, the experimental uncertainty in these determinations is intolerably large, and conceivably could obscure the small secondary deuterium isotope effect predicted for a concerted mechanism.

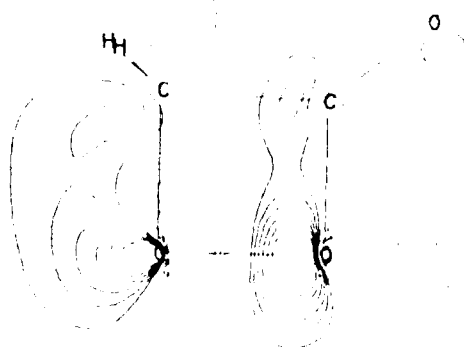


While experimental evidence on the mechanistic details is lacking, recent investigation of the structure and reactivity of the parent unsubstituted dioxetanone by self consistent field theory offers some insight into the mechanism of the reaction (Schmidt *et al.*, 1981). Of significance to the understanding of the thermal chemistry of dioxetanone is the prediction that stretching the oxygen-oxygen bond does not cause a concomitant increase in the length of the ring carbon-carbon bond. Although the calculations were not carried all the way through to the transition state, progress along the reaction coordinate was significant since the energy increase obtained is nearly half the experimentally determined activation enthalpy for dioxetanone 21. The implication of these findings is that the thermolysis of dioxetanone may proceed through the biradical state formed by crossing of the 14a' and 16a' orbitals (Figure 5) as a result of cleavage of the oxygen-oxygen bond. A similar conclusion was reached by Harding and Goddard (1977) for dioxetane using GVB calculations.

The results of the computation which implicate a biradical intermediate for the dioxetanone reaction suggest an explanation for the difference in total excited state yields, as well as the difference in triplet to singlet excited state ratios obtained from thermolysis of dioxetanone 21 and dioxetane 3. Cleavage of the oxygen-oxygen bond in both cases leads to a biradical presumably initially in a singlet state. Intersystem crossing to the triplet biradical is therefore in competition with cleavage of the ring carbon-carbon bond



a



b

Figure 5. Molecular orbital contour plots of the occupied orbital 14a' (a) and the virtual orbital 16a' (b) of dioxetanone, full and dotted lines refer to different phases of the orbitals.

(Figure 6). For the case of dioxetanone the loss of CO_2 competes with intersystem crossing; for dioxetane it is the loss of a simple carbonyl compound that is in competition with intersystem crossing. The former is more exothermic and, therefore, is probably more rapid, giving the biradical less opportunity to cross to the triplet manifold. Consistent with this postulate is the experimental observation that the yield of excited singlet acetone from thermolysis of 21 and 3 is quite similar (0.1% and 0.2%, respectively), but the yield of triplet acetone from 21 is considerably reduced (1.5 vs. 30%).

While the unimolecular chemiluminescence of dioxetanones appears to fall easily within the framework of conventional dioxetane chemiluminescence, the chemiluminescence of dioxetanones in the presence of certain fluorescers falls resoundingly outside that framework. Adam *et al.* (1974) noted that the addition of rubrene to solutions of dimethyldioxetanone gave a yield of light twenty times that obtained when an equivalent concentration of 9,10-diphenylanthracene was added. Importantly, the apparent dissimilarity between rubrene and diphenylanthracene is unaccounted for by any conventional dioxetane decomposition mechanism. Also, significantly, Adam *et al.* (1974) observed an increase in the first-order decay constant of the dioxetanone with the addition of rubrene, an observation for which he was not able to offer an explanation. Sawaki and Ogata (1977) also observed, in the base-catalyzed decomposition of α -hydroperoxvesters, for which a dioxetanone intermediate was proposed (equation 25), an unusual dependence of the chemiluminescence yield on the identity of added fluorescer.

Recent work by Schmidt and Schuster (1978a, 1980a) has shown that the addition of any of several easily oxidized, fluorescent, aromatic hydrocarbons or amines to solutions of 21 results in greatly enhanced chemiluminescence. Moreover, addition of these molecules accelerates the rate of reaction of 21. The catalyzed

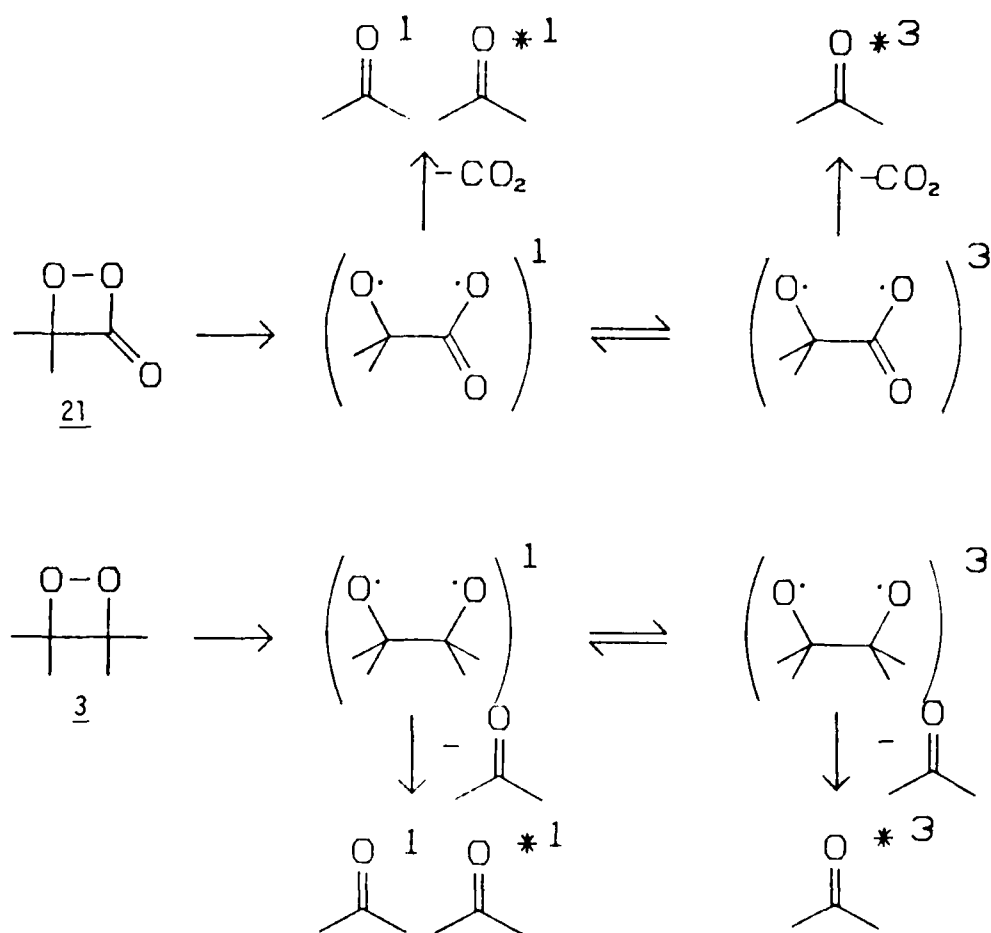


Figure 6. Biradical intermediates, intersystem crossing, and C-C bond cleavage in the chemiluminescent reactions of dimethyldioxetanone (21) and tetramethyl-1,2-dioxetanone (3).

reaction is first order in both 21 and aromatic hydrocarbon or amine (which is termed the activator, ACT). Activator 21 is still produced quantitatively. Moreover, the hydrocarbon is not consumed in the reaction, but rather serves as a catalyst for the decomposition of the dioxetanone. The kinetic behavior is thus described by the simple rate law of equation 27, where k_1 is the rate constant for unimolecular reaction and k_2 is the bimolecular rate constant for the activator-catalyzed reaction. While the unimolecular rate constant k_1 is

$$k_{\text{OBS}} = k_1 + k_2[\text{ACT}] \quad (27)$$

independent of activator identity, the bimolecular rate constant k_2 , is highly dependent on the nature of the activator. In fact, k_2 in benzene at 24.5°C is over 13000 times larger for N,N-dimethyldihydrophenazine (DMP) than it is for rubrene. There is a broad relationship between the one electron oxidation potential of the activator and the magnitude of k_2 . In general the more easily oxidized activator (lowest E_{ox}) has a larger k_2 associated with it, suggesting an endergonic one electron transfer from activator to dioxetanone in the rate-determining step of the catalytic reaction.

The chemiluminescence observed when these activators are added to solutions of 21 is fluorescence from the excited singlet state of the activator. The relative initial chemiluminescence intensity is highly dependent upon the nature of the activator employed; a 100,000-fold range in intensity is observed. The corrected relative intensity is uniquely predicted by the one electron oxidation potential of the activator. This relationship, shown in Figure 7, demonstrates that the chemiluminescence results from a bimolecular catalytic reaction (of rate constant k_{cat}) which may involve an endergonic one electron transfer from activator to dioxetanone in the rate-determining step.

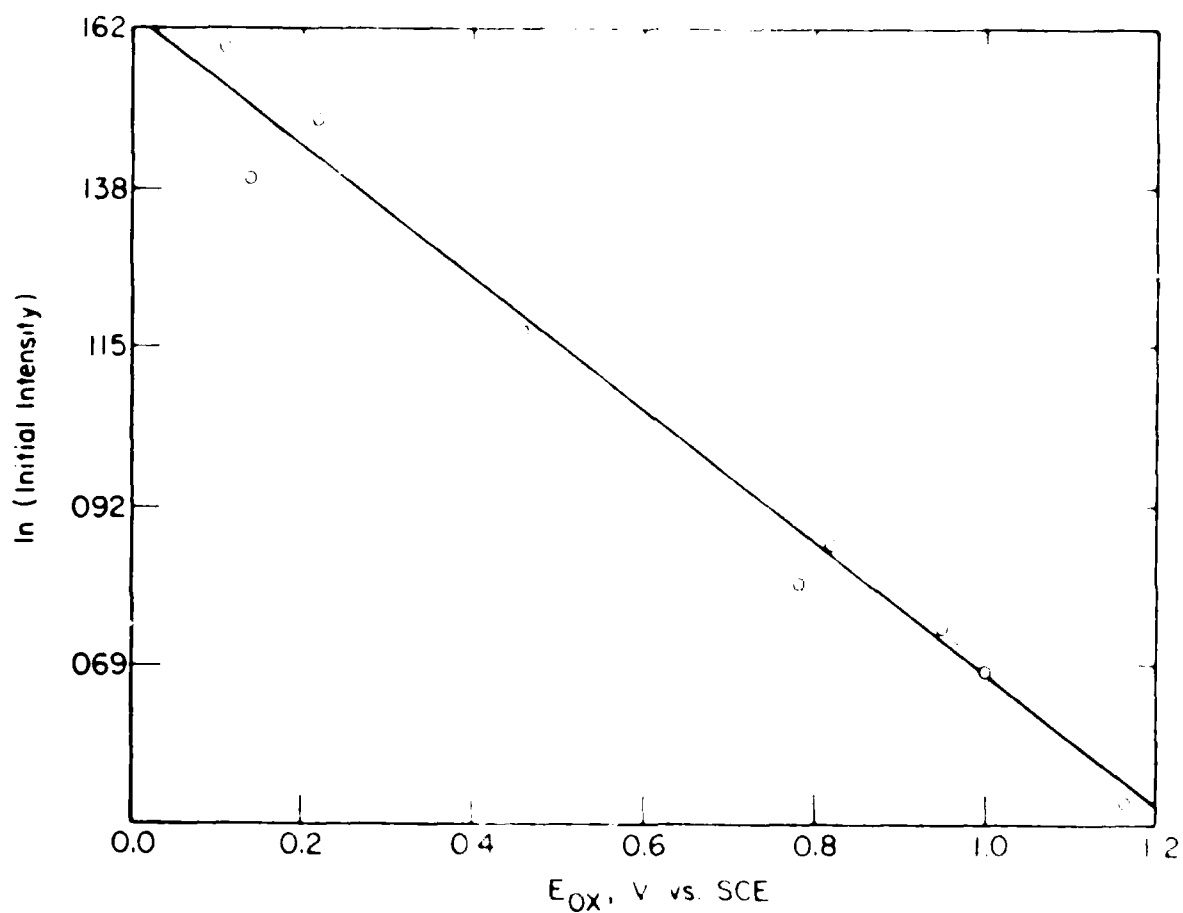
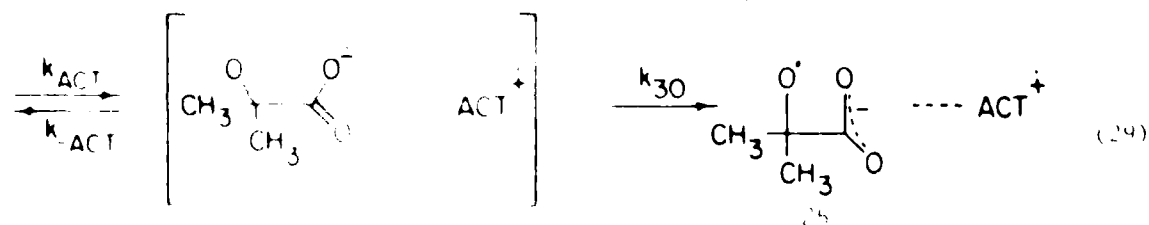
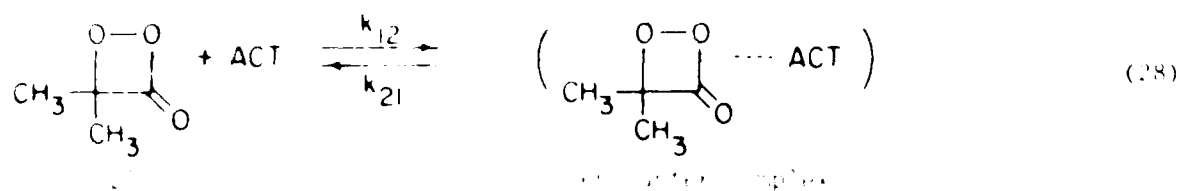
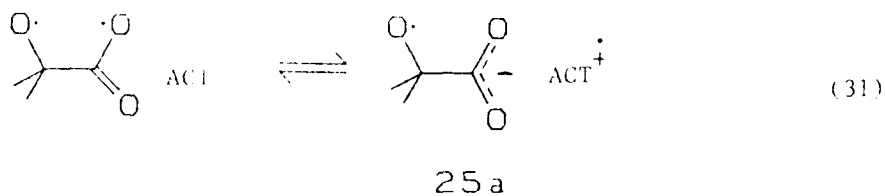


Figure 7. Correlation of the initial chemiluminescence intensity for 21 inorganic at 2.0 μ s, with the fluorescence efficiency and photoluminescence and monochromator response, with the oxidation potential of the various inorganic activators.



2. The reaction of the actin with catalyzed chemiluminescence
 of actin with actin monomer, chemically initiated
 chemiluminescence (CHFL).

yielding a new complex of activator and 1,4-biradical. In Figure 9 this path is shown as the correlation of the encounter complex (ACT---O—O) with the state ACT--($\dot{O}$ $\dot{O}$). There is, however, another electronic configuration available to the bond-cleaved state, one in which an electron has been transferred from ACT to the fragmented peroxide, equation 31.



The relative energies of these two species can be estimated from electrochemical measurements. Comparison of the electrochemical oxidation potential of the activators with that of alkyl carboxylate anions (the electrochemical oxidation of alkyl carboxylates is irreversible, use of this potential therefore provides only a lower limit to energy separation of the two states) (Reichenbacher *et al.*, 1968) which must be used as a model for 25a predicts that the state $\text{ACT}^+ - - \text{O}^- \text{O}$ may lie as much as 18 kcal/mol lower in energy than the biradical state. Thus, stretching the oxygen-oxygen bond of the peroxide-activator encounter complex leads to an avoided crossing (Ramunni and Salem, 1976) of the biradical and electron-transferred state and thus simply stretching the oxygen-oxygen bond provides a path for activation of the electron transfer.

The results of the SCF calculation on dioxetanone bear on this mechanism (Schmidt *et al.*, 1981). These calculations show that stretching the oxygen-oxygen bond of dioxetanone results in a remarkable decrease in the energy of the unoccupied $16a'$ orbital. The net result of this decrease in orbital energy is to facilitate dramatically the electron transfer. Thus the activating process for the electron transfer in the CIEEL mechanism is most likely the stretching of the oxygen-oxygen bond.

The vibrationally excited radical ion pair shown in brackets in equation 29, may be an intermediate or, more likely, a transition state. Back electron transfer from dioxetanone radical anion (with the oxygen-oxygen bond intact) (k_{-ACT}) is exergonic and therefore might be anticipated to be competitive with oxygen-oxygen bond cleavage. Cyclic voltammetric measurements have indicated that the reduction of peroxesters is irreversible, presumably due to rapid oxygen-oxygen bond cleavage. This may indicate that the oxygen-oxygen bond of the state shown in brackets in equation 29 cleaves rapidly ($k_{30} \gg k_{-ACT}$), giving the radical ion pair 25.

The SCF calculations bear also on this description. Of prime importance is the total energy of the radical anion obtained by placing an electron in the $16a'$ orbital. This orbital is antibonding between the peroxide oxygens. The striking result obtained is that on increasing this bond distance $0.2 \text{ \AA}$ from its equilibrium value the total energy of the radical anion drops by ca. 52 kcal/mole. This result is taken to indicate that the oxygen-oxygen bond of the radical anion of dioxetanone is dissociative and that irreversible cleavage follows immediately the receipt of the electron. This conclusion is entirely consistent with the experimental observations of the dioxetanone system.

A controversial feature (Walling, 1980, see, however, S. J. Lein et al., 1981) of the proposed rate limiting electron transfer has been the interpretation of the linear free energy relationships of the type shown in Figure 7 for dimethyldioxetanone. The initial chemiluminescent intensity plotted in Figure 7 is directly proportional to the magnitude of k_{cat} . The free energy for electron transfer from activator to peroxide can be estimated from the oxidation potential of activator, the reduction potential of the peroxide and coulombic work terms (which are small in polar solvent) according to eq. 32, where K is a constant incorporating the equilibrium constant for encounter complex formation and other factors. The factor c is similar to the well-known transfer coeffi-

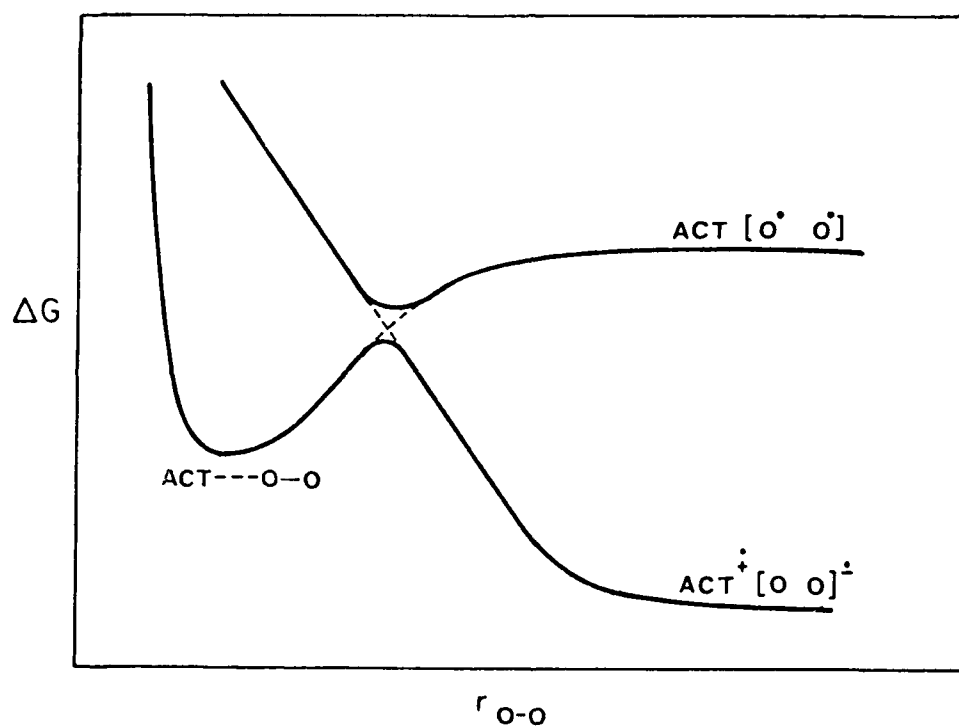


Figure 9. State correlation diagram for the activated electron transfer with simultaneous cleavage of the oxygen-oxygen bond.

$$\ln k_{cat} = \ln(K) + \frac{-(E_{red} + E_{coul})}{RT} - \frac{\alpha(E_{ox})}{RT} \quad (32)$$

cient which generally takes a value between 0.3 and 0.7 for electrode reactions (Delahay, 1965).

For the chemiluminescent reactions of dimethyldioxetanone with the aromatic hydrocarbon and amine donors the value of α is 0.3. For thermodynamically irreversible electron transfer reactions, as is postulated for this case, the value of α can be interpreted to reflect the angle formed by the potential energy curves in the region of the intersection of reactant and product. It is important to emphasize that the value of α is not related to the fraction of charge transferred in the electron transfer step. It should be noted, however, that observation of a linear free energy relationship between the rate and free energy of electron transfer does not constitute proof that a rate-limiting complete electron transfer is involved. A reaction that occurs through an intermediate with greater or lesser charge-transfer is expected to show similar trends.

One notable feature of the correlation of relative initial chemiluminescence intensity with activator oxidation potential in Figure 7 is the widely varying nature and structure of the activators that follow this relationship. Several significant exceptions are the zinc and magnesium tetraphenylporphyrins (Schmidt and Schuster, 1980b). These metalloporphyrins behave as the other activators in the reaction with dimethyldioxetanone in that the reactions follow first order kinetics, the porphyrin is not consumed by the peroxide, and equation 27 is followed. The initial chemiluminescence intensity, however, is about 100 times greater than predicted by the oxidation potential of the porphyrin and the data of Figure 7. The bimolecular rate constants, k_2 , moreover, are consistent with the large intensity. That is, k_2 too is about 100 times greater than is predicted by the oxidation potential of the metalloporphyrin.

The special chemiluminescent catalysis of the zinc and magnesium porphyrins appears to be a result of ground-state complex formation between the metallo-porphyrin and the dioxetanone. Stable complexes of these metalloporphyrins with nitrogen donors such as pyridine are well-known (Hambright, 1971). Weaker complexes with oxygen donors such as diethyl ether are known as well. Certain porphyrins such as silver tetraphenylporphyrin and the non-metallated free-base porphyrins are known not to form complexes with such donors (Miller, and Dorough, 1952). Significantly these porphyrins do not display any special catalysis; the magnitude of the bimolecular rate constant and the initial chemiluminescent intensity are simply predicted by the measured oxidation potentials of these porphyrins.

The magnitude of k_{cat} , the experimentally determined bimolecular rate constant for chemiluminescence, is related to several of the rate constant specified in Figure 8. The data on the hydrocarbon or amine-activated chemiluminescence indicated that $k_{30} \approx k_{-ACT}$. Thus simple analysis of the kinetics shows that:

$$k_{cat} = K_{12} k_{ACT} \quad (33)$$

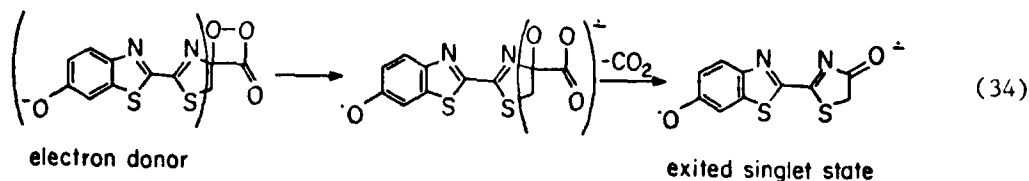
where K_{12} is the equilibrium constant for complex formation. For the amine and aromatic hydrocarbon activators K_{12} is evidently independent of the structure of ACT and probably depends, as in the Weller model (Rehm and Weller, 1970) only on diffusion. However, ZnTPP, MgTPP, CoTPP, CdTPP, etc. form ground state complexes with peroxide 21 and the magnitude of k_{cat} is therefore the product of K_{12} for the complex and k_{ACT} . Indeed, if it is assumed that complexation does not affect k_{ACT} then the increase in the magnitude of K_{12} resulting from ground-

state complex formation is directly reflected in the increased k_{cat} .

Further evidence for ground-state complexation as the cause of the special catalysis was obtained by a spectroscopic study in a model system. Such complexes are typically characterized by a shift of the maximum of the porphyrin Soret absorption band relative to that of the non-complexed porphyrin. In the presence of a high concentration of tetramethyl-1,2-dioxetane, used as a model for the coordinating ability of 21, the absorption maximum of ZnTPP was determined to be shifted 1.2 nm.

Final evidence for involvement of a ground-state complex with 21 on the catalytic chemiluminescence pathway comes from the inhibition of the special catalysis by the addition of donor molecules capable of competitive complexation. Both the rate constant for the reaction of 21 catalyzed by MgTPP and the initial chemiluminescence intensity are decreased markedly by the addition of diethyl ether and even more dramatically by the addition of pyridine. This inhibition of catalysis apparently derives from complexation of the diethyl ether or pyridine to MgTPP. The added donor competes with 21 for the formation of the weak ground state complex, thereby inhibiting the otherwise effective catalysis. The special catalysis of ZnTPP and MgTPP is thus fully consistent with and readily accommodated by the CIEEL mechanism.

The involvement of the CIEEL process in the thermolysis of 21 immediately offers new insight into many previously perplexing proposals of dioxetane or dioxetanone intermediacy in various chemi- and bioluminescent reactions. For example, the discovery of activated chemiluminescence for 21, and the finding that intramolecular electron transfer can generate a very high yield of electronically excited singlet (Horn et al., 1978-79), prompts speculation that an intramolecular version of the CIEEL mechanism is operating in the bioluminescence of the firefly (Koo et al., 1978). This general mechanism may in fact

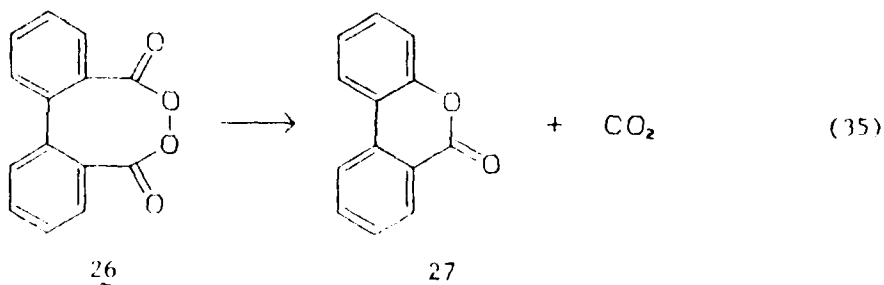


be typical of many chemi- and bioluminescent systems, for our experience with 21, and other peroxides capable of reactions releasing sufficient energy to populate electronically excited states, indicates that the most important light-generating process is the CIEEL reaction.

D. Diphenoyl Peroxide Chemiluminescence.

The chemiluminescent reaction of diphenoyl peroxide (26) with easily oxidized, aromatic hydrocarbons, reported by Koo and Schuster (1977b, 1978), was the first well-defined example of an electron exchange chemiluminescent reaction of an organic peroxide. Its study led to the postulation of chemically initiated electron-exchange luminescence as a generalized mechanism for efficient chemical light formation (Schuster, 1979 ; Schuster et al., 1979).

Although apparently energy sufficient, the thermal decarboxylation of 26 does not generate detectably excited states of the product, benzocoumarin (27) (equation 35). However, addition of easily oxidized hydrocarbons such as



rubrene leads to efficient formation of the excited singlet state of the hydrocarbon and readily observed chemiluminescence.

The kinetics of the chemiluminescent reaction are first order in both peroxide and hydrocarbon. The hydrocarbon, not consumed in the reaction, functions as a catalyst for decarboxylation of 26. The kinetics for consumption of 26 follow equation 27, just as is the case for dimethyldioxetanone. It was also demonstrated that the electronically excited activator is formed as a direct consequence of the bimolecular reaction.

Of utmost import is the correlation which is found between the magnitude of k_{CAT} and the one-electron oxidation potential of the activator, the more easily oxidized activators having the larger values of k_{CAT} . This indicates that a one-electron transfer from the activator to 26 may occur in the rate-determining step of the bimolecular reaction and determine, in part, the magnitude of k_{CAT} . The mechanism proposed to account for the experimental observations on the chemiluminescence of 26 is shown in Figure 10.

The initial electron transfer is followed by oxygen-oxygen bond cleavage and loss of CO_2 , generating benzocoumarin radical anion, a powerful reducing agent, and the activator radical cation. Annihilation of the caged radical ion pair generates the singlet excited state of the activator. Evidence that the light-generating sequence occurs within the initial solvent cage is provided by the lack of effect of oxygen or trace amounts of water on the chemiluminescence efficiency. Further evidence that electronic excitation of the hydrocarbon occurs while in the cage with benzocoumarin is provided by the observation of thermally generated exciplex emission when N-phenylcarbazole or triphenylamine is employed as activator. This emission is ascribed to an exciplex of benzocoumarin and amine.

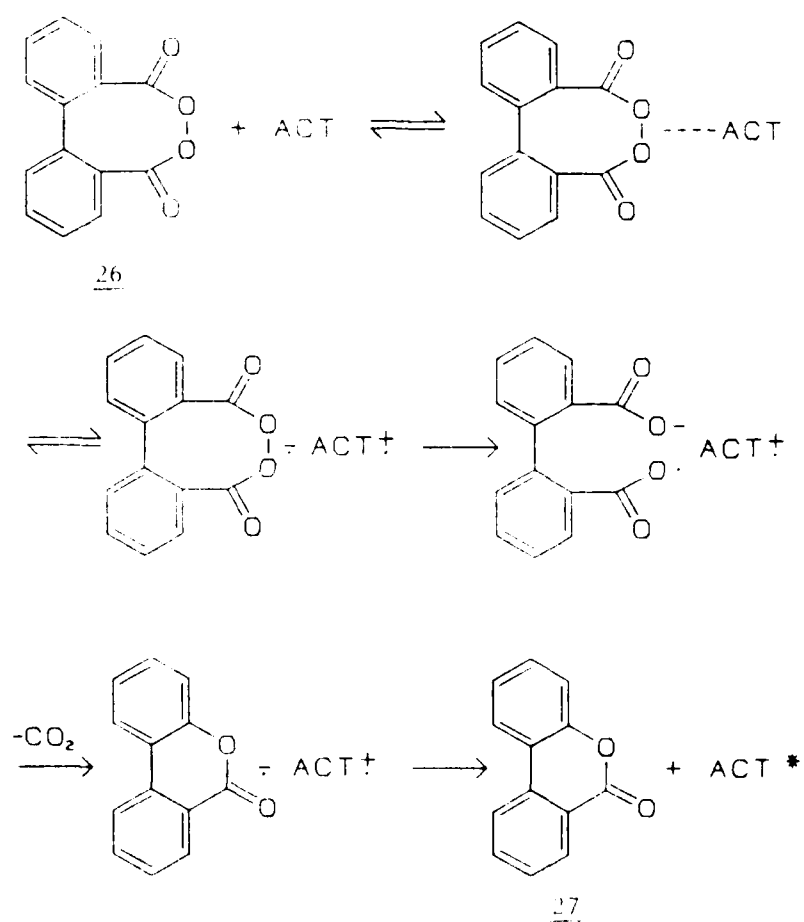
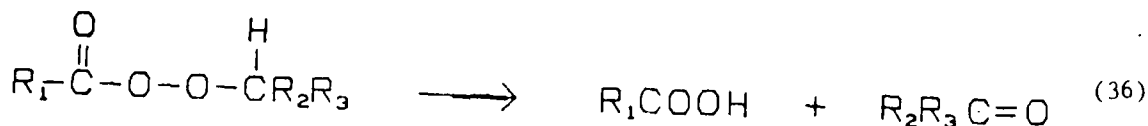


Figure 10. The CIEEL mechanism for the thermal reaction of diphenoyl peroxide (26) with aromatic hydrocarbons (ACT).

More recently, direct experimental verification of the existence of radical ions in the reaction of 26 with activators, and of their intermediacy in the chemiluminescence process, was obtained by applying nanosecond laser spectrophotometric techniques to the study of this reaction (Horn and Schuster, 1979). Excited singlet pyrene was generated by irradiation with a nitrogen laser. The fluorescence of pyrene was quenched by diphenoyl peroxide and the absorption spectrum of the transient products formed from this reaction were recorded 200ns after excitation. The spectrum was that of pyrene radical cation. Determination of the yield of cage-escaped pyrene radical cation, the rate constant for the reaction between pyrene singlet and 26, and the quantum efficiency of that reaction led to the conclusion that pyrene singlet is regenerated from the cage-radical ion pair resulting from its reaction with 26 thus confirming a key tenet of the CIEEL mechanism. Finally, a "kinetic link" was established between the excited state activators and the previously investigated ground state activators. The reaction of triplet anthracene with 26 proceeds with a rate constant predictable from its oxidation potential and the oxidation potential-bimolecular rate constant correlation established with ground state activators. This finding confirms that rate-limiting electron transfer to form a radical ion pair is the initiating step in the CIEEL reaction of diphenoyl peroxide.

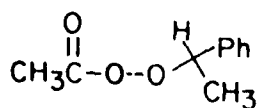
E. Chemiluminescence of Acyclic Secondary Peroxyesters.

Hiatt, Glover and Mosher (1975) reported that the thermolysis of acyclic secondary peroxyesters generates a carboxylic acid and the appropriate carbonyl compound; equation 36. Thermochemical calculations using the group equivalent method (Benson, 1976) indicate that the prototypical reaction is exothermic by ca. 60 kcal/mole. When this exothermicity is combined with the reaction activation

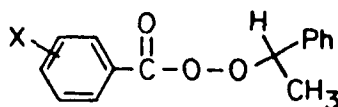


energy it is clear that there is sufficient energy available at the transition state of the secondary peroxyester reaction for the formation of the excited state of the carbonyl compound.

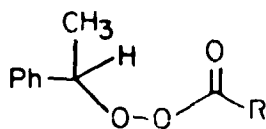
Dixon and Schuster (1979 , 1981) have reported the results of their investigation of both the thermal and electron donor induced reactions of 1-phenylethyl peroxyacetate (28) and a series of substituted 1-phenylethyl peroxybenzoates (29a-29e). They report the direct generation of electronically excited states from unimolecular thermolyses, as well as generation of light by the chemically initiated electron-exchange luminescence mechanism.



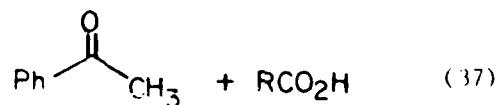
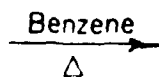
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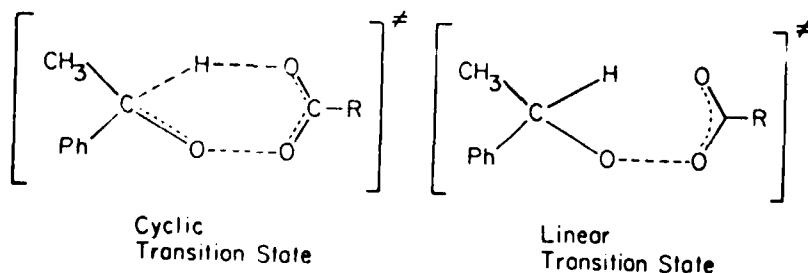
- | | |
|-----|--------------------------|
| 29a | X = H |
| 29b | X = p-OMe |
| 29c | X = p-N(Me) ₂ |
| 29d | X = p-NO ₂ |
| 29e | X = m-NO ₂ |



R = CH₃, Ar



The rates of thermolysis of the peroxyesters in argon purged benzene can be followed conveniently by their direct, indirect, or activated chemiluminescence. In all of the cases reported peroxyesters in benzene solution show clean first order reaction for low initial peroxide concentrations (10^{-5} - 10^{-3} M). The activation parameters for the peroxyester thermolyses reveal some important details of the reaction mechanism. The activation enthalpy obtained for peroxyester 28 is quite similar to that reported by Hiatt et al. (1975) for related secondary peroxyesters in the vapor-phase, but it is considerably higher than the values obtained by these workers for solution-phase reactions. Similarly, the activation entropies reported for 28 are more closely aligned with the vapor-phase values of Hiatt. This observation is of significance since the rather small activation enthalpy and negative activation entropy reported by Hiatt et al. were used to support the notion of a cyclic transition state for these reactions. In contrast, the activation parameters reported by Dixon and Schuster for peroxyacetate 28 resemble closely the values measured for tertiary peroxyesters where the cyclic transition state is not possible and simple oxygen-oxygen bond homolysis is the accepted mechanism (Pyror and Smith, 1971).



The degree of carbon-hydrogen bond involvement in the rate determining step of the unimolecular thermolysis of 28 was probed by measuring the kinetic isotope effect that results from replacement of the methine hydrogen of 28/ with deuterium. In benzene at 100° k_H/k_D is 1.11 ± 0.10 , a value considered to be too small to be indicative of significant cleavage of the carbon-hydrogen bond at the reaction transition state. For an exothermic reaction with an early transition state the expected isotope effect observed might be quite small. However, Mosher has observed an isotope effect for thermolysis of some di-secondary peroxides of about three (Durham and Mosher, 1960). Thus, in contrast to the modified Russel mechanism proposed by Hiatt and coworkers, the linear representation for the reaction transition state appears to be more accurate.

The activation parameters reported for the substituted peroxybenzoates show a slight dependence on the nature of the substituent which has statistical significance only for the dimethylamino substituted peroxybenzoate 29. In this case both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are considerably smaller than for the other structures examined. The measured kinetic deuterium isotope effect when the methine hydrogen of this compound is replaced by deuterium is 1.18 ± 0.04 which also fails to indicate significant involvement of the carbon-hydrogen bond at the transition state.

In sum, the thermal and isotopic data indicate that the mechanism for thermolysis of these peroxvesters has as the rate-determining step the cleavage of the oxygen-oxygen bond without much, if any, carbon-hydrogen bond cleavage.

The substituent on the benzene ring influences the relative position of the transition state in the reaction coordinate diagram more, or less, electron density on the oxygen atom is developed as this bond cleaves. The neutral substituent effect of methyl is observed from 28 indicates that transfer of the electron pair to generate the final products competes successfully with escape of the radical from the solvent cage and with decarboxylation. This mechanism is shown schematically in Figure 11.

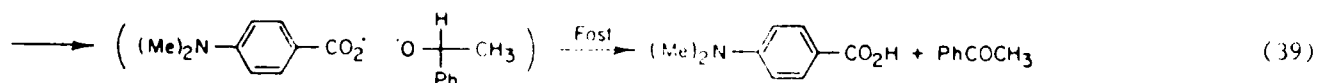
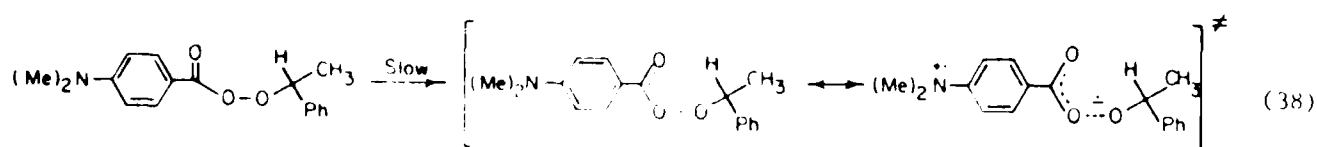


Figure 11. Mechanism of thermolysis of secondary peroxyesters.

The thermolysis of peroxyacetate 28 and substituted peroxybenzoates 29 gives both direct and indirect chemiluminescence. Thermolysis of peroxyacetate 28 in benzene solution at 100° gives very weak direct chemiluminescence. The emission is so weak that an emission spectrum could not be obtained. When biacetyl, which has a considerably higher phosphorescence quantum efficiency than acetophenone (Bäckström and Sandros, 1958), is used as an energy acceptor a reasonably strong chemiluminescent emission results. The spectrum of this emission is identical to that of biacetyl phosphorescence. This observation indicates that either the excited state formed in the thermal reaction is a triplet, or that intersystem crossing of the first formed state is more rapid than singlet-singlet energy transfer to biacetyl. In either case,

the structure of the first formed excited state from thermolysis of peroxyester 28 is assigned to acetophenone. The yield of excited acetophenone formed under these conditions is reported to be about 0.62% (Dixon and Schuster, 1981).

The direct and indirect chemiluminescence measured for the substituted peroxybenzoates is remarkably dependent upon the nature of the substituent. The parent peroxybenzoate (29a), and the *o*-NO₂ (29b), *p*-NO₂ (29d), and *m*-NO₂ (29e) substituted peroxybenzoates show very little direct chemiluminescence, a result similar to that obtained for the peroxyacetate. Also, the indirect chemiluminescence with 9,10-dibromoanthracene (DBA) as an energy acceptor is very weak with these peroxides. In contrast to these results, the dimethylamino substituted peroxybenzoate (29c) gives reasonably intense direct and indirect chemiluminescence.

Thermolysis of peroxide 29c in benzene solution gives a fluorescence emission whose spectrum is identical to the fluorescence spectrum of photo-excited *p*-dimethylaminobenzoic acid under similar conditions. Thus the direct chemiluminescence is attributed to the formation of the singlet excited acid. (Dixon and Schuster, 1981). The yield of directly generated excited acid is reported to be 0.24% / Since none of the other peroxybenzoates generate detectable direct chemiluminescence it was not possible to compare this yield to the other peroxides. However, by extrapolation it was concluded the dimethylamino substituted peroxide generates excited singlet products at least one thousand times more efficiently than does the peroxyacetate or any of the other peroxybenzoates examined.

Indirect chemiluminescence with DBA as the energy acceptor is unusual in that the DBA is able to accept energy from sufficiently energetic triplets and form its emissive excited singlet state (triplet to singlet energy transfer) (Wilson and Schaap, 1977 ; Ferro et al., 1974b). Thus it is possible to use the indirect chemiluminescence of DBA as an indicator of excited triplet state

formation. The yield of directly formed triplet dimethylaminobenzoic acid and benzoic acid obtained from thermolysis of the peroxyesters is indicated by DBA and 0.002% respectively. indirect chemiluminescence to be 3.8%. The yields of triplet acid generated from peroxybenzoates 29a, 29b, 29d, and 29e as indicated by the DBA indirect chemiluminescence intensity are also about 500 times less than that of 2c.

Evidently, the p-dimethylamino substituent greatly alters the ability of these secondary peroxybenzoates to generate electronically excited state products. Two likely rationalizations for this effect have been proposed. The first is that the powerfully electron-donating amino substituent somehow alters the reaction transition state to facilitate excited state formation. Or, second, the lower energy of the excited singlet state of dimethylaminobenzoic acid (the singlet energy of benzoic acid and p-dimethylaminobenzoic acid are 98.3 and 83.5 kcal/mole, respectively) directs the reaction to excited products. The lowered excited state energy explanation, however, does not appear to hold for the formation of triplet acids. The triplet energy of p-dimethylaminobenzoic acid is 73.3 kcal/mole, which is only 3.8 kcal/mole below the triplet of benzoic acid. Yet the yields of triplet excited states differ by a factor of ca. 500. At this time no unambiguous explanation for the increased excited state yield from peroxybenzoate 29c has been offered. However, we note that a similar effect of amino substitution has been reported in the luminol series (see below).

Activated chemiluminescence is observed from these secondary peroxyesters as well. When the thermolysis of peroxyacetate 28 in benzene solution is carried out in the presence of a small amount of an easily oxidized substance the course of the reaction is changed. For example, addition of N,N-dimethyl-dihydrodibenzo[ac]phenazine (DMAC) to peroxyester 28 in benzene accelerates the rate of reaction and causes the generation of a modest yield of singlet excited

DMAC. This is evidenced by the chemiluminescence emission spectrum which is identical to the fluorescence spectrum of DMAC obtained under similar conditions. Spectroscopic measurements indicate that the DMAC is not consumed in its reaction with peroxyester 28 even when the peroxyester is present in thirty fold excess. The products of the reaction in the presence of DMAC remain acetophenone and acetic acid. These observations indicate that DMAC is a true catalyst for the reaction of peroxyester 28. The results of these experiments with DMAC, plotted according to equation 27 give $k_2 = 9.73 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$.

DMAC is not unique in its ability to catalyze the reaction of peroxyacetate 28 and provoke the formation of excited singlet states. The chemiluminescent intensity (corrected for changes in fluorescence efficiency, and photomultiplier and monochromator spectral response) was shown to be a sensitive function of the nature of the activator. Under conditions of low, but constant, activator concentration the magnitude of this corrected chemiluminescent intensity is related to the one electron oxidation potential of the activator. The inverse linear relationship between the log of the corrected chemiluminescent intensity and the oxidation potential of the activator is prima facie evidence for the operation of the CIEEL mechanism, Figure 12. This reaction is postulated to

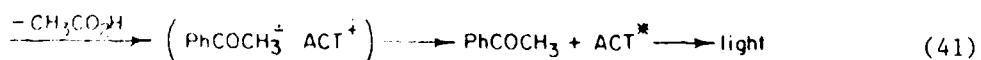
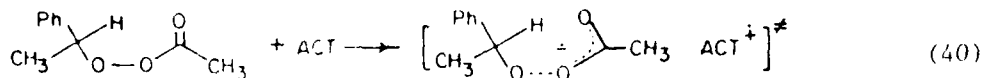


Figure 12. CIEEL mechanism for secondary peroxyesters.

be initiated by the thermally induced transfer of an electron from the activator to the peroxyester, cleavage of the oxygen-oxygen bond of the reduced peroxide and transfer of hydrogen to form acetic acid, thus leaving acetophenone radical anion and activator radical cation within a solvent cage. Annihilation of these oppositely charged radical ions leads to the formation of the excited singlet state of the activator that is detected by its luminescence.

The one exception to the correlation of corrected chemiluminescence intensity and oxidation potential reported for this system is for dimethyldihydrophenazine (DMP). However, this is readily understood with the CIEEL mechanism. In order to form an electronically excited state by an ion annihilation, the energy released by the annihilation must be at least as great as the energy of the excited state. The energy released on annihilation ($\Delta E_{+/-}$) can be estimated using available redox potentials. The energy of the target excited state, in this case the singlet, (ΔE_S^0) is estimated from optical absorption and emission data. It is clear from the data that for all of the activators used except DMP there is sufficient energy released to form the excited singlet. DMP remains a catalyst for the reaction of peroxyacetate 28, but it cannot be promoted to its excited singlet state on annihilation because insufficient energy is released. This observation offers further convincing evidence for the intermediacy of radical ions in the activated chemiluminescence of the peroxyacetate.

The response of the peroxybenzoates to the CIEEL activators depends remarkably on the nature of the substituent. The unsubstituted peroxybenzoate 29a behaves in a fashion nearly identical to that observed for the peroxyacetate 28. The dimethylamino substituted peroxybenzoate 29b behaves quite like the parent, but the nitro substituted compounds 29d and 29e and the p-dimethylamino substituted peroxybenzoate 29c behave quite differently. The properties of these compounds, however, can be understood within the CIEEL mechanism. For example, the nitrosubstituted peroxybenzoates 29d, and 29e exhibit k_2 with DMAC approximately ten times greater than for the unsubstituted peroxide 29a. Yet the yield of excited singlet DMAC generated by 29d and 29e is 700 times less than from 29a. This seeming inconsistency can be easily understood. In the postulated CIEEL path, the reduction of the peroxide results in its fragmentation to acetophenone and an acid. One of these species must be a radical anion. For the peroxyacetate and all of the substituted peroxybenzoates examined, with the exception of the nitro substituted examples, the more easily reduced species of this pair is acetophenone. Thus, in these cases the annihilation takes place between acetophenone radical anion ($E_{red} = \text{ca. } -2.3 \text{ V vs. SCE}$) (Mann and Barnes, 1975 ; Loutfy and Loutfy, 1972) and the activator radical cation. The reduction potentials of the nitro substituted acids are below the reduction potential of acetophenone (Arai, 1968). Thus when these reduced peroxides fragment the radical anion species is probably the acid. Annihilation between the nitro-substituted acid radical anions and the activator radical cations is not sufficiently energetic to form the excited singlet state of the activator.

For the dimethylamino substituted

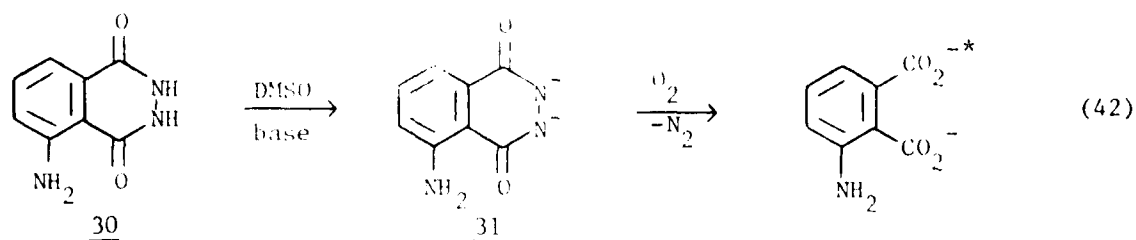
peroxyester 29c a third type of behavior is observed. The corrected chemiluminescence intensity obtained is independent of the structure of the activator. This is just what is expected for simple indirect chemiluminescence where the activator is excited by energy transfer from some first-formed singlet state. As indicated above, the initial excited state in this system is p-dimethylaminobenzoic acid. Evidently, the electron donating p-dimethylamino substituent renders the peroxybenzoate 29c sufficiently difficult to reduce that the value of k_2 is so small that the bimolecular path never is able to compete successfully with unimolecular decomposition.

The most significant conclusion reached from investigation of the chemistry of the secondary peroxyesters is that the energy released on thermal conversion to the ketone and the carboxylic acid can be directed to the formation of excited state products. However, the specific structure of the secondary peroxyester controls the specific mechanism of chemiexcitation and the yield of excited state product obtained. These findings point the way to further exploration of the chemistry of these compounds.

F. Chemiluminescence of Luminol

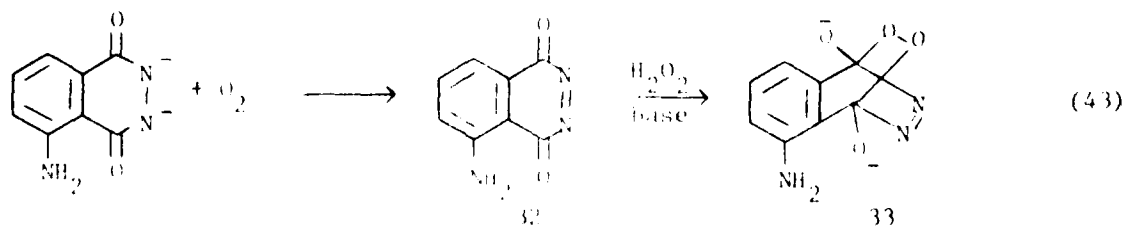
The organic chemist's interest in chemiluminescent phenomena was aroused first by Albrecht's (1928) report of light emission from the reactions of luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) 30. Since that time there have been innumerable investigations of this system and its close relatives. There have also been excellent reviews of much of this work, the most recent being by Roswell and White (1978). Herein we will present a broad summary of this work and some comments on recent work on analogous compounds.

It appears that there may be several paths leading to eventual generation of electronically excited state products from luminol. In non-protic solvent, in particularly DMSO, the reaction apparently proceeds through the luminol dianion as an intermediate. Reaction of the dianion with oxygen results in the formation of 3-aminophthalate in the excited state, equation 42. White and Roswell

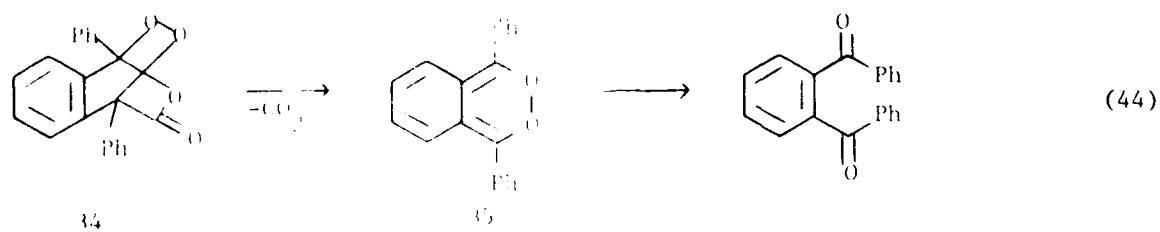


(1970) have shown that under these conditions the chemiluminescence is due to emission from the excited phthalate.

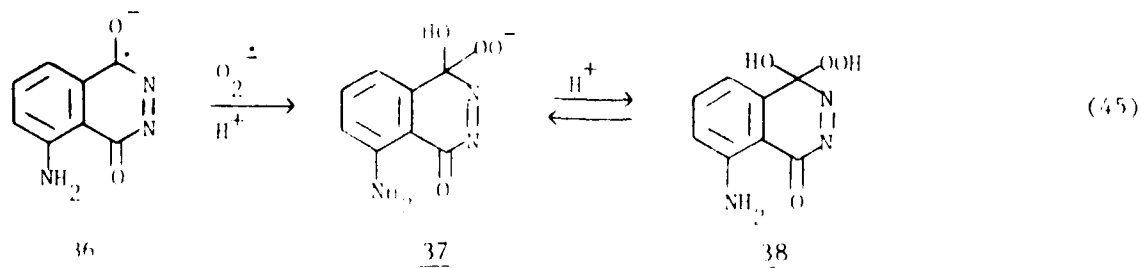
The precise nature of the chemiexcitation step for luminol remains poorly defined. Evidently some product formed by interaction of the dianion with O_2 is capable of giving excited states. Unfortunately, there is very little direct experimental evidence concerning the structure of this product. One possibility is the azaquinone (32) that results from two electron oxidation of the dianion. It has been confirmed independently (Gundermann, 1968; White *et al.*, 1968) that azaquinones generate electronically excited phthalates on reaction with basic hydrogen peroxide. This observation has led to the suggestion that azoendoperoxide 33 may be the immediate precursor to the electronically excited phthalate, equation 43. Alternatively, endoperoxide 33 might be formed directly from the reaction of dianion 31 with O_2 .



Smith and Schuster (1978) have reported the observation of chemiluminescence from endoperoxide 34 which is structurally related to proposed luminol intermediate 33, equation 44. This observation suggests yet another possibility for the structure of the key chemiluminescent intermediate from luminol, the o-xylylene peroxide analogous to 35.



It is apparent that the details of the mechanism of luminol chemiluminescence in aprotic solvent are still obscure. In protic solvent, in particular water, the situation is even more complicated. In this case the radical anion of luminol (36) has been suggested as a possible intermediate. It has been shown recently (Merényi and Lind, 1980) that the generation of this species by pulse radiolysis is consistent with its participation in the chemiluminescent reaction. Moreover, the radical anion was shown to react with superoxide to form an intermediate capable of partitioning between a light-generating path and a dark path. The pH dependency of this partitioning led to the suggestion that azaquinone adduct 37 is a key intermediate involved, equation 45, and that it can go on to form the excited amino phthalate

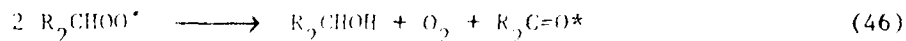


whereas intermediate 38 goes on to give only ground-state products. Further dissection of luminol chemiluminescence awaits the clearer definition of the immediate precursor to electronically excited aminophthalate.

C. Miscellaneous Chemiluminescent Reactions

There are several chemical systems that have been observed to generate light whose mechanisms have not been clearly defined. Many of these reactions suffer the same difficulty as does luminol. That is, the key intermediate has not been isolated, hence its structure is not known, and its properties must be inferred from indirect experimental results. In this section we will introduce some of these systems and review them briefly.

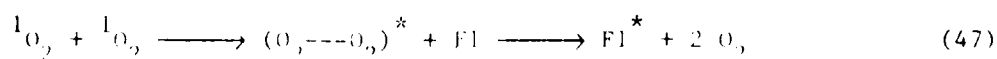
Oxidation of organic materials nearly always results in the production of detectable chemiluminescence. The most extensive investigations of this phenomenon have been carried out by Shlyapintokh (1966) and by Vassil'ev (1967). The mechanism for excited state generation is complex, and the nature of the excited state produced is not well-defined. However, from kinetic evidence, and on the basis of there being sufficient energy released, it has been postulated that the chemiexcitation step is the combination of two alkylperoxy radicals to form oxygen, an alcohol, and an excited state carbonyl compound, eq. 46. Although the yield of light from this process is very low, about one



photon per 10^9 combinations (Kellog, 1969). This phenomenon has been used analytically to study autoxidation of hydrocarbons and many other materials (Mendenhall, 1977).

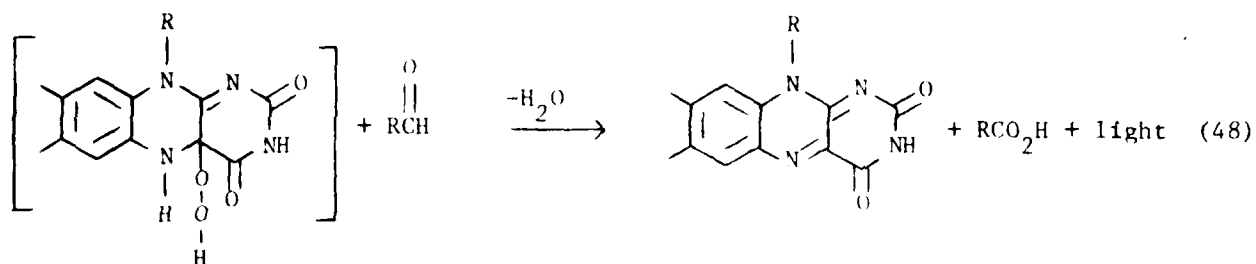
A striking and unusual example of chemiluminescence from an oxidation is the reaction of molecular oxygen with some α -alkoxy Grignard reagents. This reaction was discovered nearly 60 years ago (Gatford et al., 1923; Dufford, 1928) (Evans and Diebenhorst, 1976) but its mechanism is still poorly understood. Recent studies (Bolton and Kearns, 1970) have implicated free radicals and have identified the emitting species as biphenyl derivatives.

The elimination of singlet oxygen (1O_2) from certain peroxides has been shown to be capable of causing visible chemiluminescence (Kahn and Kasha, 1963). The excitation energy of singlet oxygen is rather low (23 kcal/mole) and thus the direct emission from this state is in the infra red spectral region. Indeed, this emission has been detected in the gas-phase and in solution first by Peters et al. (1972) and more recently by Kahn (1980). Visible light can result from the simultaneous transition of two 1O_2 molecules. This reaction is capable of generating a photon of red light or of transferring energy to a suitable fluorescent acceptor, eq. 47. It was claimed that this chemiluminescent process



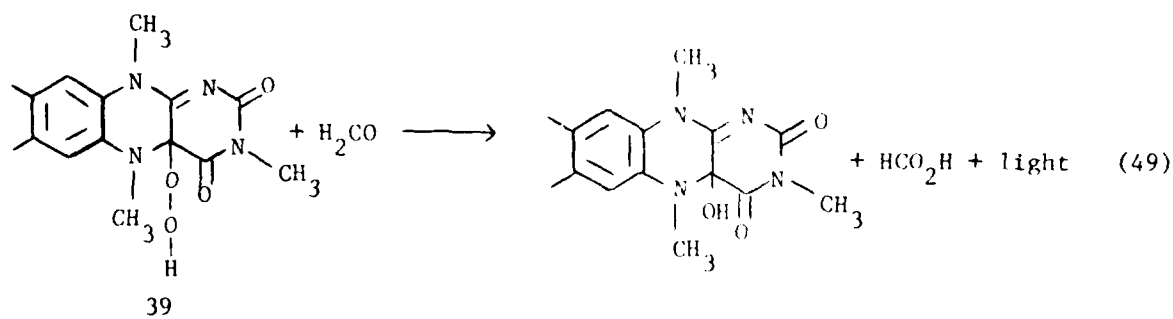
may be responsible for many of the observed weakly luminescing systems (Kahn and Kasha, 1966). It has been suggested for example, that this is the operative mechanism in the chemiluminescence of pyrogallol, with formaldehyde and hydrogen peroxide (Bowen and Lloyd, 1963).

The bioluminescence of certain bacteria appears to involve the reaction of a flavin hydroperoxide with an aldehyde. This reaction proceeds through one or more intermediates to generate eventually an electronically excited state, eq. 48 (Bastings, 1975). An example of the efficient bioluminescent

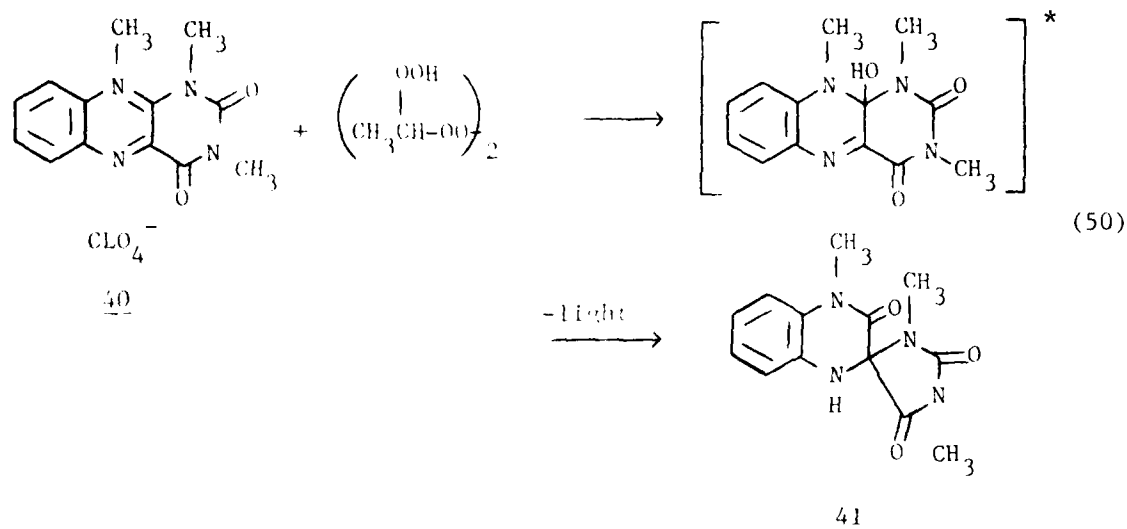


process several weakly chemiluminescent reactions have been investigated.

Kemal and Bruice (1976) prepared and isolated some 4a-hydroperoxy-5-alkyl-3-methylisolumiflavine derivatives (39) and showed that reaction of these compounds with aliphatic aldehydes gives the corresponding acid and some chemiluminescence in dioxane or water solution, eq. 49.



Similarly, McCapra and Leeson (1976) have reported that reaction of some dimeric peroxides with 1,3,10-trimethylisolumiflavine perchlorate (40) gives light. These authors suggest that this reaction proceeds by addition of the hydroperoxide to the 10a position to give eventually the spirohydantoin 41, eq. 50.



Whether these intermediates, or some others, are involved in the bacterio-luminescence process is still uncertain. The details of the chemiexcitation step will, of course, depend upon the specific structures involved. However, there has been some recent speculation on the nature of this process. In analogy to the chemistry of secondary peroxvesters Schuster *et al.* (1979) have proposed an intramolecular electron transfer. Kosower (1980) has invoked a similar mechanism. Verification of these proposals awaits further experimental investigation.

V Conclusions

Chemiluminescent phenomena are much better understood today than they were ten years ago. Indeed, the investigations of the last decade have finally begun to provide rational mechanistic explanations for many chemiluminescent reactions. These explanations so far have revealed three general mechanisms for the transductions of chemical potential energy to electronic excitation. These are the CIEEL process, ion annihilation reactions, and unimolecular thermolyses of high energy content reagents. Within each of these groups the details of structure and reactivity still remain mostly unexplored. Thus, it is not yet possible to predict accurately the yield of excited state product by knowing the structure of the reagent.

The practical applications of chemiluminescent reactions are numerous. They can function as sources of light, markers, analytical systems, and mechanistic probes, to name only a few. These applications, and the very spectacular nature of the phenomena, will work together to encourage further examinations of these reactions.

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