THE CHEMILUMINESCENCE OF
ORGANIC COMPOUNDS

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ABSTRACT
The chemiluminescence of organic compounds in solution is briefly surveyed
with some emphasis on the mechanisms which result in relatively efficient
population of an excited state of a product molecule. This is done in terms
of the relation $\Phi = \Phi_C \times \Phi_E \times \Phi_F$ with particular reference to peroxide
compositions.

INTRODUCTION
The study of chemiluminescence mechanism in a persistent and systematic
fashion is an activity largely confined to the last decade. This is not surprising
when one considers that the problems associated with ground–excited state
interactions must be multiplied by the complexities of a vigorous oxidative
reaction for a full description of a chemiluminescent reaction. A general
survey of the phenomenon discloses that, with almost no exceptions,
oxidation is involved, the mechanism ranging from the relative simplicity
of an electron transfer reaction to the confusion of a many step, bond cleavage
process. The excitation step in certain bioluminescent reactions is of particular
interest as an example of the latter kind. Although luminescence in the gas
phase has been comparatively well understood for a long time, there are
various reasons why the problem of chemiluminescence in solution must be
approached differently. All gas phase reactions emitting light involve di- or
tri-atomic molecules and often atom recombination. The restriction of the
degrees of freedom in small molecules and the near absence of collision in the
gas phase leads to a non-equilibrium distribution of the energy derived
from the exothermic reaction. If one assumes that the reactants in an
exothermic reaction in solution are, within the lifetime of an excited species,
in equilibrium with the surrounding solvent, then it is obvious that in this
case vibrational energy, no matter how great, is an unlikely source of
electronic excitation. Thus of the various mechanisms for organic chemi-
luminescence, electron transfer is particularly attractive. Conversely, there is
no well proven instance of the emission of light from a radical recombination
reaction in solution, although the bonds formed in such a process usually
release more than sufficient energy to populate an electronically excited state.
A further consequence of the conditions under which most organic chemi-
luminescent reactions occur is the observation that emission is from the first
excited singlet state, the triplet state being easily quenched. However, there

has never been any reason to suppose that triplet states are not likely to be formed efficiently, and low levels of light emission and chemical reactions from the state confirm the possibility.

A complete description of a chemiluminescent reaction would account for the magnitude of the chemiluminescence quantum yield, Φ, in terms of the details of the product

$$\Phi = \Phi_C \times \Phi_E \times \Phi_F$$

where Φ_C is the chemical yield of the primary excited molecule, Φ_E is the number of molecules of product appearing in an excited state, and Φ_F is the fluorescence quantum yield of the product. All three terms include their own particular subtleties. For example, Φ_F which is normally not subject to much experimental manipulation, can involve a further subdivision to include energy transfer. However, the real challenge lies in understanding the factors affecting Φ_C and Φ_E and in the alteration of conditions and structure to enhance their value. The reactions to be discussed in this paper are being actively examined in each of these three factors in our own and other laboratories.

ELECTRON TRANSFER REACTIONS[1]

In a search for a general mechanism this reaction, as mentioned above, has particular advantages, opportunities for vibrational deactivation being small in the short lifetime of the transfer. Since electron transfer may in fact be present as a hidden, final excitation step in an ostensible bond cleavage process, a brief examination of some of its characteristics is desirable. The most easily controlled method of generating such a system involves electrolysis of a polynuclear aromatic hydrocarbon. The radical anion and cation can be generated in the same volume of the solution by electrolysis.

$$Ar^{+\cdot} + Ar^{-\cdot} \rightarrow Ar^\star + Ar$$
$$Ar^{-\cdot} + [Ox.] \rightarrow Ar^\star + [Red.]$$
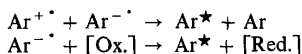
Alternatively the radical anion formed by reduction by dissolving metals may be oxidized by a variety of oxidizing agents, but significantly, not by oxygen. A simple description of the process in molecular orbital terms is shown.

$$Ar^{-\cdot} \quad + \quad Ar^{+\cdot} \longrightarrow Ar^\star \quad + \quad Ar$$
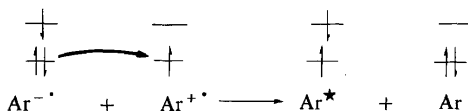
It has been shown[2] that the greater the enthalpy change between the ground state reactant and the state of the product to be formed, the higher is the activation energy for the formation of that state (see *Figure 1*). That is, removal of a *bonding* electron occurs at a rate competitive with that of the removal of the electron in the antibonding orbital. One may reasonably have expected exclusive removal of the latter electron by consideration of factors such as overlap of orbitals and ionization potential.

The assumption of little change in configuration (as is implied in the diagram) cannot be made for reactions which involve rearrangements in bonding, but it would be reasonable to expect that as the energy of any
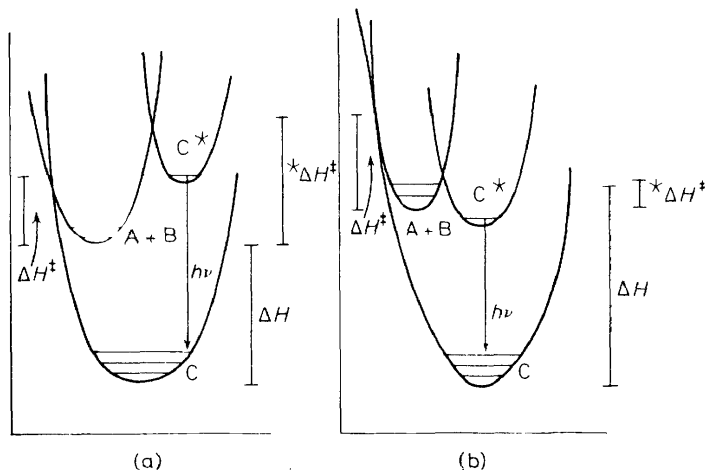
Figure 1. (a) The reaction $A + B \rightarrow C$ is not chemiluminescent. (b) The activation energy for formation of $C^\star$ is less than that for the ground state, and C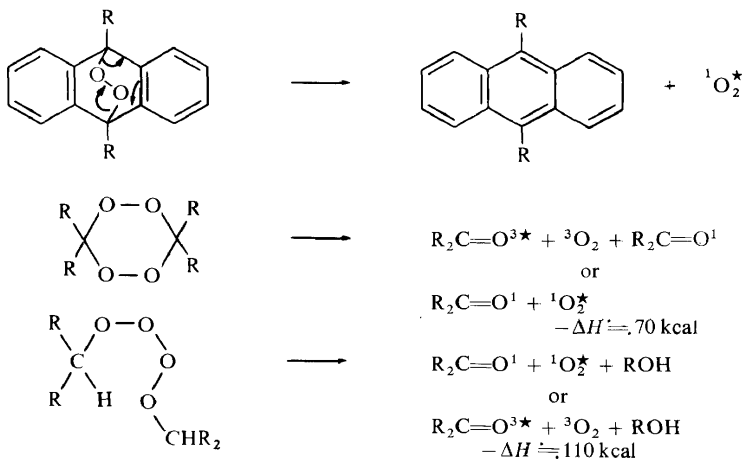 is formed from the excited state. Note that $h\nu = \Delta H + \Delta H^{\ddagger}$ and must be identical to $h\nu$ of emission in fluorescence.

excited state is lowered, then its population would be favoured. At the present time there is no good evidence for electron transfer reactions as a general excitation mechanism in reactions involving bond fragmentation processes, although they should always be considered in oxidative reactions.

REACTIONS CONTROLLED BY SPIN CONSERVATION

The ionic reaction of hydrogen peroxide and chlorine or bromine in alkaline solution must necessarily result in singlet oxygen, such excited states requiring energy (22.4 and 37.8 kcal/mole) which is available. It is interesting to note that a popular kinetics text[3] hinted at this now well known

Scheme 1

$$R_2C{=}O^{3\star} + {}^3O_2 + R_2C{=}O^1$$
or
$$R_2C{=}O^1 + {}^1O_2^{\star}$$
$$-\Delta H \doteq 70 \text{ kcal}$$

$$R_2C{=}O^1 + {}^1O_2^{\star} + ROH$$
or
$$R_2C{=}O^{3\star} + {}^3O_2 + ROH$$
$$-\Delta H \doteq 110 \text{ kcal}$$

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source of singlet oxygen before more recent work[4] confirmed the possibility. That excited oxygen molecule pairs themselves radiate is well established[5], the most apparent emission being the red (45 kcal/mole) radiation from two $^1\Delta_g$ molecules. Other concerted reactions which involve oxygen are the decomposition of arene endoperoxides[6], alkalidene peroxides[7], and linear tetroxides[8]. In the last two cases, the carbonyl products formed may also be expected to appear in an excited triplet state (see Scheme 1).

Visible radiation attributable to singlet oxygen and triplet carbonyl products (by energy transfer and annihilation reactions) has been observed[7, 8].

EXOTHERMIC FORMATION OF SMALL MOLECULES

Although quite specific mechanisms for the preferential population of excited states are discernible, it is nevertheless important to consider an alternative, more general source of excitation[9]. The reactions involved in chemiluminescence are by definition exothermic by amounts greater than can be accommodated in easily accessible vibrational levels of the product molecules. If the products are small molecules, or there is an obstacle (e.g. rigidity) to rapid vibrational equilibrium within a larger molecule, then we might expect that a concerted reaction releasing as much as 100 kcal/mole would result in the appearance of an electronically excited product. At the present time this general explanation appears to be the only satisfactory one for hydrazide luminescence, although more specific mechanisms may yet be discovered. For example the sequence shown for the oxidation of luminol[10] while still lacking certain details, provides for the formation of the proven emitter in a final concerted step which releases 135 kcal/mole.
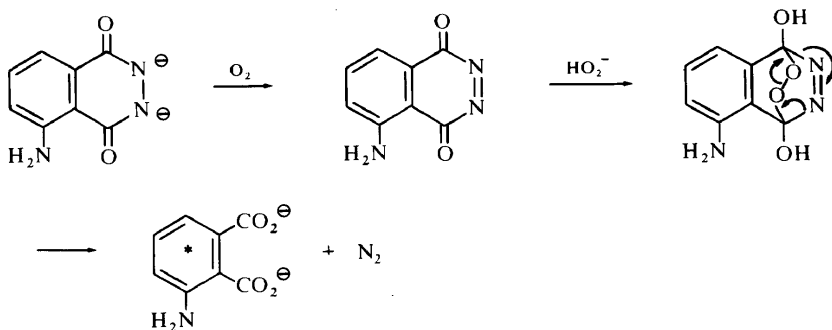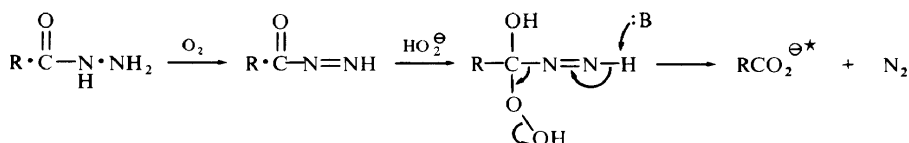

A complementary reaction[11] which also releases nitrogen (but with less energy) is dark.
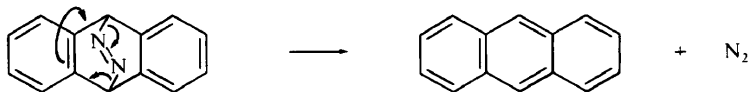
Knowledge of both these reactions is largely owing to E. H. White, who has probably contributed most to the subject of organic chemiluminescence in

recent years. A suggestion for chemiluminescent linear hydrazides can also be made on the same lines:

Reactions which produce CO_2 as the sole product (of the emission step) are obvious candidates for this category, and it is worth noting that the precursor carbon atom hybridization imposes a geometry on the product of this and similar reactions more appropriate to the excited than to the ground state.

CHEMILUMINESCENCE FROM PEROXIDE DECOMPOSITION

It has long been recognized that oxygen plays a major role in organic chemiluminescence. This is particularly marked in bioluminescence, although recently several intriguing cases[12] of this natural phenomenon have been found not to require oxygen (in the system as isolated) perhaps because a peroxide is already present or because the mechanism is entirely different. Previous suggestions for the involvement of oxygen include energy transfer from excited oxygen pairs[13] (as a general mechanism this is now seen to have little application) and as a triplet substrate complex[7].

The acceptance of peroxide decomposition as a principal pathway to excited states has provided both an explanation for the excitation step in bioluminescence and the most efficient purely chemical sources of light. The reactions of bioluminescence can result in the astonishing formation of the excited state of the product to the virtual exclusion of the ground state and the simple oxalyl ester series is not significantly less effective. A general solution to the problems in bioluminescence is obviously not possible in view of the very small number of systems in which the substrate and product are known. There are in fact only three at this stage of development at the present time and the reactions are shown below.
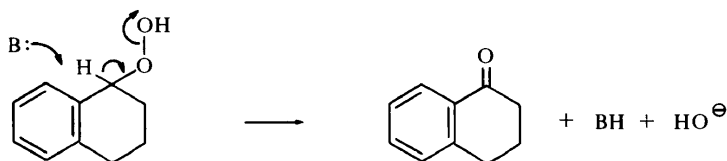
Firefly (*Photinus pyralis*)[14]

Cypridina hilgendorfii[15]

O_2
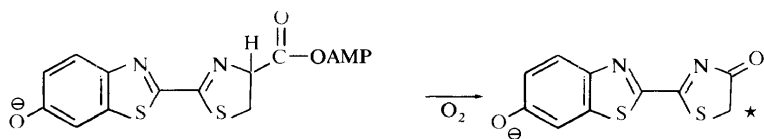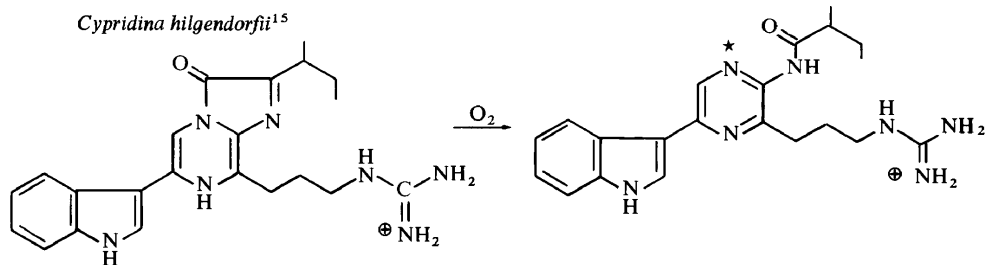
Latia neritoides[16]

O_2
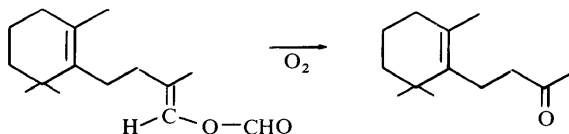
Although the substrate is as yet unknown in luminescent fungi, a carbonyl product of the reaction is implied[17]. Thus the simplest suggestion (or a free radical variant thereof) is indicated below.

+ BH + HO$^{\ominus}$

However, even where the product is highly fluorescent no light is emitted by this route. An earlier proposal[18] that a free radical reaction related to the above simple scheme is operative has been modified[19] and is now seen as the spin controlled reaction of the tetroxide previously described. The base catalysed reaction in particular would release about 60 kcal/mole, and there is little doubt that a significant proportion of this would reside in the BH bond. Thus on energetic grounds alone such a process would not account for most observed reactions (blue light, $hv = 65$ kcal/mole). A mechanism which appears common to all the luciferins shown is represented in Scheme 2 where XH is a stronger acid than ROOH.
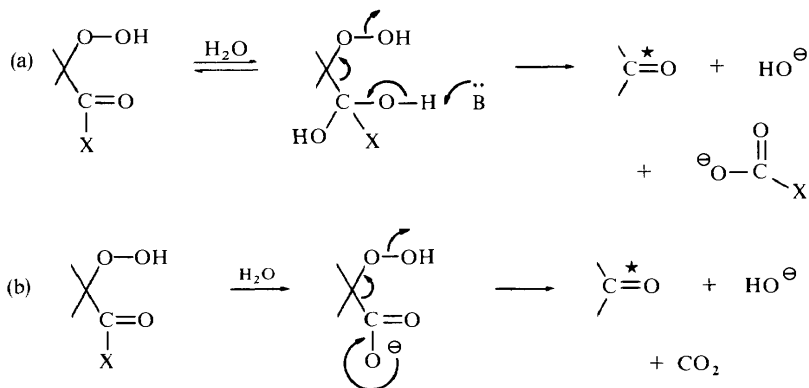
Scheme 2

O_2

$\longrightarrow$ $\overset{\star}{=}O$ + CO_2

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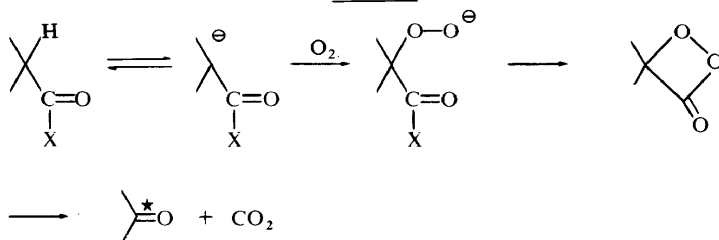
Although the steps shown above have ample analogy, alternative schemes cannot be excluded on this basis. For example the products could well arise by two related but significantly different routes (Scheme 3).
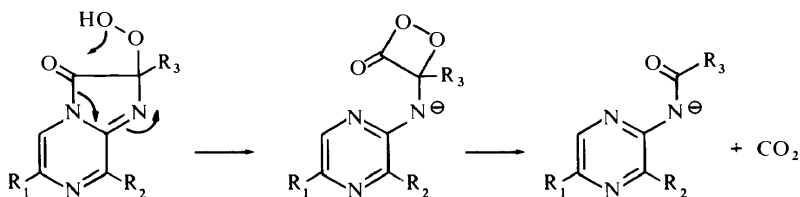
Scheme 3

All of these paths have in common the simultaneous formation of *two* carbonyl groups, although the enthalpy changes are not the same in the crucial excitation step. Since this class of reaction is undoubtedly responsible for the almost exclusive formation of an excited state in particular cases, its examination in detail is obviously important. Scheme 3(b) is the least energetic of the routes and may in fact not provide sufficient energy to account for the emission of blue light. Solvation unfortunately increases the uncertainty in the estimation of the exothermicity of the step. In Scheme 3(a) the resonance energy of the carboxylate grouping is gained on decomposition, not lost as in 3(b) and here the exothermicity closely rivals that of the decomposition of the strained dioxetanone in 2.

It has been shown, by the study of both model compounds and the actual luciferins[14, 15, 16], that in general these mechanisms apply. Until recently our own and other laboratories seemed agreed that the *Cypridina* and firefly oxidative reaction was best described as shown.


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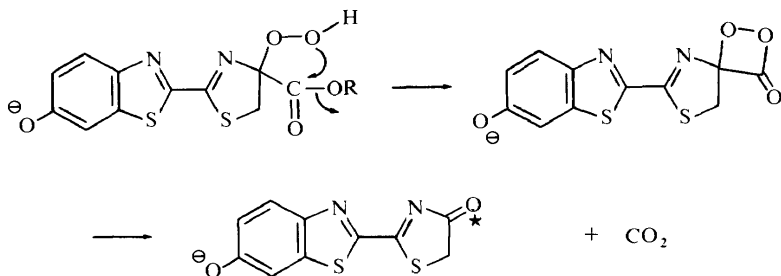
The arguments for this choice of Scheme 2 are several. Both molecules (and the various model compounds) have carbonyl groups substituted so as to predispose them to attack by peroxide rather than external hydroxyl ion or water. It is well known that peroxides are about 35 times more nucleophilic towards such carbonyl derivatives than is water, and that peroxide anion is about 10^4 times better as a nucleophile than is hydroxide[20]. Since the peroxide has an intramolecular advantage over hydroxyl ion, there seemed little doubt about the choice of mechanism. However, while chemilumine-scence seems to obey the conclusions above, very recent work[21] using both $O_2{}^{18}$ and H_2O^{18} favours, in the enzymically catalysed reaction, Scheme 3.

The generality of our earlier proposals is apparently maintained in chemiluminescence, and our recent work has been much concerned with providing sufficient detail to allow us to distinguish between the possibilities in Schemes 2 and 3.

We had earlier[22] chosen certain acridine derivatives as an easily studied series of chemiluminescent compounds. This series would appear to be among the least ambiguous and best understood of the examples of organic chemiluminescence at the present time. The product of the reaction, N-methyl-acridone, is formed in over 95 per cent yield in a smooth reaction which occurs at a convenient rate in a large variety of conditions. The emission is unquestion-ably from the singlet excited state of N-methylacridone, formed to the extent of at least ten per cent of the overall yield of ketone. The acridan esters provide fairly close models of the luciferins, while being an interesting class in themselves. The variation of quantum yield and rate with substitution is informative (*Figure 2**).
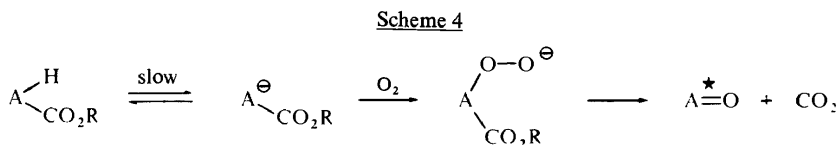
Scheme 4

The reaction can be carried out in dry, polar non-hydroxylic solvents, but since water is not consumed in Scheme 3 it is possible that traces of water are present to initiate the reaction. However, considering the precautions taken, and the fact that added water does not significantly affect either the rate or quantum yield in the phenyl esters, we feel that Scheme 2 is favoured.

* The use of Swain and Lupton[37] parameters gave a better correlation, using data from Schowen[23] and Ryan and Humffray[38] for phenyl ester solvolysis. The reaction constant is actually that derived from the use of Hammett σ constants.

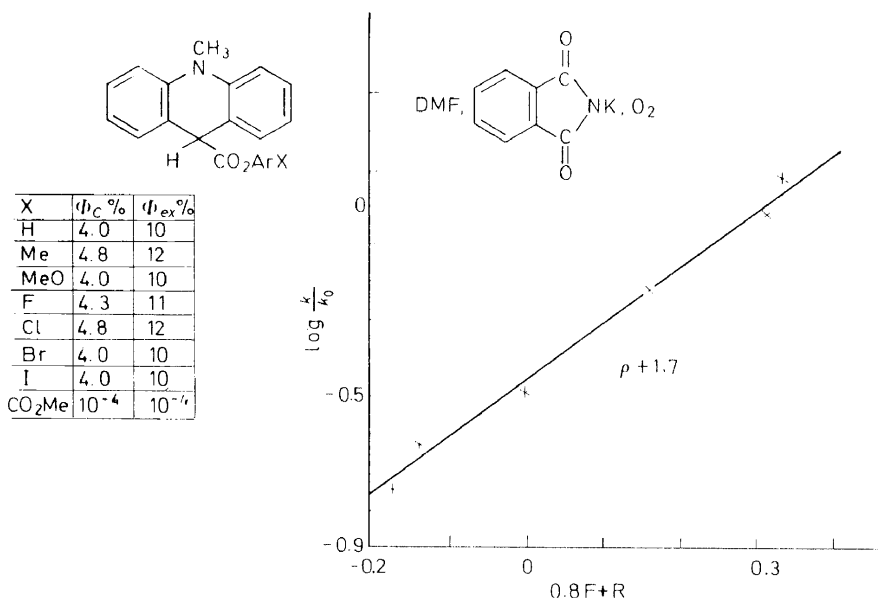| X	Φ_C %	Φ_{ex} %
H	4.0	10
Me	4.8	12
MeO	4.0	10
F	4.3	11
Cl	4.8	12
Br	4.0	10
I	4.0	10
CO_2Me	10^{-4}	10^{-4}

Figure 2. Effect of substitution (see footnote, page 618) on rate and quantum yield of acridan chemiluminescence (Φ_{ex} includes Φ_F of 0·42 for NMA).

In the series of substituted phenyl esters (Scheme 4), the slow step would appear to be the reversible formation of the anion. There is a marked dependence on the H^- value of the solution (the rate of reaction of the isolable intermediate peroxide is considerably greater at a given pH or H^- value). The reaction constant ρ in the Hammett equation is $+1.7$, in qualitative agreement with this view. The rate of reaction in this, and in the acridinium series, was determined by following both the increase in concentration of N-methylacridone and by the decrease of light intensity with time.

If the intermediate peroxide is first formed (by another route) then, as will be discussed below, a very different value for the reaction constant is found. It is noteworthy that the reaction of firefly luciferin shows an isotope effect for the removal of the equivalent proton.

Since the early slow step obscures the details of the critical excitation step, we turned our attention to the complementary acridinium salt series. In this case the addition of hydroperoxide to the 9-position occurs rapidly and the resulting peroxide can be isolated before reaction takes place, if necessary. It is now possible to examine in detail the later steps of the reaction. Apart from the greater sensitivity to base and the enhanced rate of reaction (which can be as high as 13 sec^{-1} at pH8) the major difference observed is in ρ, now surprisingly high at $+4.4$ in DMF and $+4.6$ in aqueous ethanol. For the solvolysis of phenyl esters the value is about $+2.0$[23]. The high rate of reaction is a function of the peroxide since the ψ-base is stable under the same conditions. The nitrile is also chemiluminescent and since attack of hydroxyl ion would directly form an intermediate amide (which is *not* chemiluminescent) we conclude that peroxide ion is again responsible for the reaction.

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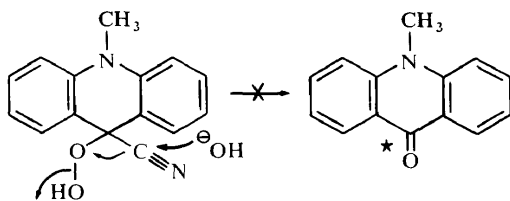
It would therefore appear that attack of hydroxyl ion at the carbonyl group is not rate-determining. We eliminate, at this stage, route 3(b) by the observation that the peroxide of the carboxylic acid is decomposed by base rapidly and quantitatively forming N-methylacridone, *without detectable light emission* at the concentrations used. In most of our work with peroxides of this type we have noted that reduction (by solvent or base) of the peroxide is a major competing dark route also. The dark reaction of the carboxylic acid may be associated with the deficiency in energy available (the excited state requires about 65 kcal/mole). Thus in firefly luciferin (50 kcal/mole required) this route *may* lead to emission.

We have already presented evidence showing that we are doubtful about route 3(a), and confirmation of these doubts was sought. In the conditions used for optimum quantum yield it was feared that exchange reactions would render ambiguous the use of O^{18}. By taking advantage of the reactivity of acridinium salts a peroxide incapable of cyclization was made (*in situ*) using methyl hydroperoxide.
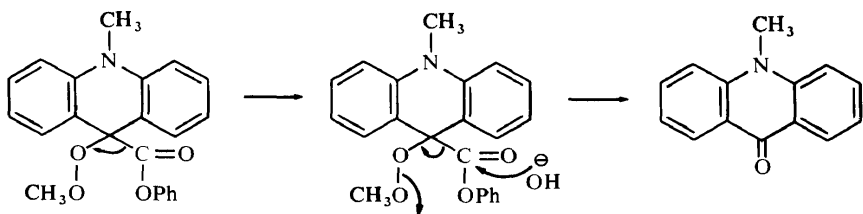
Decomposition by route 2 is precluded, and a mechanism in accord with the recent isotopic work on firefly luciferin seems inescapable. No significant emission of light is observed, in spite of the formation of an almost quantitative yield of N-methylacridone.
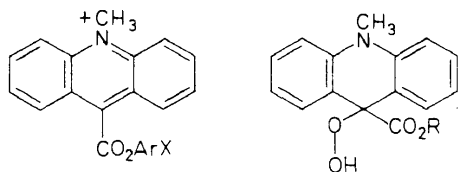
Returning briefly to the extremely high sensitivity to inductive effects ($\rho = +4.6$) we note that ρ for ionization of phenols is $+2.1^{24}$, so that we conclude that a high degree of bond breaking is occurring in the transition state. Looking more closely at the reaction sequence, we might account for the unusually high value of ρ by noting that not only is the attacking nucleophile (hydroperoxide) of comparable acidity to the leaving group (phenol) but the partition of the tetrahedral intermediate should favour return to the initial hydroperoxide. Thus inductive effects which enhance the forward reaction are of considerable importance.
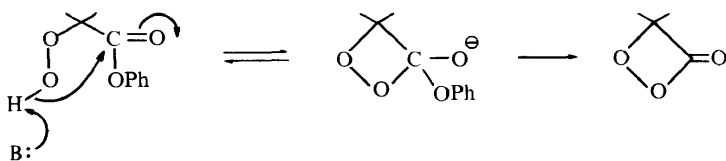
Similar results would be expected if the reaction proceeds directly via a transition state rather than an intermediate. In this connection, we note that the exothermic decomposition could occur equally well at the intermediate dioxetane or final dioxetanone stages. Both decompositions are sufficiently exothermic to populate (to the extent of ten per cent) an excited state of about 70 kcal/mole in energy. We have made no particular effort to improve the quantum yield, and this is probably a minimum value.

Although the general scheme is capable of rationalizing many existing examples of chemiluminescence and of predicting others, many details remain to be understood. Thus extension of our detailed investigations to another

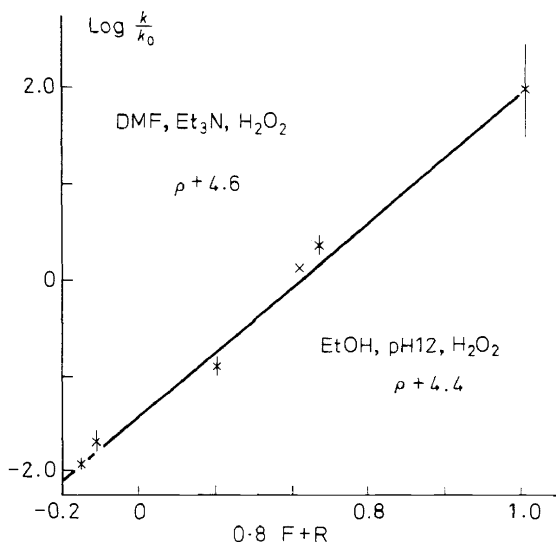| X	Φ_c%	
	DMF	EtOH
H	1.2	1.2
Me	1.5	1.2
MeO	1.8	1.0
F	1·6	
Cl	1.4	
Br	1.2	1.4
I	0.17	
NO_2	>0.7	1.2
CN	10^{-3}	10^{-2}
CO_2Me	10^{-3}	10^{-6}

Figure 3. Effect of substitution* on rate and quantum yield of acridinium salt chemiluminescence.

* The use of Swain and Lupton[37] parameters gave a better correlation, using data from Schowen[23] and Ryan and Humffray[38] for phenyl ester solvolysis. The reaction constant is actually that derived from the use of Hammett σ constants.

series, whose luminescence has been briefly reported[25], provides a related yet different scheme, with opportunities to broaden the scope of the questions asked of the system. More than one product is formed, and since the proven emitter can exist as an anion or as two different tautomeric neutral species, the identification of the excited molecule is potentially more difficult. The reaction (carried out in dimethylsulphoxide both dry and aqueous) is catalysed by strong base, and occurs at a suitable rate only when the activity of the peroxide anion is enhanced by a high concentration of DMSO.
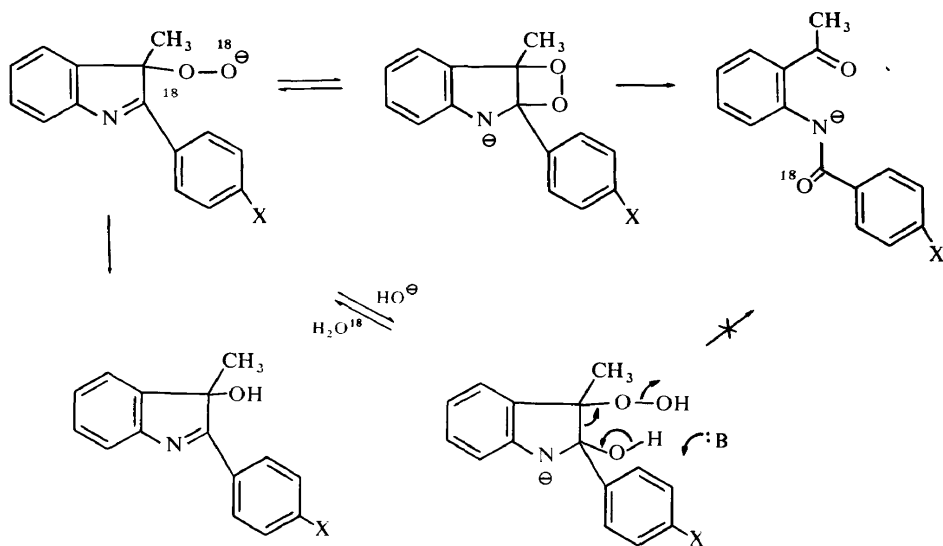
The identification of the anion shown as the emitter is easy and secure when the emission is strong, but in the weaker cases considerable absorption by coloured impurities prevents a complete correspondence between fluorescence and chemiluminescence spectra. However, in all cases only the two products are formed accounting for more than 90 per cent of the reaction in aqueous DMSO. Both reactions are first order in peroxide, and the reaction was followed both by light emission and by appearance of the products. A perfect isosbestic point is observed in the transformation (note that the alcohol and peroxide have the same ultra-violet spectrum). Thus no detectable concentration of intermediate is formed, perhaps more as a result of the equilibrium than of its instability.

We took advantage of the fact that oxygen exchange for an amide is a slow reaction. Thus the alternative mechanism involving addition of hydroxyl ion (in 85 per cent aqeous DMSO) is totally excluded within the limits of experimental error. This is taken as confirmatory evidence of the overwhelming tendency for intramolecular peroxide attack. A Hammett plot is obtained for the overall reaction ($\rho = +1.1$); although the rate-determining step is not thereby fully distinguished, it would appear to be the nucleophilic attack by peroxide on the imine. The yield of alcohol obtained shows that the two rate constants are of comparable magnitude. Although there is some trend

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Table 1

| X	k $\sec^{-1}$	Overall chemi-luminescence yield $\Phi \times 10^6$	Fluorescence yield $\Phi_F \times 10^3$	Yield of amide $\Phi_c\%$	Yield of product in excited state $\Phi_E\%$	Fluorescence maximum λ_F nm
NMe$_2$	0.10	2.0	0.6	5.2	6.7	490
OMe	0.14	3.2	2.8	32.3	0.4	470
H	0.28	0.2	2.2	47.7	0.02	450
F	0.29	0.4	2.6	60.4	0.02	450
Cl	0.54	0.07	1.9	66.0	0.005	450
Br	0.53	0.04	0.9	71.9	0.006	450

Indolenyl peroxides
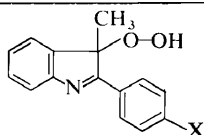
in 85 per cent aqueous DMSO and 0.04 M sodium methoxide.

observable in the chemiluminescence quantum yield, there is none of signifi-cance in the fluorescence efficiency. (The dimethylamino-compound is strongly coloured, exhibiting much self-absorption of the emission in both fluorescence and chemiluminescence.) When fluorescence efficency, and the total yield of product are taken into account, one obtains the fraction of molecules entering the excited state. There is a strong trend with substitution in a direction opposite to that of the rate of the overall reaction. Thus there is a large difference of 10^3 in the rate of population of the excited state with dimethylamino-substitution as against substitution by halogen. The chemi-luminescence quantum yield is moderately temperature-sensitive, falling with rise in temperature by about the same degree as the fluorescence efficiency of the emitter. Although the overall quantum yield is decidedly low, this is very largely owing to the exceedingly low fluorescence efficiency. This series of compounds has resisted all our efforts to improve on this by sub-stitution. It might be said that the *o*-amidoacetophenone chromophore 'dominates' all others. Under certain conditions yellow light is seen, perhaps as a result of emission from the neutral species. The intensity of fluorescence at 520 nm is markedly solvent-dependent, but also appears to be unaffected by substitution. There is a shift to longer wavelength in the anion in the same direction as Φ_E with substitution. However, the difference in energy that this represents can only result in a factor of three if activation energy were the sole influence. The obvious parameter which is of importance is ionization potential, and this may operate most effectively in the transition

$\lambda_{max.}$ emission

420 nm

520 nm

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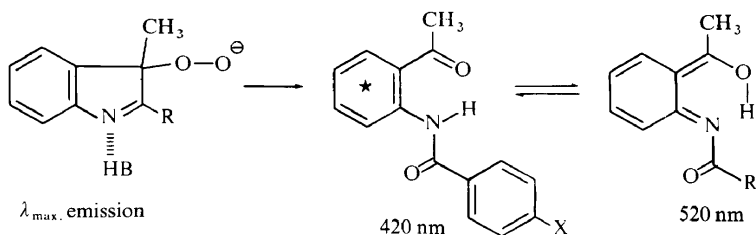
state. Returning to the case of firefly luciferin it is noteworthy that the methyl ether is not significantly chemiluminescent (the product is fluorescent) whereas the free phenol (as anion) is very effective (estimated $\Phi = 10$ per cent). This feature would appear to play a very important part in the extraordinary efficiency of the enzymic firefly system ($\Phi = 88$ per cent).
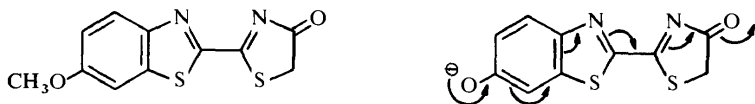
Other reactions which resemble these discussed above are the oxalyl ester series[26]. This has been studied in great detail with the resulting abbreviated sequence shown below.
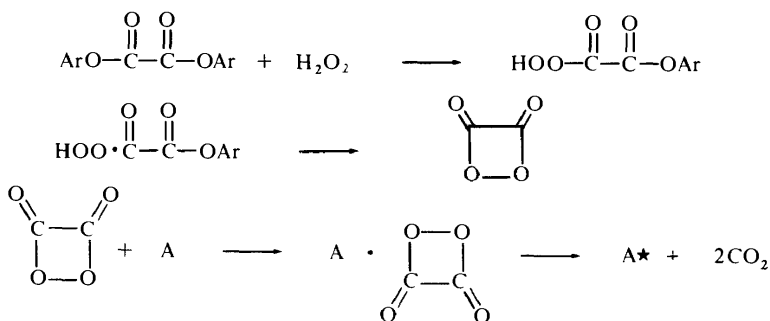
The evidence for the dioxetanedione is largely indirect although a mass spectrum has been obtained[27]. Although this route undoubtedly provides the most efficient chemical system yet discovered, an intermediate dioxetanedione is not essential for at least significant chemiluminescence. By replacing hydrogen peroxide by methyl hydrogen peroxide the reaction is about one thousandth as efficient, although much slower. A reasonable mechanism in this case would be:
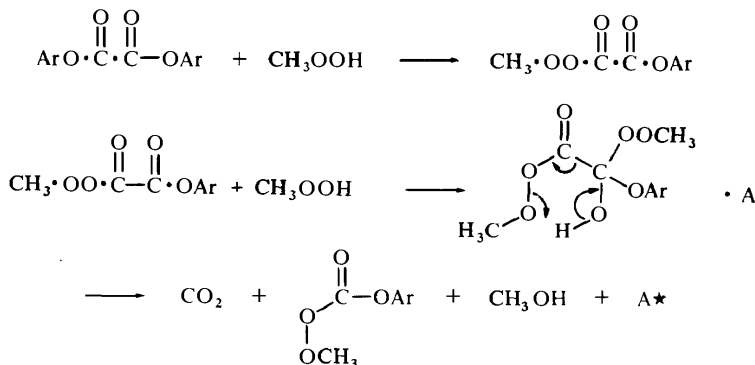

This reaction also forms two new carbonyl groups, and should be capable of exciting the fluorescers used. We are now studying this reaction in detail.

It has been argued[28] that Dewar benzene owes its existence to the fact that its decomposition is inhibited by symmetry prohibitions. Much the same may be said of the dioxetanedione—a carbon dioxide dimer! It is perhaps not surprising, that other dioxetanes of proven structure show remarkable stability— requiring fairly high temperatures for rapid decomposition. A value of 25 kcal/mole[29] has been quoted for the activation energy in spite of the potential enthalpy change of well over a 100 kcal/mole obtainable merely by electron reorganization.

However, the stability of dioxetanes associated with large molecules is considerably less, and attempted preparations which are successful in the less substituted cases decompose spontaneously with the emission of light, for example:
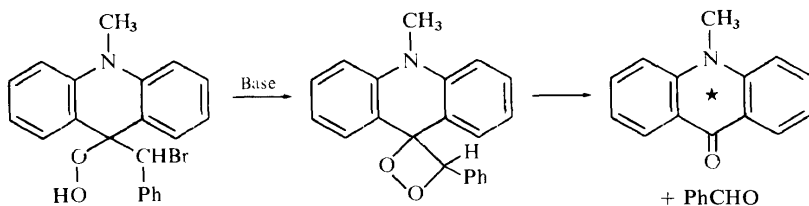

There are a variety of possible reasons, but one which we single out here is again the mixing of states which result from charge transfer interactions, aided at least in part by a reduction in ionization potential. Exactly the same observation has been made[26] concerning the intermolecular reaction between the dioxetanedione and fluorescers of various structures. In connection with other studies we have been able to observe, at low temperatures, the enormous catalytic effect of aromatic hydrocarbons on the decomposition of solutions of what appear to be the isolated dioxetanedione.

Recently[30] the addition of singlet oxygen to simple olefins has afforded several isolable dioxetanes, all of which emit light on decomposition. We have
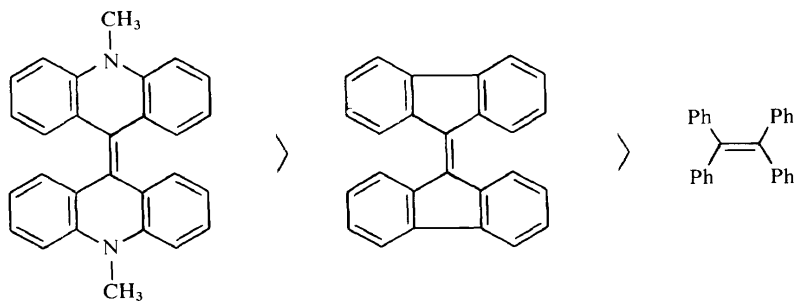
noted previously[31] the presumption of such intermediates in a number of cases of bright chemiluminescence. While we were less concerned with the isolation of the intermediates, we were aware of the factors which would lead to successful oxygen addition. In the series of compounds shown the order of reactivity with singlet oxygen can be inferred[32]. Unfortunately the series does not distinguish between the two most likely mechanisms, since the order of electron density in the double bond decreases in the same direction as the
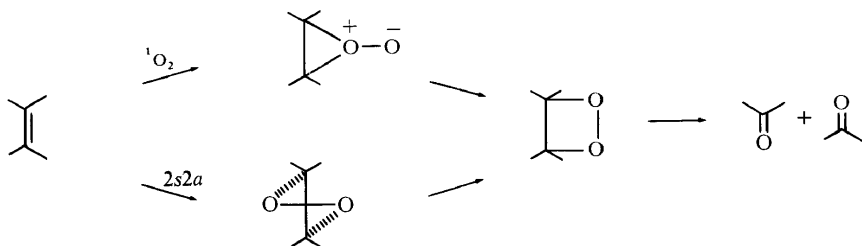
degree of twisting, the latter factor assisting the $2s2a$ addition. It would seem that the interference from the non-bonding electrons on oxygen would adversely affect the concerted addition in the transition state. We have noticed a moderate solvent effect suggestive of the polar addition but other experiments are in hand to help resolve the problem in this particular case. Interestingly ozonolysis, if carried out by adding instantly a large excess of

quantum yield between this reaction and that of singlet oxygen is 10^7. If, however, time is allowed for reaction with solvent, some light is emitted from excited N-methylacridone—perhaps from traces of singlet oxygen produced by reaction of the solvent with ozone[33]. The reaction of singlet oxygen with dimethylbiacridylidene in the solid state in near vacuum results in emission from the excited state of N-methylacridone. It is difficult on simple stoichiometric grounds alone to account for its formation by any other route. It must be emphasized that this reaction of singlet oxygen differs from the energy-pooling process perhaps involved in some other cases[13,34].

Experiments like those cited in this paper seem to demonstrate the participation of dioxetanes in some kinds of chemiluminescence. Work on the decomposition of simple dioxetanes bears out our contention that they are an important source of excited carbonyl products[35]. If it is necessary to provide *in one step* energy approaching 100 kcal/mole for the formation of an excited state, energy 'storage' is needed and a dioxetane provides a suitable 'capacitor'. In summary:

(1) From the stability associated with these molecules and the insight provided by Woodward and Hoffmann[36], we may conclude that this is an effective way of storing an exceedingly large amount of energy, to be released merely by electron reorganization.

(2) In addition to this feature, the rules indicate that an excited state formed in this decomposition will possess a lower energy of formation than it might otherwise have in another concerted reaction.

(3) Charge transfer would seem to play a significant part, perhaps allowing a mixing of states, and providing a lower pathway for the excitation.

(4) The difficulty of accommodating energy equivalent to an electronic excitation in vibrational modes of a ground state, a sort of chemical 'vertical transition', is a consideration supplementary to (1).

However, it is possible to discuss the dioxetane in somewhat more specific terms by means of a correlation diagram.

The most notable differences between the dioxetane and the now classical[29] cyclobutane–ethylene interconversion are the enthalpy change (100 kcal/mole), the lesser symmetry and the non-bonding electrons on oxygen. In the case of the last feature it can be seen that direct formation of an $n \rightarrow \pi^\star$ state is as symmetry-forbidden as it is in the carbonyl group itself. We would therefore expect a $\pi \rightarrow \pi^\star$ state, with singlet and triplet $n \rightarrow \pi^\star$ states formed in the usual way. Unfortunately there does not seem to be any definitive way of deciding this question. Whether the observed singly excited state is to be considered S or A in the diagram is not important, although it does alter the details of the indicated crossing. Crossing occurs twice using A states and, depending on whether the non-crossing rule is strictly obeyed, only once with
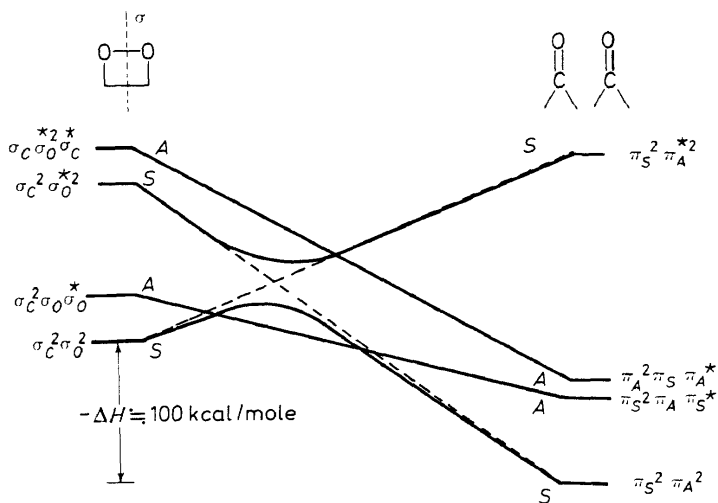
Figure 4. The concerted $2s + 2s$ decomposition of a dioxetane. Essential features of this route to chemiluminescence are the release in one step of about 100 kcal/mole and a low-lying excited state. The level of the $\pi \rightarrow \pi^\star$ state formed is here shown as that of the whole fluorescent molecule. In simple carbonyl compounds this state is inaccessible and crossing to the much lower $n \rightarrow \pi^\star$ level must occur.

S states. It is interesting that the surface crossing is obtained by the breakage of the very weak O—O bond, and that the two (in the limit) degenerate excited $\pi \rightarrow \pi^\star$ states give a charge transfer stabilized interaction. However, the exact details of the decomposition are probably best discovered by less qualitative methods. In this connection the allowed $2s2a$ process is to be seen as a competitive path, and may well account for some of the dark portion of the reaction. If the activation energy to entry into the excited state is comparable to that of the distortions necessary to consummate the allowed path then an excited state pathway is possible.

Perhaps one of the main reasons why symmetry arguments do not provide further examples of chemiluminescence is the difficulty, in other systems, of satisfying the thermodynamic requirements of the available excited state.

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For example, the decomposition of Dewar benzene can be seen as an intended formation of the $^1B_{1u}$ state which is certainly not to be achieved with the
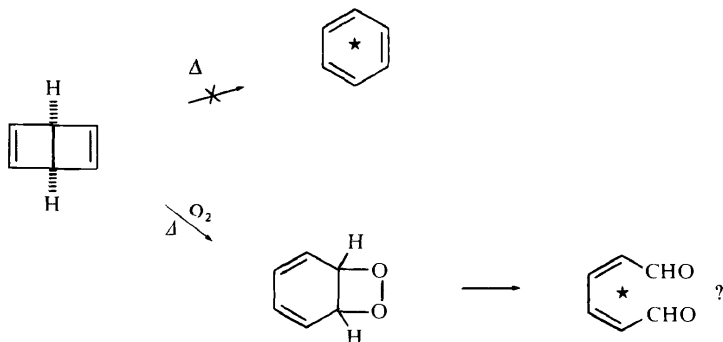
energy available ($ca.$ 90 kcal/mole). Even a crossing to the lower energy $^1B_{2u}$ state is similarly impossible. Light observed from the heating of Dewar benzene seems to be dependent on the presence of oxygen and a possible explanation is shown. Perhaps reaction occurs via the suggested[35] diallyl radicals or their equivalent. Nevertheless by a suitable choice of substituted valence isomers a direct formation of a hydrocarbon excited state is possible. This requires some synthetic effort, which is in hand.

ACKNOWLEDGEMENTS

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