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THE MECHANISM OF CHEMILUMINESCENCE:
A NEW CHEMILUMINESCENT REACTION

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The mechanism of light production by chemical reactions in solution has been the subject of many papers[1] since the discovery of the more efficient substrates. Among these, lucigenin,[2] 10,10'-dimethyl-9,9'-biacridinium nitrate (III) is considered to be one of the most powerful.

We wish now to report a new chemiluminescent reaction which provides some insight into the mechanism of the more effective, and still puzzling, older members of this class of compound. Indeed the prediction of the occurrence of luminescence in this compound (I) was made[3] on the basis of a probable general mechanism.

9-Cyano-10-methylacridinium nitrate (I), prepared by oxidation of 9-cyano-10-methylacridan[4] (II) by dilute nitric acid, when treated with alkaline hydrogen peroxide in ethanolic solution gave a blue glow which was emitted for 15 minutes under favourable conditions.

Measurement of this emission by means of a Hilger and Watts f4.6 spectrometer and an RCA 7265 photomultiplier tube gave a spectrum with a maximum at 442 mμ, identical in all respects to the fluorescence spectrum of N-methylacridone, measured under the same conditions. This latter compound was isolated from the reaction mixture in almost quantitative yield. The mechanism of light emission probably thus involves the formation of N-methylacridone in an excited state.

The similar oxidation of 9-cyano-10-methylacridan (II) was slightly more efficent. Conditions for the reaction included passage of oxygen through an ethanolic solution of the acridan nitrile, with the emission of light depending on oxygen concentration and temperature. Although oxidation by a radical chain process is possible, this mechanism does not seem to be involved. No catalytic effect was observed with added potassium ferricyanide, ferrous sulphate or cupric bromide.[5] Addition of arsenious oxide,[6] cyanide ion or hydroquinone did not inhibit light production. Several mechanisms are possible in this case, but detailed comment must await further work. The acridinium nitrate, however, must react by initial nucleophilic attack by peroxide anion.

The probable mechanism for the oxidation of the nitrate (I) is thus depicted in Fig. I and bears some analogy to the oxidation of α-diketones. In the latter case, four-membered peroxide intermediates (or transition states) are involved,[7] and it is anticipated that a similar mechanism will be found to operate here.[*] Oxidation of the acridan (II) to N-methylacridone has been observed earlier,[4] and we consider that this reaction is completely analogous to the peroxidic oxidation of similar nitriles. Recently[8] a four membered peroxide ring has been advanced to account for the production of isocyanate and a ketone in the oxidation of a secondary nitrile by oxygen in strong base. Oxidation of the unsubstituted N-methylacridinium salts, although giving N-methylacridone in high yield, does not produce light.

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[*] The exact nature of the intermediate need not be defined at this stage, although the breakage of the C-C and O-O bonds is likely to be concerted.

A reaction of energy sufficient to excite a molecule electronically, thereby producing the possibility of a radiative return to the ground state, will emit light providing that the energy produced is directed into the system of a potentially fluorescent product molecule. It is therefore attractive to consider constrained four-membered peroxide intermediates, because it is less likely that loss of the needed energy will occur by 'dark' (e.g. vibrational or translational) routes. The dark nature of the oxidation of acridinium salts, in contrast with the behaviour of the nitrile, is considered as an indication of this possibility. The ubiquitous nature of oxygen in chemiluminescent reactions could be associated with

(a) the low energy required to break the resulting O-O bond, such facile fission occurring concomitantly with

(b) the formation of a carbonyl group, with its high resonance energy, capable of conjugation with a potentially fluorescent π system.

Although all chemiluminescent reactions need not be of this pattern, by analogy with our findings a mechanism consistent with present evidence[9] for the oxidation of lucigenin is given in Fig. I. It is known[2] that the pseudo-base (IV) can be a precursor in the light reaction. This has led to suggestions[9(a)] that direct oxidation of the diol is responsible for the light, but heterocyclic pseudo-bases are known[10] to form peroxides by equilibration with the much more nucleophilic[11] peroxide anion. The efficiency of lucigenin could well be the result of the decomposition of the highly symmetrical peroxide (V), all energy produced then residing in the fluorescent product molecule. The nitrile would be expected to be less efficient, since nothing is known at present of the distribution of energy in the intermediate postulated, or in any resulting ion-pair. The dark reaction depicted in Fig. I also reduces the efficiency.

It is of interest that White's work with luminol[12] gives rise to a similar possibility and his description[13] of the reaction could be construed in this way.

While this manuscript was in preparation, the suggestion was made[14] that chemiluminescence does not involve bond breaking or bond formation, but simply electron transfer. The description of the formation of the electronically excited molecule in the reactions discussed here is made difficult by the fact that the excited molecule is produced by a relatively complex mechanism. In the present case a complete description must, of necessity, include bond cleavage and formation steps, although we are aware that the ultimate cause of excitation is not thereby necessarily defined.

Investigation of the suggestions made here is being carried out by isotopic tracer methods, and the results will be reported shortly.

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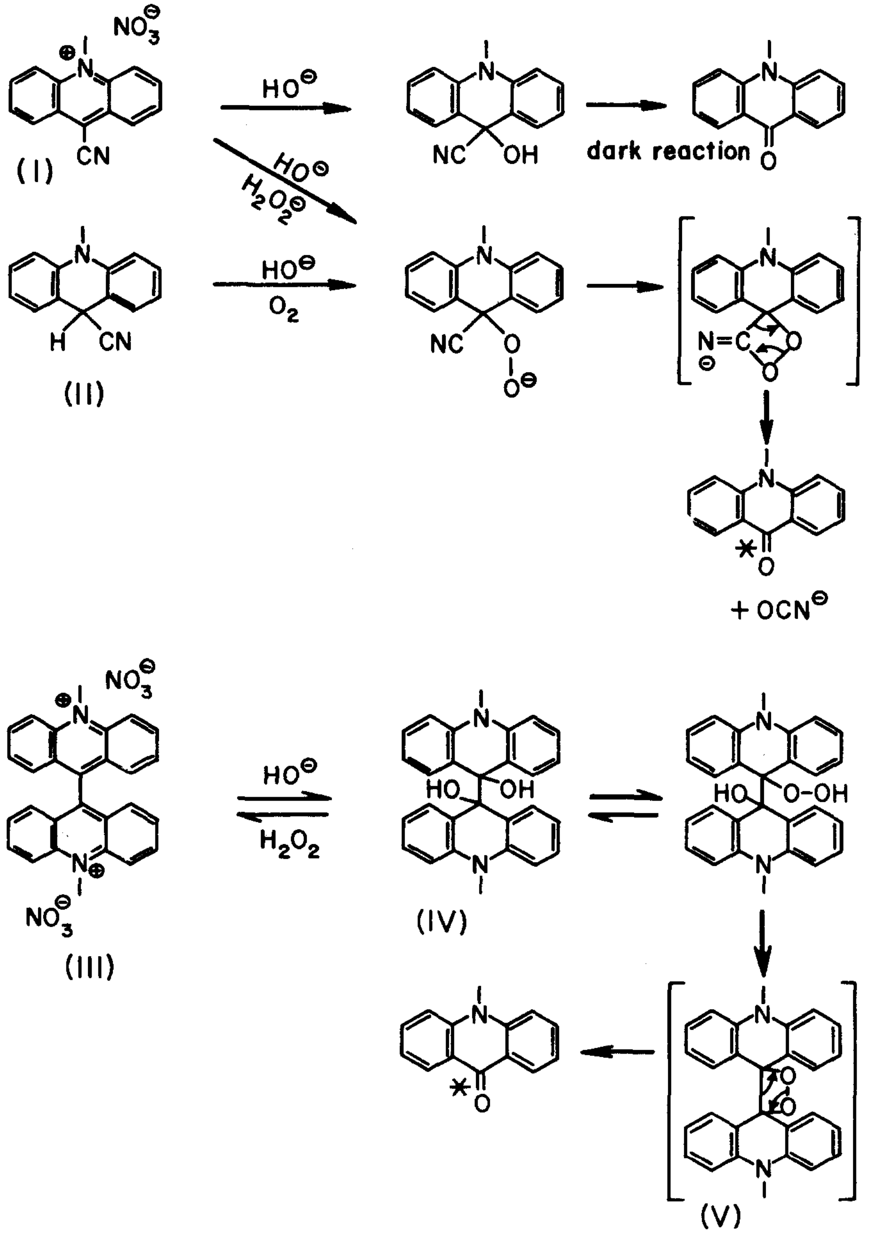
FIG. I


NO3⊖
CN
(I)
HO⊖
NC OH
dark reaction
O
HO⊖
H2O2⊖
H CN
(II)
HO⊖
O2
NC O O⊖
N=C O O
+ OCN⊖
NO3⊖
NO3⊖
(III)
HO⊖
H2O2
HO OH
(IV)
HO O-OH
O O
(V)
O

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