The Chemiluminescent Reaction of Singlet Oxygen with 10,10′-Dimethyl-9,9′-biacridylidene

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THE involvement of singlet oxygen in some chemiluminescent processes is well known.[1,2] The energy required for the elevation of the emitting molecule to an excited state is usually derived from the $^1\Delta g$ molecular pair. Radiation observable from the pair itself indicates an available energy of 44·8 k.cal.mole^{-1} (635 nm.). Energy sufficient for the excitation of the many organic systems which give rise to light in the region of 400 nm. requires the transfer of energy from two $^1\Sigma_g$ oxygen molecules. The ease with which this species is quenched[1] makes the implication of two of these

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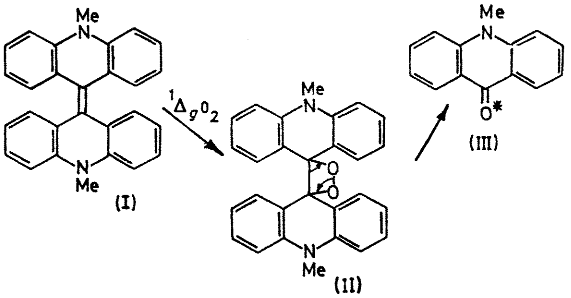
molecules in solution chemiluminescence unlikely. Nevertheless the suggestion[2] that the generation of singlet oxygen provides a general mechanism for chemiluminescence in solution deserves consideration. Further investigation is also made desirable by the application[3] of the suggestion to bioluminescence, a suggestion not in agreement with our own conclusions. We therefore find significant the observation of chemiluminescence in the presence of excess singlet oxygen which is *not* the result of transfer of energy, but is almost certainly derived from the decomposition of a 1,2-dioxetan.

10,10 -Dimethyl-9,9′-biacridylidene is reported[4] as being spontaneously chemiluminescent on solution in methanol. A pure sample[5] prepared by us is not visibly chemiluminescent in this solvent. The compound can be recrystallised from hot pyridine in good yield and the solution is again not visibly chemiluminescent on exposure to oxygen.

It was our expectation that singlet oxygen should be capable of addition to a double bond in the manner shown (by analogy with the reactions of enamines[6]) and this possibility has been theoretically confirmed.[7] Addition of an excess of triphenyl phosphite–ozone complex[8] to a pyridine solution of the biacridylidene in pyridine at 0° resulted in a bright blue light, λ_{max} 440 nm. Bromine and ethanolic alkaline hydrogen peroxide gave a brilliant emission whose spectrum was identical to that of the fluorescence of *N*-methylacridone, formed in high yield in the reaction. In the case of the triphenyl phosphite reagent we were able to show that a radical process was unlikely by a series of experiments to be reported later. The reagent itself does not appear to be the oxidant[8] and lucigenin (a biacridinium salt) is not an intermediate. An important observation is that ozonolysis, while forming *N*-methylacridone in high yield, is a dark reaction. The presence or absence of water was without effect on the emission of light, suggesting $^1\Delta_g$ rather than $^1\Sigma_g$ oxygen as the reactant and excluding pseudo-bases as intermediates.

Confirmation of these conclusions was provided by the exposure of a pyridine solution of the biacridylidene at −70° to singlet oxygen generated by a radiofrequency discharge.[‡] It was possible to show that *only* $^1\Delta_g$ oxygen caused emission and the information already given indicates a probable concerted reaction. The easily visible emission decayed in about 30 sec. on removal of singlet oxygen. Thus it should be possible to measure the activation energy for the decomposition of the dioxetan. The obviously lower value for this example contrasts with the value of 25 kcal.mole^{-1} found for 3,3,4-trimethyl-1,2-dioxetan,[9] presumably owing to the much lower electronic states available to the highly conjugated *N*-methylacridone.



We have observed no excitation of the green (λ_{max} 515 nm.) biacridylidene fluorescence, neither is *N*-methylacridone caused to emit light except by oxidative formation from the biacridylidene. The light reaction is at least as efficient as that of lucigenin with alkaline hydrogen peroxide. This work also explains the observation[4] of a long lived "phosphorescence" on irradiation of the biacridylidene in the presence of oxygen, as a photosensitised oxygenation forming (II), followed by its chemiluminescent decomposition.

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