

Infrared Chemiluminescence from an Organic Compound

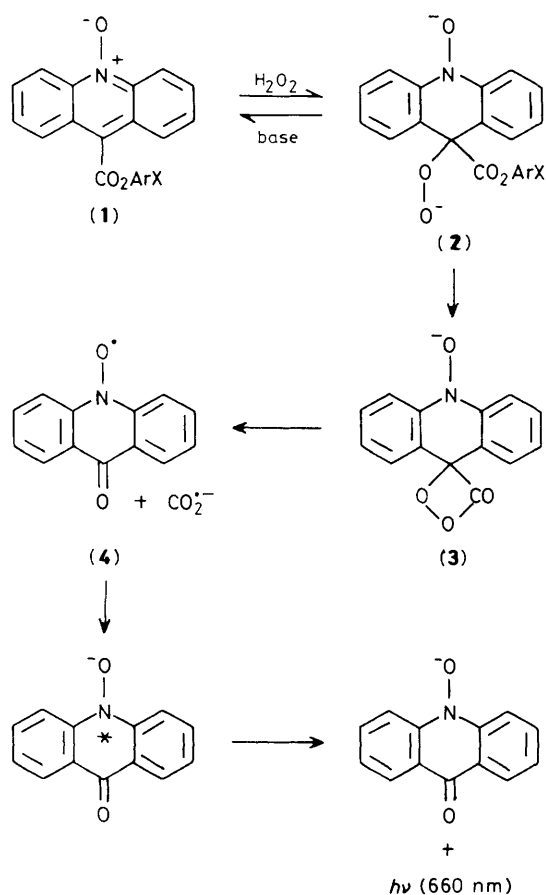
Frank McCapra* and M. Taheri-Kadkhoda

School of Chemistry and Molecular Sciences, The University of Sussex, Brighton BN1 9QJ, U.K.

Chemiluminescence which extends into the infrared has been observed during the oxidation of acridine *N*-oxide phenyl esters in solution.

There are two established mechanisms for the generation of bright chemiluminescence from organic compounds in solution.¹ However, the principles which govern the efficiency of light emission are not fully understood. It is expected² that, in the electron transfer mechanism proposed³ for reactions which proceed by formation of a dioxetanone, lowering the energy of formation of the radical ion pair (see Scheme 1) should have an effect on the efficiency. In the case of the compounds described in this report, we intended to achieve this by taking advantage of the well known stability of the nitroxyl radical (4). This radical is expected to result from the transfer of an electron from the intermediate (3), formed by the intramolecular cyclisation of the peroxide (2).

A short series of acridine *N*-oxide phenyl esters (1), X = H, Me, OMe, Cl, F, and NO₂, was synthesised by standard methods.[†] Treatment of the esters in solution in either



[†] All compounds cited are new and gave n.m.r., i.r., u.v., and mass spectral data in accord with their structures. Satisfactory microanalyses were also obtained for all compounds.

methanol or dimethylformamide (DMF) with alkaline hydrogen peroxide resulted in easily visible red light. The spectrum obtained (Figure 1) clearly demonstrated emission in the i.r. region, extending beyond 850 nm.[‡] Most of the quantitative work was done in DMF.[§]

The chemical mechanism of the reaction is assumed to be analogous to that of the acridinium esters,⁴ although there is a very substantial difference in one respect. The Hammett reaction constant ρ is 0.94 for the *N*-oxide series, and 3.90 for the acridinium esters. This points to a difference in rate determining step, in which, in the compounds studied in this work, the addition of peroxide anion to the 9-position is the slow step. The addition of hydroxide to the 9-position can be easily followed in the absence of H₂O₂ by the change in the u.v. spectrum of the starting ester, but the peroxide adduct completes the remaining steps too quickly for the analogous observation. By contrast, there is no doubt that dioxetanone formation is the slow step in the reaction of acridinium esters.⁴ The product from the *N*-oxide esters, *N*-hydroxyacridone, is formed in >90% yield. The chemiluminescence quantum yield[¶] is low (0.03%), largely as a result of the low fluorescence yield of the oxy-anion (1.8%) as expected for a low-energy excited state. The yield of excited states is, however, similar to that of the acridinium esters at 2.0% (independent of substitution in the present case).

There is usually a clear relationship between the ionisation potential of the donor molecule and efficiency in other, inter-molecular, chemiluminescent reactions, thought to proceed by an electron transfer mechanism.² In general, the lower the ionisation potential, the higher the quantum yield. Since the ionisation potential of a molecule which fluoresces in

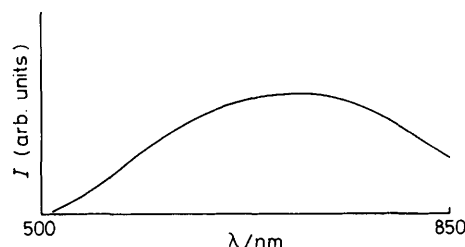


Figure 1. Chemiluminescence from the esters (1).

[‡] Fluorescence and chemiluminescence spectra were obtained on a Spex Fluorolog 112X spectrometer, using a cooled red-sensitive photomultiplier.

[§] Excellent pseudo-first-order plots of the light decay rate were obtained, but to keep the rate sufficiently slow for measurement, succinimide and potassium *t*-butoxide were used as a buffer system. We recommend this novel approach for the control of H₂ in dipolar aprotic solvents.

[¶] The fluorescence quantum yield was measured by reference to diphenylanthracene and chemiluminescence quantum yields by reference to luminol (H. H. Seliger, *Methods Enzymol.*, 1978, 57, 560).

the i.r. may safely be assumed to be extremely low, it is noteworthy that the efficiency of population of the excited state is no higher than that of the acridinium esters which give rise to a blue emission (λ_{max} 440 nm). Thus it may be that the mechanism does not involve discrete electron transfer, but occurs by way of a charge transfer state formed during the decomposition of (3). The distinction may be subtle, but it has great importance in the design of experiments to intercept, and attempt to prove the existence of, the postulated radical ion pairs.

Although the expectation of enhanced efficiency of excited state formation has not been fully realised, this reaction is the first example, to our knowledge, of an *intrinsic*** i.r. emission

** I.r. chemiluminescence can be obtained from active oxalate esters by the addition of fluorescent acceptors known to fluoresce in that region (M. M. Rauhut, B. G. Roberts, D. R. Maulding, W. Bergmark, and R. Coleman, *J. Org. Chem.*, 1975, **40**, 330).

from a chemically generated *electronically* excited state in solution.

Received, 4th December 1987; Com. 1751

References

- 1 K. D. Gundermann and F. McCapra, 'Chemiluminescent Organic Compounds,' Springer Verlag, Berlin 1987; F. McCapra, *Proc. Roy. Soc. Lond., Ser. B.*, 1982, **215**, 247; T. Wilson, *Int. Sci. Rev. (2)*, 1976, **9**, 265; G. B. Schuster and S. P. Schmidt, *Adv. Phys. Org. Chem.*, 1982, **18**, 1982.
- 2 G. B. Schuster, J. J. Zupancic, and K. A. Horn, *J. Am. Chem. Soc.*, 1980, **102**, 5279; J.-Y. Koo and G. B. Schuster, *ibid.*, 1978, **100**, 4496; P. Lechtken and N. J. Turro, *Mol. Photochem.*, 1974, **6**, 95; P. A. Sherman, J. Holzbecher, and D. E. Ryan, *Anal. Chim. Acta*, 1978, **97**, 21.
- 3 J.-Y. Koo, S. P. Schmidt, and G. B. Schuster, *Proc. Natl. Acad. Sci. U.S.A.*, 1978, **75**, 30; F. McCapra, *J. Chem. Soc., Chem. Commun.*, 1977, 946.
- 4 F. McCapra, *Acc. Chem. Res.*, 1976, **9**, 201.