METAL CATALYSED LIGHT EMISSION FROM A DIOXETAN

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Summary   The photosensitised oxidation of 9-(2-adamantylidene)-N-methylacridan affords a
compound whose properties are best explained by a dioxetan structure   Its decomposition is
catalysed by lanthanide chelates with energy transfer

The chemistry of dioxetans continues to excite much interest   Of special significance are
the effects of substituents and of catalysts on light emission, particularly where electron
transfer may be involved[1]   Except in rare cases catalytic decomposition does not result in the
expected emission of light[2]   The reactions of dioxetans substituted by electron releasing groups
with metals are not easily examined since such compounds are inherently unstable[1,3 4]   We have
therefore synthesised and further investigated the only readily isolable example[3]

Related unstable dioxetans 1 and 2 based on the acridan nucleus also emit light as they
decompose[4,5], but investigation can be difficult   For example the synthesis of 1 by the photo-
oxygenation of 9-methylene-N-methylacridan gave a complex mixture, with no component sufficiently
stable as to allow isolation[5]   The most stable compound found in the mixture was assigned the
dimeric tetraoxocane structure 4   In view of this behaviour we have re-examined the oxidation of
9-(2-adamantylidene)-N-methylacridan[6]   Photo-oxygenation of 5 in CH_2Cl_2 at $-72^\circ C$ using methylene
blue[7] as sensitiser gave a quantitative yield of a single compound, 3 (as judged by n m r spectro-
scopy) in 20 min   The n m r spectrum was obtained at room temperature, and the absence of
N-methylacridone (NMA) is in marked contrast to the results obtained in the photo-oxygenation of
1   Photo-oxidation of enamines, particularly likely to give dimeric and polymeric material also
gives monomeric dioxetans by careful choice of conditions[8]   The plot of light emission from 3
against a rise in temperature from $-20^\circ C$ to $+60^\circ C$ showed no peaks of intensity again in contrast
to the behaviour of the mixture obtained from oxidation of 9-methylene-N-methylacridan[5]   This
stabilisation of dioxetans by spiroadamantyl substitution has recently been shown to be general[9]
Establishing the molecular weight by the freezing point method proved difficult   Although

monomer was indicated the results were unreliable owing to the precipitation of an insoluble material during cooling in most solvents with useful cryoscopic constants However vapour pressure osmometry gave a molecular weight of 357 ± 86 in acetone and 369 ± 101 in $CHCl_3$[10] The value required for $\underline{3}$ is 359 Allowance was made for traces of NMA and adamantanone, formed in these solvents during the determination

It has been noted[2] that lanthanide metals catalyse the decomposition of simple dioxetans, such as tetramethyl dioxetan The mechanism of this reaction is of interest particularly with regard to dioxetans such as $\underline{3}$ which uniquely give mainly singlet rather than triplet excited states When the shift reagent $Eu(fod)_3$ was added to a solution of $\underline{3}$ in toluene at room temperature, bright red light was seen The usual blue light is not observable from such a solution at room temperature unless the reaction is catalysed[3] We have therefore examined the effect of several lanthanide chelates (Table) with the following results

Catalysis occurs by formation of a complex between $\underline{3}$ and the lanthanide Thus the initial light intensity is directly proportional to the concentration of both lanthanide and $\underline{3}$, whereas the total light is independent of the concentration of lanthanide That the emission of red light is not simply the result of energy transfer from excited NMA is also confirmed by the effect of solvent In toluene, with $Eu(fod)_3$ the emission occurs entirely from the lanthanide $(\lambda_{max}$ 540, 557, 582, 594, $\underline{614}$ and 625 nm), whereas in EtOH the strongest maximum is observed at 423 nm, characteristic of uncomplexed NMA In toluene as solvent, acetone, pyridine or Et_3N compete for the catalyst The octacoordinate europium tris(thenoyltrifluoroacetonate-1,10-phenthroline does not significantly catalyse the decomposition of $\underline{3}$

The kinetic behaviour is not simple, since the ketonic products of the reaction complex with and compete for the catalyst as they form, and we have not attempted a full kinetic examination However by using initial intensities and approximate pseudo first order rates the order shown in the Table is obtained This follows that expected for the decreasing Lewis acidity across the lanthanide series

The catalytic decomposition of simple dioxetans by Lewis acids has been shown to be a dark reaction[11] and it has been suggested[2] that the metal may lift the orbital symmetry restrictions against a concerted (dark) reaction In the present case at least this does not appear to be so It seems that although the metal lowers the activation energy for decomposition the likelihood of light emission depends on whether the product-metal complex radiates or not Thus in the case of catalysis by Eu chelates, the NMA-Eu complex is strongly fluorescent, and energy transfer is virtually complete With $Pr(fod)_3$ (weakly fluorescent)and in particular $Dy(fod)_3$ (non-fluorescent) strong quenching of both the chemiluminescence and the fluorescence of NMA occurs In the latter two cases very weak emission at ca 440 nm is observed, typical of the spectrum of general Lewis acid broadened NMA fluorescence We therefore conclude that the catalytic event does not of itself lead to ground state products Catalysis may be the result of the increase in oxidation potential of the peroxide on complexing with the Lewis acid[12] A schematic interpretation of this mechanism is shown
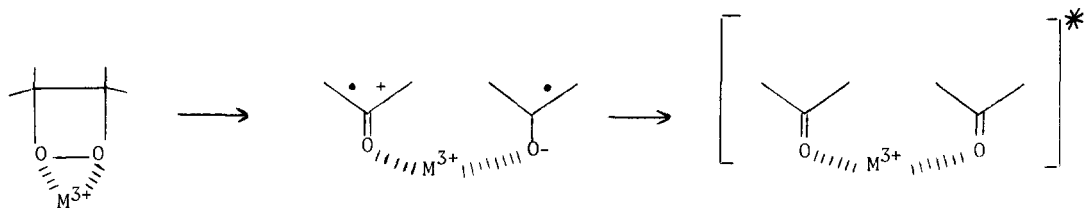
TABLE

Catalyst	Rel rate	λ emission (nm)
Pr(fod)$_3$	65	440, 602
Eu(fod)$_3$	30	614[†]
Dy(fod)$_3$	6 5	436
Yb(fod)$_3$	1 0	435
None	6 5 x 10^{-4}	423

[†]Main peak only, see text, solvent toluene, 25°C
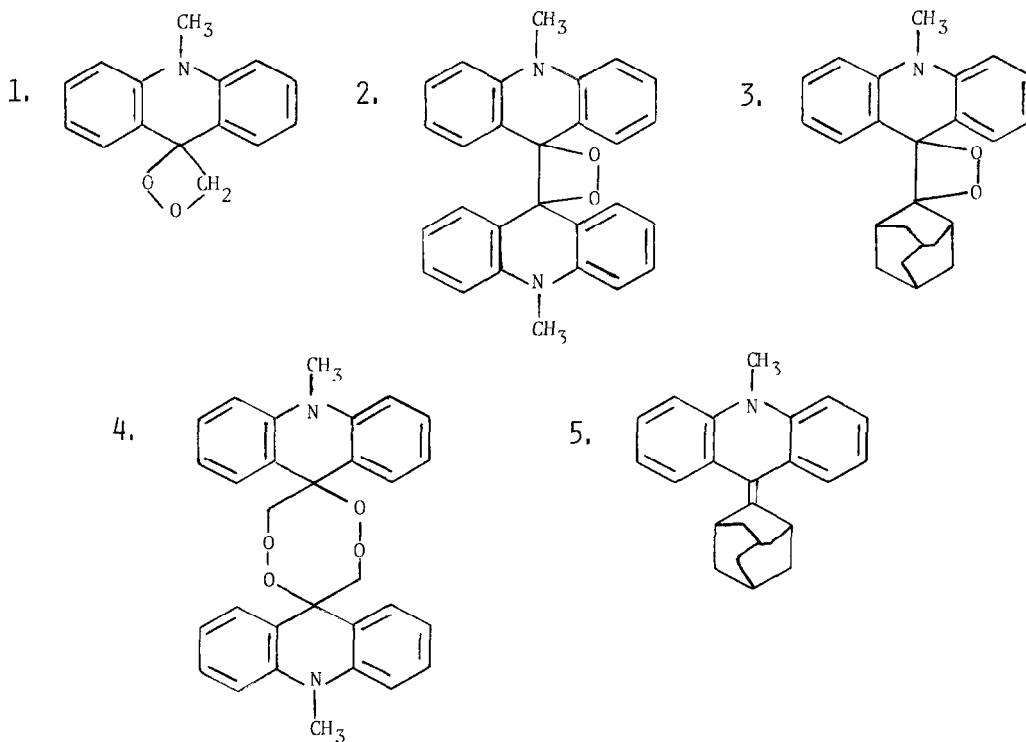
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5. F H White, N Suzuki and W H Hendrickson, Chem Lett , 1979, 1491

6. The olefin was synthesised from N-methylacridonethione and adamantanone p-tolylhydrazone by the method of D H R Barton, F S Guzec and I Shahak, J Chem Soc , Perkin I 1974, 1794

7. It was more convenient to use the easily separated polymer-supported Rose Bengal as sensitiser in preparation runs, but some photodecomposition occurred   A solution (0 02 M) of 2-amino-4-nitrotoluene in ethanol was used as an optical filter

8. C S Foote, A A Dzakpasu and J W-P Lin, Tetrahedron Lett , 1975, 1247

9. W Adam, L A Arias and D Scheutzow, Tetrahedron Lett , 1982 2835

10. The error quoted in these determinations is the propagated standard deviation of all the errors in calibration, the determination of molecular weight and the estimation of contaminating NMA and adamantanone concentrations

11. T Wilson, M E Landis, A L Baumstark and P D Bartlett, J Am Chem Soc , 1973, 95, 4765

12. Similar interpretations are possible in related cases of acid catalysis of light emission from dioxetans (see ref 3 and K A Zaklika, T Kissel, A L Thayer, P A Burns and A P Schaap, Photochem Photobiol , 1979, 30, 35)