Singlet Excited States from Dioxetan Decomposition

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Summary Isolable dioxetans usually afford triplet rather than singlet excited products but we now show that high yields of excited singlet states are obtainable from stable dioxetans by appropriate substitution; a remarkable rate acceleration of the chemiluminescent reaction by surfaces is observed.

DIOXETANS are now accepted[1] as a principal source of chemically generated excited states. They were originally proposed[2] as intermediates in visible chemiluminescence and as such must produce high yields of excited singlet states, usually of π,π^* character. However, with only one exception[3] triplet states are virtually the exclusive products of the dioxetans so far characterised. In addition in the one case so far studied it seems that n,π^* states are formed in preference to π,π^* states even if the latter are of lower energy.[4] The rate of decomposition is not increased by substitution[5] with the exception[3] previously noted suggesting that the reaction is not concerted. This is in agreement with kinetic[5,6] and some theoretical studies[7] which indicate a diradical mechanism. Other treatments and calculations[8] seem to suggest that the reaction is concerted but that the formation of triplets is expected on theoretical grounds.

All the preceding observations cast doubt on the role of dioxetans in bright chemiluminescence and, by implication, of dioxetanones in bioluminescence.[9] It is therefore important to examine these points and we now report a study of three dioxetans which shows that none of these accepted properties of dioxetans is general.

Photo-oxidation of 9-benzylidene-*N*-methylacridan in toluene at −78 °C gave an unstable compound (**1**) ($t_{\frac{1}{2}}$ at 25 °C, 8 min) which emitted light on warming in solution. The optimum quantum yield was obtained by the use of dilute solutions and addition of radical inhibitors such as galvinoxyl. Destruction by traces of transition metals was not a problem in this solvent. The result is a remarkable singlet excited state yield of 25%, and an abnormally short lifetime for the dioxetan which incidentally prevents its isolation. However, the n.m.r. spectrum showed a singlet at δ 6·44 (as predicted from a consideration of model compounds) whose disappearance was directly related to the appearance of the benzaldehyde signal at δ 10·01 and the decay of light emission. The same dioxetan was prepared by cyclisation of 9-hydroperoxy-9-bromobenzyl-*N*-methylacridan and showed identical behaviour.

Since singlet efficiency appears to accompany a reduced lifetime it has been suggested[10] that isolation of such dioxetans is unattainable. However the dioxetan (**2**) prepared in similar fashion to (**1**) from the corresponding olefin, seemed likely to be more stable, assuming that the transition state for decomposition involves a high degree of initial O–O bond stretching. Study of molecular models suggests that this stretching would be resisted by com-

TABLE 1. Decomposition of the dioxetans (3)

Dioxetan	k/s^{-1} (25 °C)	E_a/kcal mol^{-1}	log A	ϕ_{NMA^*} %[b]	Solvent
(1)	$1{\cdot}3 \times 10^{-3}$	19·7	11·6	25·0	Toluene
(2)	$1{\cdot}0 \times 10^{-7}$[a]	26·3	11·5	12·0[a]	Xylene
(3)	$1{\cdot}3 \times 10^{-3}$	—	—	5·9	CH_2Cl_2

[a] By extrapolation from results at higher temperatures. [b] Yield of NMA excited states calculated from chemical and fluorescence yield in each experiment, using luminol as chemiluminescence standard, J. Lee, A. S. Wesley, J. F. Ferguson, and H. H. Seliger, in 'Bioluminescence in Progress,' eds. F. H. Johnson and Y. Haneda, Princeton University Press, New Jersey, 1966, p. 35.

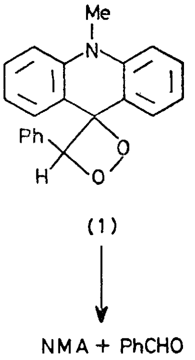
pression of the acridan and adamantyl residues.[11] There is a considerable increase in activation energy (Table 1) and the lifetime is now sufficient to allow crystallisation. Acceptable analytical and spectral data were obtained for this dioxetan.† During attempts to isolate it by t.l.c. we were surprised to find that its lifetime was very considerably less than expected from the kinetic data. Treatment of solutions of the dioxetan with solids (Table 2) gave very large increases in the rate of decomposition.[12] The catalysis of dioxetan cleavage normally results in exclusive enhancement of competing dark reactions.[1,13] Given the problems in optical geometry which prevent a precise measurement of the yield of excited molecules, it is clear that with a greater than million-fold increase in rate, it must be roughly true that the dark and light paths are equally catalysed. For example, if the dark reaction were catalysed exclusively, as is usual, the quantum yield on adsorption would have been $3{\cdot}4 \times 10^{-5}$, a difference very much greater than that observed (Table 2) and which may, in any case, be more apparent than real. We see this as an indication that excitation occurs after the transition state. It is possible that enzyme binding could exert a similar catalytic effect on intermediates in bioluminescence which, in isolation, have too great a lifetime to account for the typical flash of light exhibited by many organisms. Trimethyldioxetan[14] and bisadamantylidenedioxetan[15] did not decompose significantly faster in contact with solids. There are several possible explanations for this difference, one of which is considered in the accompanying paper.[16]

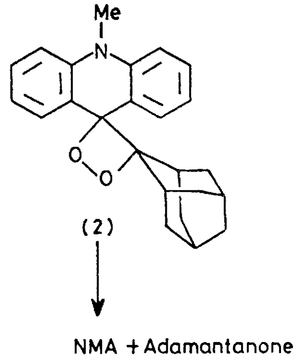
TABLE 2. Decomposition of the dioxetan (2) by adsorption on solids

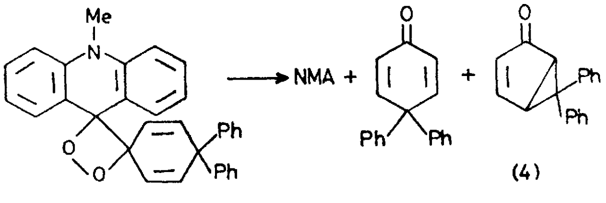
Solid[a]	k/s^{-1} (25 °C)	ϕ_{NMA^*} %
Alumina	$0{\cdot}27 \pm 0{\cdot}05$	0·9
Silica gel	$5{\cdot}0 \pm 2{\cdot}0 \times 10^{-2}$	—[c]
MgO	$7{\cdot}5 \pm 1{\cdot}0 \times 10^{-3}$	—[c]
None	1×10^{-7}[b]	9·2

[a] Added to xylene solution of (2). [b] By extrapolation from Arrhenius plot. [c] Not measured.

The remaining problem is that of the competition in the fragmentation between n,π^* and π,π^* states. Previous work[4] indicated that the carbonyl product with a lowest excited state of n,π^* character did not lose excitation to the carbonyl product of π,π^* character even though the former was at higher energy than the latter. The results already described suggest that this is not general since *N*-methylacridone (NMA) has a lowest π,π^* excited state but give no indication of the energy distribution in the fragments.


(1)


(2)


(3) (4)

However, decomposition of the dioxetan (3) gives a carbonyl product whose rearrangement [to (4)] is indicative of triplet n,π^* excitation[17] and fluorescence from NMA as before allows measurement of the π,π^* excitation yield (Table 3). We were unable to measure the amount of triplet NMA formed, but the ratio of π,π^* to n,π^* excitation is sufficiently large as to show that preference for n,π^* triplet states is not universal. For experimental reasons to be discussed in detail elsewhere, this ratio is almost certainly underestimated. It may be that only n,π^* states of both fragments

TABLE 3. Distribution of excitation energy in products of decomposition of the dioxetan (3)

Solvent (25 °C)	Yield of (4) %[a]	ϕ_{NMA^*} %[b]	ϕ_F NMA[c]
Toluene	1·3	5·1	0·07
CH_2Cl_2	1·3	5·9	0·63

[a] Based on yield of unrearranged ketone. [b] Based on total yield of NMA and its fluorescence efficiency in the solvent used. [c] Fluorescence efficiency of NMA.

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† Satisfactory analyses and spectra were obtained for all new compounds including the starting olefins although microanalysis of dioxetans (1) and (3) was not possible owing to their short lifetime.

are initially populated, and that the observed states are the result of rapid internal conversion and intersystem crossing. It may also be significant that although the fluorescence of NMA is much affected by solvent polarity, the effect being ascribed to the mixing of adjacent n,π^* and π,π^* states,[1] no change in the ratio was observed (Table 3).

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