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3,3-(9,9-FLUORENYL)-4-METHOXY-1,2-DIOXETANE AND 3,3-DIPHENYL-4-METHOXY-1,2-DIOXETANE: KINETIC PARAMETERS OF THERMAL DECOMPOSITION

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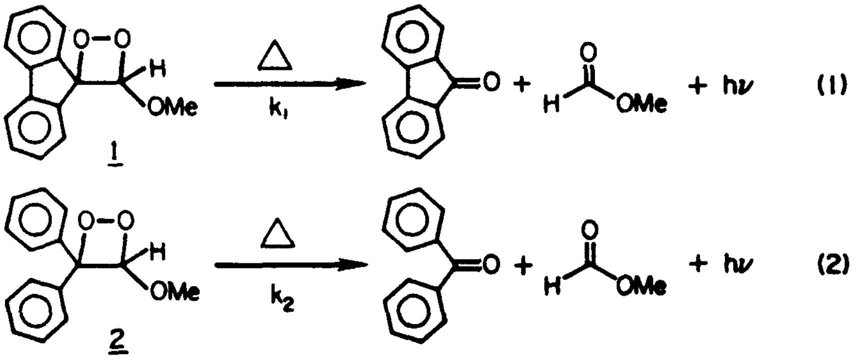
The thermal decomposition of 1,2-dioxetanes has been shown to produce two carbonyl fragments, one of which can be generated in an excited electronic state.[1,2] Dioxetanes capable of generating carbonyl products with excited states of known π,π^* configuration and good fluorescence efficiency have resisted isolation until now.[3] We report here the properties of 3,3-(9,9-fluorenyl)-4-methoxy-1,2-dioxetane 1, and show that its decomposition (reaction 1) generates excited singlet (π,π^*) fluorenone. We also compare 1 to the closely related 3,3-diphenyl-4-methoxy-1,2-dioxetane 2, expected to generate excited benzophenone with n,π^* excited states upon thermolysis (reaction 2).



The activation parameters for the thermolysis of 2 are found to be similar to those of other trisubstituted dioxetanes[2], however the activation energy for the thermolysis of 1 is significantly lower than expected. 1 is one of the least stable dioxetanes so far isolated.

1 and 2 were obtained in approximately 10% yield by the method of Kopecky[1a] by ring closure of the corresponding bromohydroperoxides.[4] 1 and 2 were purified by low temperature (-60°) column chromatography (alumina, CH_2Cl_2 as eluent).

The thermal decomposition of 1 [nmr in CCl_4: δ 3.40 (s, 3H); δ 5.92 (s, 1H); δ 7.0-7.5 and 7.7-8.0 (m, $\sim$ 8H)][5] produced fluorenone and methyl formate [nmr in CCl_4: δ 3.66 (d, J = 0.4 cps, 3H) and 7.90 (q, J = 0.4 cps, 1H)] as the sole products and was accompanied by chemiluminescence. The emitter in the thermolysis of 1 was shown to be excited singlet (π,π^*) fluorenone by the following evidence: a) chemiluminescence spectrum (λ_{max} = 486 nm in benzene) matching the fluorescence spectrum of fluorenone[6], b) no observable quenching of the chemiluminescence by conjugated dienes (up to 1 M), c) red shift of the luminescence in polar solvents[6], and d) parallel between initial luminescence intensities in various solvents and the solvent dependent fluorescence efficiency of fluorenone.[6]

The thermal decomposition of 2 [nmr in CCl_4: δ 3.38 (s, 3H); δ 6.06 (s, 1H); and δ 7.2-7.5 (m, $\sim$ 10 H)[5b]] resulted in a weak luminescence and produced benzophenone and methyl formate as the sole products. 9,10-Diphenylanthracene (DPA, a singlet energy acceptor) and 9,10-dibromoanthracene (DBA, a good triplet energy acceptor) increased the intensity of the luminescence (by an order of magnitude) although the increase caused by DBA was not as great as in the case of tetramethyldioxetane for example.[1d,2] However, the major excited product is expected to be triplet excited benzophenone (E_T = 68-9 kcal) which might not efficiently transfer energy to DBA (E_S = 70.2 kcal).[2] This hypothesis is supported by the much larger intensity increase (a factor of 10^{+2} over that observed with DBA) in the presence of europium tris-(thenoyltrifluoroacetonate)-1,10-phenanthroline (ligand $E_T \approx 58$ kcal).[2]

The rates of thermal decomposition of 1 and 2 were determined by monitoring the decay of chemiluminescence intensity in aerated benzene (or xylenes), with or without added fluorescers. These rates showed strict first order dependence over at least 4-5 half-lives. The activation parameters for 1 and 2 (from Arrhenius plots) are listed in Table I. In view of the known

TABLE I

Activation Parameters for the Thermal Decomposition of 1 and 2

Dioxetane[a]	k_1 sec^{-1} at 65°	E_a[b]	log A[b]	E_a[c] from T drop
1	7.6×10^{-3}	21.0 ± 1	$11.6 \pm .6$	21 ± 1[d]
2	7.0×10^{-4}	26.1 ± 1	$13.5 \pm .6$	25.5 ± 1[d,e]

[a] Concentration range 10^{-2}-10^{-4} M in benzene.

[b] Calculated from Arrhenius plots (T-range = 45°, correlation coefficient > .99).

[c] $E_a = E_{chl} - E_{fl}$.[9]

[d] No added fluorescer, E_{fl} taken as zero.

[e] DPA as added fluorescer.

sensitivity of dioxetanes to catalytic complications[7], the activation energy for the luminescent decomposition of 1 and 2 were independently checked by the temperature drop method.[8] The good agreement between the values of E_a obtained by these two methods indicates that dark catalytic processes are unimportant (Table I).

The structural change of coupling the ortho hydrogens of the diphenyl groups of 2 (to produce the rigid fluorenyl group) caused a large change in the activation parameters. Removal of steric interactions of the substituents is expected to lower the activation energy. The additional possibility exists that the difference in the electronic configuration of the two ketones (π,π^* instead of n,π^*) allows a change of mechanism of dioxetane cleavage (from a two-step mechanism to perhaps a concerted cleavage). Such a change of mechanism might explain the observed differences between the properties of most isolated dioxetanes (n,π^* products) and the dioxetanes postulated to be intermediates in many cases of intense chemiluminescence and bioluminescence.[9]

Work is in progress to determine the absolute yields of excited singlet and triplet products produced in the thermolysis of 1 and 2.

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Soc., *97*, 3527 (1975) have reported that the thermolysis of 3,3-(4,4-diphenyl-cyclohexadienyl)-4-methyl-4-β-naphthyl-1,2-dioxetane did not produce π,π^* triplet excited β-acetonaphthone but rather the more energetic n,π^* triplet of 4,4-diphenylcyclohexadienone.

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5. a) **1** undergoes some decomposition during the recording of the nmr spectrum; b) Some ketone (cleavage product) present due to slight decomposition during the concentration of the dioxetane-containing fractions from the chromatographic purification.

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