Alternative Mechanism for Dioxetan Decomposition

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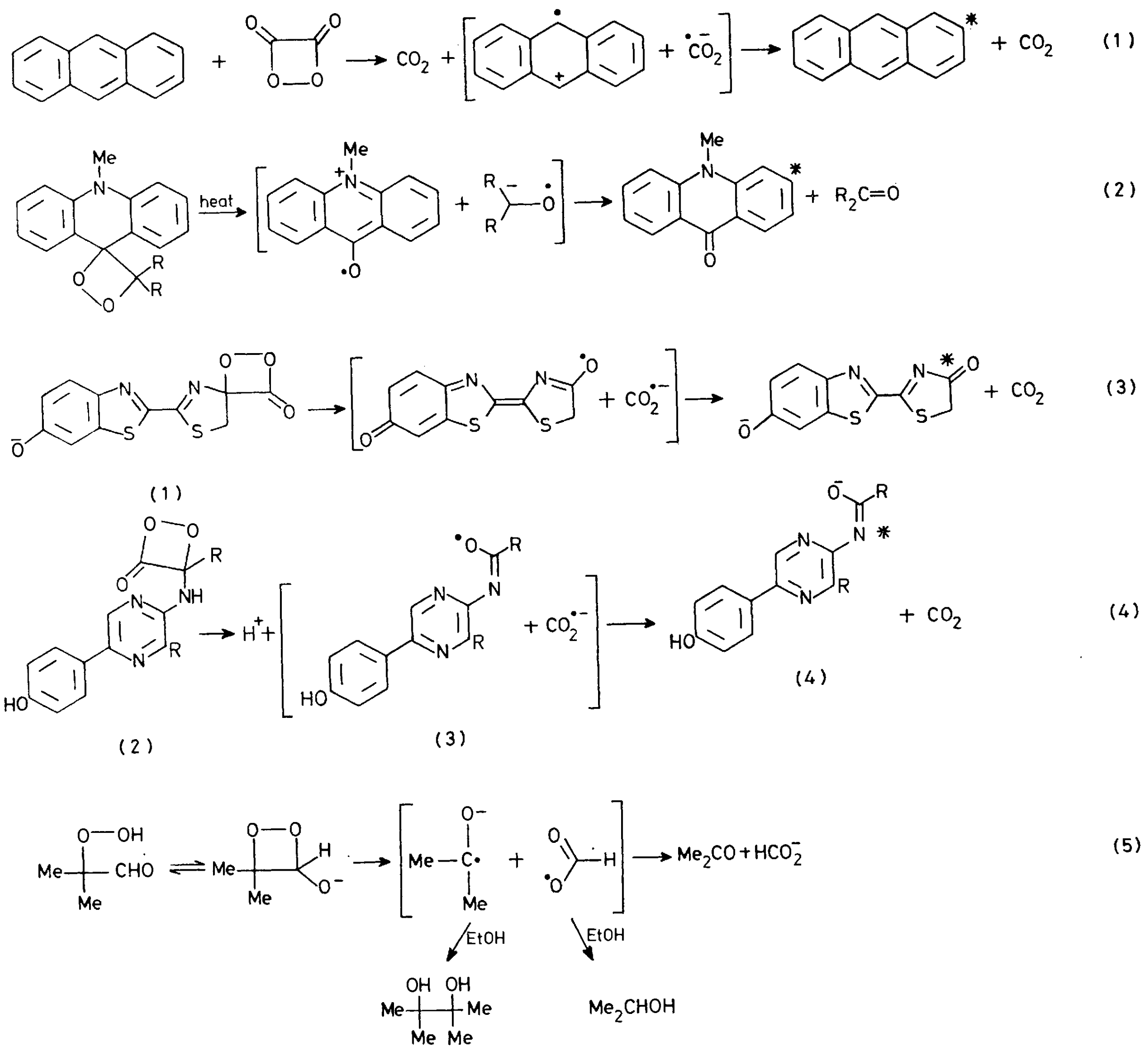
Summary It is suggested that dioxetans substituted by, or reacting with, compounds with strongly electron-donating groups decompose *via* radical ions and that excitation occurs by electron transfer.

The thermal decomposition of isolable dioxetans has been well studied in the last few years.[1] During this time, evidence for less stable dioxetans, distinguishable from the first type by substitution, fast rate of decomposition, and a high yield of excited singlet states has accumulated,[2–4] It has been suggested that the latter type of dioxetan undergoes concerted decomposition,[1,5] whereas the former decomposes by a two-step diradical mechanism.[6]

An alternative to concerted decomposition which is strongly suggested by the structure of the brightest compounds and which deals effectively with some anomalies is shown in the Scheme. A characteristic of active oxalate ester chemiluminescence is the catalytic effect of the hydrocarbon on the presumed intermediate, dioxetandione.[7] Equation (1)[8] explains why the catalysis is greatest with hydrocarbons of low ionisation potential. Experimental evidence for this mechanism has been obtained for the decomposition of other peroxyesters.[9] Stabilisation of the radical is probably required for this mode of decomposition and the heterocyclic radicals of equations (2)[2,3] and (3)[2] have structures related to well known stable radicals (anthranol and galvinoxyl, respectively). Methylation of the phenolic hydroxy group of firefly luciferin [shown as the derived dioxetanone (**1**)] leads to a drastic diminution in quantum yield as would be expected since the quinonoid radical structure is blocked.

The chemiluminescence of the coelenterate luciferin analogue [shown as the derived dioxetanone (**2**)] exhibits a striking anomaly[10] nicely explained by the hypothesis. Chemiluminescence of (**2**) generates the monoanion (**4**) as shown by the emission spectrum. Any attempt to produce the fluorescence of this anion by adding base to the neutral amide fails since the more acidic phenol ionises first. At best the emission of the dianion is produced. The reduction of the radical (**3**) at a pH too low to allow ionisation of the phenol will generate the excited state of the amide anion, which will emit light before proton transfer. Emission of a photon before protonic equilibrium is achieved is a well known phenomenon.[11]

A remarkably high yield of photoproducts recently observed[12] during the peroxidase catalysed oxidation of isobutyraldehyde can also be explained on this basis (equation 5). Pinacol and propan-2-ol may well be the results of trapping of the ketyl by a hydrogen donor before electron transfer (equation 5) rather than a result of a reaction of triplet acetone formed by decomposition of the dioxetan. If this interpretation is correct, it suggests a means of confirming the hypothesis in those cases where



Scheme

electron transfer is not fast as compared with potential trapping reactions.

The accompanying communication commented on the problem of explaining the distribution of excitation energy in some dioxetan decompositions. In electrochemiluminescence and electron-transfer luminescence generally, the redox potentials of the partners are crucial to the efficiency.[13] It may be significant that where there is sufficient energy to produce the excited singlet the quantum yield of visible light is very high.[14] On the other hand energy-deficient systems (those in which electron transfer cannot yield sufficient energy to populate the singlet excited state directly) produce triplet states efficiently and singlets are inefficiently formed by triplet–triplet annihilation.[13] Thus some of the puzzling yields may be associated with the 'hidden' electron-transfer step, rather than with an ostensible non-ionic dioxetan cleavage.

The status of dioxetans such as tetramethyldioxetan is probably not affected by these suggestions. This may be true partly because the necessary stabilisation of the radical ions is insufficient. We noted in the accompanying communication that trimethyldioxetan showed no increased rate of decomposition on solid surfaces in marked contrast to the dioxetan (**2**).[4b] Our suggestion that the light-producing step occurred after the transition state for decomposition is in accord with the possibility that the solid surface promotes ion formation. The expected solvent effect on all three dioxetans in the accompanying communication is present with decomposition occurring progressively faster as solvent polarity is increased, the reaction rate being about 100 times faster in $CHCl_3$ than in toluene. Again no change in quantum yield is observed, and tetramethyldioxetan decomposes at the same rate in polar and non-polar solvents.[1]

We would like to suggest that subsequent theoretical investigations of dioxetan decomposition take increased account of electron correlation and possible charge transfer states in an effort to determine whether there are two distinct mechanisms or whether certain inherent properties of a single mechanism are enhanced by substitution.

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