INGOLD LECTURE

Four-membered Rings and Reaction Mechanisms

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1 Introduction

By the time I entered the chemical profession, C. K. Ingold had written about one-third of his eventual 443 publications, and had established the style and tempo that left such an important mark on the chemistry of our time. His work, entwined with the conviction that intimate details of structure and mechanism were knowable, was important from the start in my own approach to chemical research.

Ingold's first paper on four-membered rings was in 1922. His last publication, the second edition of his great book in 1969, contains a review and perceptive discussion of [2 + 2] cycloaddition to yield four-membered rings. As far as our research group is concerned, the novelty and excitement in the field of four-membered rings today centres about singlet oxygen, which appears to be the only known reagent that reacts vigorously and stereospecifically both in the Diels–Alder manner and in [2 + 2] addition to the double bond.

Ordinary oxygen does not behave like ethylene, but is extremely reactive toward free radicals. This behaviour is associated with its existence in a triplet ground state, with unpaired electrons in two equivalent π orbitals. In the longest-lived singlet state of oxygen ($^1\Delta_g$), 22.5 kcal mol^{-1} higher in energy than the triplet, these two electrons are paired and the properties of this species are those of a very reactive olefin. The higher singlet state, $^1\Sigma_g{}^+$, is so short-lived as to undergo no chemical reactions in competition with quenching. It is now recognized[1] that the photosensitized oxygenations, produced when oxygen is bubbled through an irradiated solution of reactant and a light-absorbing substance such as methylene blue or a porphyrin, are reactions of singlet oxygen ($^1\Delta_g$) produced by energy transfer from the excited dye.

2 Four-membered Rings from Singlet Oxygen

Two of the modes of reaction of singlet oxygen—1,4-addition to dienes or anthracenes [equations (1), (2)], and 'ene' reaction [equation (3)] with alkenes having allylic hydrogen—are normal reactions of the double bond distinguished for their extraordinary speed; a third mode, observed with enol ethers, enamines,

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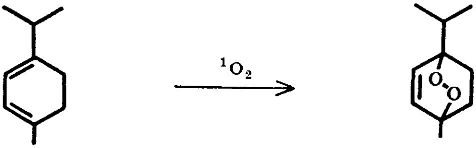
[1] (*a*) C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, 1964, **86**, 3879; (*b*) C. S. Foote, *Accounts Chem. Res.*, 1968, **1**, 104; (*c*) E. J. Corey and W. C. Taylor, *J. Amer. Chem. Soc.*, 1969, **86**, 3881.

and alkenes with hindrance to ene-reaction, is the [2 + 2] addition to yield 1,2-dioxetans [equations (4), (5)].



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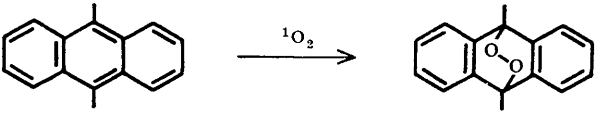

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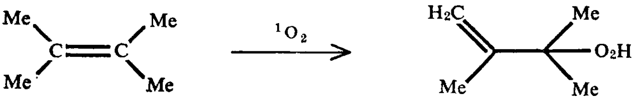

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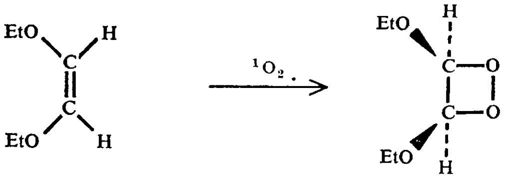

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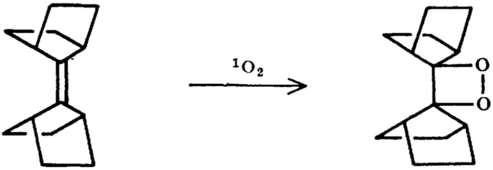


(5)[6]

The first obvious problem of mechanism raised by this behaviour is the exceptional position of singlet oxygen with respect to the orbital symmetry rules.[7] Why does not singlet oxygen, like other dienophiles that react concertedly in [2 + 4] cycloaddition, yield its [2 + 2] products by way of open intermediates which rotate internally and lose configuration?[8]

[2] G. O. Schenck and K. Ziegler, *Naturwiss.*, 1945, **32**, 157.

[3] A. Willemart, *Compt. rend.*, 1937, **205**, 866, 993.

[4] G. O. Schenck and K. Schulte-Elte, *Annalen*, 1958, **618**, 185.

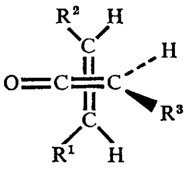
[5] P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, 1970, **92**, 3223, 6055.

[6] (*a*) P. D. Bartlett and M. S. Ho, *J. Amer. Chem. Soc.*, 1974, **96**, 627; (*b*) M. S. Ho, Thesis, Harvard University, 1974.

[7] R. B. Woodward and R. Hoffman, 'The Conservation of Orbital Symmetry', Academic Press, New York, 1970; *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[8] P. D. Bartlett and R. Wheland, *J. Amer. Chem. Soc.*, 1970, **92**, 3822.

Rationalizations for the apparent concertedness, though forbidden, of singlet oxygen's [2 + 2] cycloadditions closely resemble those offered earlier[7] for the behaviour of keten. In both cases dipolar ions are ruled out as intermediates by the absence of polar solvent effects to the degree always accompanying important charge separation at the transition state.[9] One of the remaining possibilities is antarafacial approach of the keten, as in (1), or singlet oxygen, as in (2), to the olefin, leading to favourable correlation of the orbitals in reactants, transition states, and products. Ketens and oxygen have in common a linear character which removes the serious substituent hindrance presumably responsible for the rarity of antarafacial participation of simple olefins. There is, of course, no direct way of verifying antarafacial approach of a double bond that has no configuration, as is true of both these reagents. It is noted, however, that toward ketens a *cis*-alkene is often much more reactive than a *trans*-alkene, which is suggests a geometry of the kind shown for (1). It is also observed that aldo-keten cycloadditions to *cis*-alkenes lead preferentially to the product with all three substituents (R^1, R^2, R^3) *cis*, in specific agreement with the implications of (1).[10]



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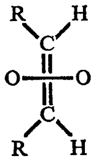
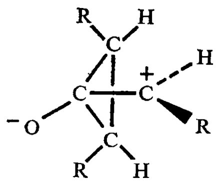


(2)

The crossed geometry of the transition state (1), with only minute modification, is also consistent with the second unique capability of the keten molecule pointed out by Woodward, namely its resemblance to a vinyl cation. Keten in the carbonyl-polarized form readily leads in an allowed [2 + 1] cycloaddition to the stage (3), which by analogy to known cases should retain configuration as it rearranges internally to the adduct (4). The geometrical requirements of (3) and



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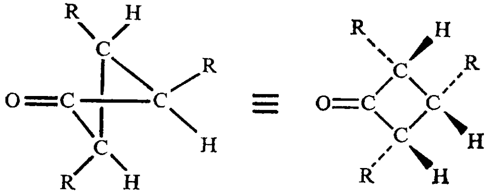

(4)

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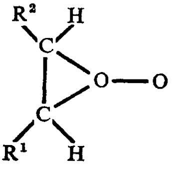
[9] P. D. Bartlett, *Quart. Rev.*, 1970, **24**, 473.

[10] (*a*) W. T. Brady, E. F. Hoff, R. Roe, jun., and F. H. Parry, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 5679; (*b*) T. DoMinh and O. P. Strausz, *J. Amer. Chem. Soc.*, 1970, **92**, 1766.

(1) are so similar that it is suggested that the actual reaction occurs in simultaneous response to the driving forces for both processes.

For singlet oxygen there is also a much-discussed mechanism analogous to (3), although the suggestion in this case arose independently.[11] It has been pointed out that a perepoxide, or peroxiran, (5), could be formed in a symmetry-allowed, stereospecific fashion and might serve equally well as a precursor of the dioxetan (6) or of the allylic hydroperoxide (7), generally produced from alkenes having allylic hydrogen atoms. Again it is possible to believe that with singlet oxygen as with keten, the factors predisposing to the approach (2) would also be compatible with the formation of (5); recent conclusions from MINDO/3 calculations[12] indicate (5) as lying on the favoured path.



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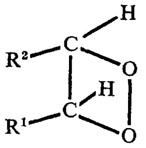

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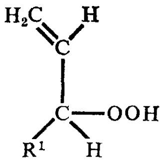


(7) [formed from (6; R^2 = Me)]

Although much of the concern with the perepoxide has centred about its intermediacy in the oxygen ene-reaction, it may be noted that the ene-reaction can proceed over a low-strain, symmetry-allowed direct path, and must do so in the best-known cases with enophiles like maleic anhydride, where no reasonable analogue of the perepoxide is available. On the other hand, it is for the concerted, stereospecific cycloaddition of singlet oxygen to the double bond that the perepoxide mechanism provides a needed rationalization for this reagent's unique position in terms of orbital symmetries.

Only indirect evidence has been generated for the intermediacy of perepoxides in reactions of singlet oxygen, and in some cases modifications have been necessary in the original interpretations.[13] However, in the related case of an episulphoxide,[14] an analogous compound has been prepared at −30 °C and rearranged at 25 °C to the allylic sulphenic acid (8) which is the sulphur counterpart of a singlet oxygen ene product.

Work with the special compounds biadamantylidene (9)[15,16] and binornbornylidene (10),[6] in which Bredt's Rule hindrance prevents the occurrence of an ene

[11] D. B. Sharp, Abstracts 138th National Meeting, American Chemical Society, New York, September 1960, No. 79 P.

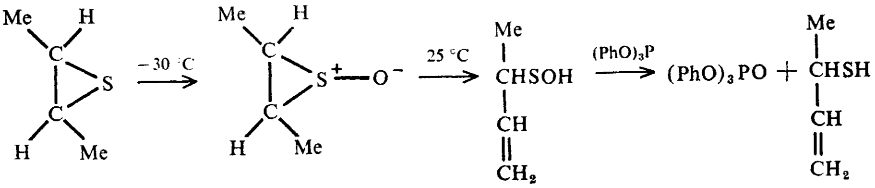
[12] M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, 1975, **97**, 3978.

[13] K. Gollnick, D. Halsch, and G. Schade, *J. Amer. Chem. Soc.*, 1972, **94**, 1747.

[14] J. E. Baldwin, G. Höfle, and S. C. Choi, *J. Amer. Chem. Soc.*, 1971, **93**, 2810.

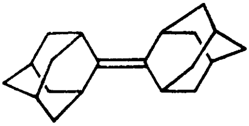
[15] J. Strating, J. H. Wieringa, and H. Wynberg, *Chem. Comm.*, 1969, 907; H. Wynberg, E. Boelema, J. H. Wieringa, and J. Strating, *Tetrahedron Letters*, 1970, 3613.

[16] J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Letters*, 1972, 169.



(8)

reaction, has shown that carbon, as well as nitrogen or oxygen substituents, can activate the double bond toward dioxetan formation with singlet oxygen. The first unusual observation about the products was that the resulting dioxetans were extraordinarily stable, withstanding temperatures more than 150 °C higher



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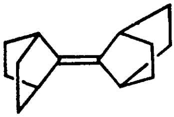

(10)

than tetramethyldioxetan does. It is also characteristic of these olefins, as of other highly hindered ones,[17] that ozonization leads simply to epoxide without the formation of an ozonide and without cleavage at the double bond. This behaviour would be compatible with endwise approach of the ozone molecule to the double bond, the trailing pair of oxygen atoms coming off as singlet oxygen.[6b]

By analogy to a literature report later shown[18] to be in error, in which pinacolone was considered to have the special property of stripping a single oxygen atom from an ozonization intermediate, Schaap and Faler conducted the photo-oxidation of biadamantylidene in pinacolone as solvent.[19] The oxidation product, in addition to the dioxetan, included 19% of the epoxide, assumed to be due to deoxygenation of an intermediate perepoxide by a Baeyer-Villiger reaction with the solvent. In the related case of binorbornylidene, however, all solvents tried yielded mixtures of dioxetan and epoxide, benzene yielding more epoxide than pinacolone, and no solvent (including pinacolone) being detectably oxidized in the process.[6] A series of comparable experiments showed that the same was true of biadamantylidene.[20] Jefford and Boschung[21] later observed that the photo-oxidation of norbornene in several solvents also yielded dioxetan

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[17] J. J. Backer, *Chem. Weekblad.*, 1939, **36**, 214; P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, 1955, **77**, 2806.

[18] K. R. Kopecky, P. A. Lockwood, J. E. Filby, and R. W. Reid, *Canad. J. Chem.*, 1973, **51**, 468.

[19] A. P. Schaap and G. R. Faler, *J. Amer. Chem. Soc.*, 1973, **95**, 3381.

[20] M. J. Shapiro, unpublished work at Texas Christian University.

[21] C. W. Jefford and A. Boschung, *Helv. Chim. Acta*, 1974, **95**, 3381.

and epoxide in proportions which reflected the same solvent order as for other olefins. Table 1 summarizes the results for these substrates.

Table 1 *Epoxide/dioxetan from photo-oxidation*

	Biadamantylidene	*Norbornene*[a]	*Binorbornylidene*[c]
$^1O_2$, CH_2Cl_2	0.09[d]	—	0.66
$^1O_2$, MeCN	—	0.64	0.85
$^1O_2$, pinacolone	0.23[b]	1.1	2.9
	0.19[d]		
$^1O_2$, benzene	0.53[d]	—	4.5
$^1O_2$, MeCOMe	—	1.86	5.1

[a] Ref. 21; [b] ref. 19; [c] ref. 6*b*; [d] ref. 20.

Despite the failure to find evidence of uptake of an oxygen atom by the solvent in any of these cases, reagents exist that are able to perform this function. Tetracyanoethylene was shown by Criegee and Günther[22] to remove the terminal oxygen atom from a carbonyl oxide in the cleavage of an initial ozonide. Dr. Ho has found that in the presence of two equivalents of tcne in acetonitrile the ratio of epoxide to dioxetan in the photo-oxidation of binorbornylidene is increased from 0.76 to 15.9.[6b] Cyanide ion in tenfold excess in methanol had a similar but much smaller effect. Since the nature of the terminal oxygen in a peroxiran is expected to be similar to that in a carbonyl oxide—co-ordinately bonded to another oxygen—this result is compatible with the involvement of a peroxiran in the formation of the epoxide in singlet oxygen reactions.

But what is the oxygen-removing reagent which is common to all the reaction media of Table 1, but is not in any case the solvent? A potential oxygen acceptor always present in singlet oxygen reactions is singlet oxygen itself, which might, if present under conditions of sufficiently long life, react with the perepoxide to yield epoxide and ozone in an approximately thermoneutral reaction. Since binorbornylidene and biadamantylidene are themselves epoxidized by ozone, presumably with singlet oxygen as the other product, the reaction of perepoxide with singlet oxygen can be treated as a chain process leading on each occurrence to two epoxide molecules without diminishing the singlet oxygen concentration. Treatment of this kind leads to the equation below in which k_e/k_d is the ratio of rate constants for the first-order rearrangement of the perepoxide and its second-order conversion into epoxide. This equation predicts that the relative importance of the epoxidation will be proportional to the steady-state

$$\frac{\mathrm{d(epoxide)}}{\mathrm{d(dioxetan)}} = 2\frac{k_e}{k_d}(^1O_2)$$

concentration of singlet oxygen, hence to the light intensity and, in dilute solution, to the sensitizer concentration, and inversely proportional to the olefin

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[22] R. Criegee and P. Günther, *Chem. Ber.*, 1963, **96**, 1564

concentration and the quenching power of the solvent for singlet oxygen. Variation of the conditions in these respects does indeed shift the product ratio in the predicted direction. A few examples are given in Table 2.

Likely as this mechanism appears for photo-epoxidation of binorbornylidene and biadamantylidene under dye sensitization,[23] it is by no means general for photo-epoxidation. Many olefins are epoxidized by photosensitization with benzil or with biacetyl under conditions where singlet oxygen, if present, would lead either to no reaction or to products entirely different from those found.[24]

Table 2 *Effect of conditions on epoxide/dioxetan ratio in photo-oxidation sensitized by tetraphenylporphin*

Olefin	*Conc.*	*Sensitizer Conc.* /10^{-5} mol l^{-1}	*Solvent*	*Epoxide/ dioxetan*	*Ref.*
(9)	0.0037	1.6	benzene	4.5	6*b*
(9)	0.00019	1.6	benzene	14, 19	6*b*
(8)	0.0011	1.0	benzene	0.53	20
(8)	0.0011	1.0	CH_2Cl_2	0.09	20

3 Opening of the Dioxetan Ring

1,2-Dioxetans cleave thermally to two carbonyl-containing fragments. Such a cleavage, if concerted and suprafacial, is required by the orbital symmetry rules to produce one of these fragments in an excited state. In good agreement with this expectancy, the decomposition of 1,2-dioxetans leads generally to chemiluminescence, although the emission directly observable from the product ketones represents a very low apparent quantum yield. Careful studies have shown that the losses are due to quenching of the excited molecules formed, and that the excitation energy can be accounted for by recovery with suitable calibrated fluorescers.[25] Thus in the thermal decomposition of dioxetans, unlike their thermal formation, there is no reason why a direct, concerted mechanism cannot be assumed.

There is a problem, however, with respect to the conservation of spin multiplicity. Rapid intersystem crossings between singlet and triplet states are well known, but it is general experience that the time of passage over a transition state does not allow an intersystem crossing to be part of a concerted reaction mechanism. The best known exceptions involve atoms heavier than those of the first row of the periodic table, such as the reaction of ^3P sulphur atoms with the carbon–carbon double bond,[26] or the excitation of 9, 10-dibromoanthracene to a singlet state by energy transfer from an excited triplet ketone.[25] It was therefore unexpected that the thermal decomposition of tetramethyl-1,2-dioxetan leads

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[23] Theoretical calculations (M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. J. Turchi, *J. Amer. Chem. Soc.*, 1975, **97**, 4439) support the perepoxide as an intermediate both in dioxetan formation and, through reaction with a second singlet oxygen molecule, in epoxidation.

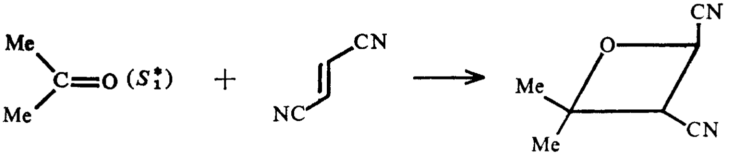
[24] N. Shimizu and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1976, **98**, in press.

[25] (*a*) V. A. Belyakov and R. F. Vasil'ev, *Photochem. and Photobiol.*, 1970, **11**, 179; (*b*) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, 1971, **93**, 4126.

[26] H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, 1966, **4**, 143.

directly to excited acetone in which the triplet molecules outnumber the singlets by about 250 to 1.

Evidence that this is so comes from several directions. First, the singlet excited ketone can be assayed by the intensity of fluorescence it induces in 9,10-diphenylanthracene, which can yield induced fluorescence only from singlet states. Fluorescence in 9,10-dibromoanthracene, on the other hand, is induced by energy transfer from either singlet or triplet excited ketone.[25] In the decomposition of tetramethyl-1,2-dioxetan the relative intensities of luminescence seen with these two fluorescers indicate that the excited acetone is mainly triplet. Second, fumaronitrile reacts with singlet excited acetone by cycloaddition, whereas triplet acetone only induces *trans–cis*-isomerization about the double bond. 'Chemical titration' of thermally decomposing tetramethyldioxetan with fumaronitrile [equations (6) and (7)] yields isomerization, indicating mainly triplet acetone as the excited species directly formed.[27] These two methods agree in indicating that triplet acetone is produced, not as a later but as a primary product in the thermal decomposition of tetramethyldioxetan.



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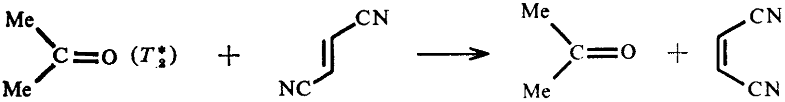

(7)

In addition, two other methods which could not have ruled out the initial formation of singlet acetone giving rapid intersystem crossing, nevertheless confirm the presence of triplet. Thermally decomposing tetramethyldioxetan produces, from benzoyl peroxide in carbon tetrachloride, chlorobenzene showing the kind of chemically induced dynamic nuclear polarization (CIDNP) signal characteristic of triplet radical pairs.[28] Triplet acetone is also indicated by the hydrogen abstraction reactions performed on 1,4-cyclohexadiene by the excited product from the dioxetan decomposition, a type of chemistry characteristic of $n\pi^*$ excited triplet states.[29]

In the case of dioxetan decomposition it is not necessary to assume that the thermal cleavage is a completely concerted process, since there is no observation corresponding to retention or loss of configuration to afford evidence on this point. The prevalent formation of triplet acetone would be less exceptional if, as

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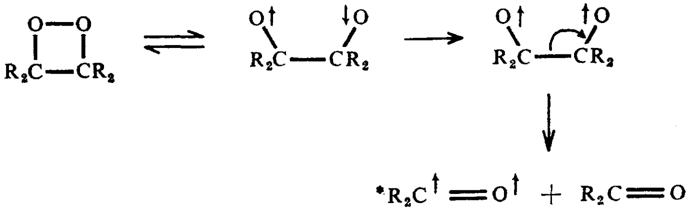
[27] N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, 1972, **94**, 2886.

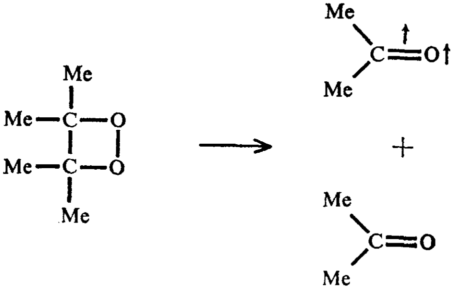
[28] P. D. Bartlett and N. Shimizu, *J. Amer. Chem. Soc.*, 1975, **97**, 6253.

[29] T. Wilson, M. E. Landis, A. L. Baumstark, and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1973, **95**, 4765.

proposed by O'Neal and Richardson[30] (Scheme 1) the O—O bond breaks reversibly and the change of multiplicity occurs in an intermediate biradical. By this view the triplet is the preferred product because it best accommodates the energy change in the cleavage, the singlet formation being endothermic and the formation of two ground-state molecules liberating an amount of energy not so efficiently disposable. Turro, on the other hand, proposes that the common feature of concerted processes with intersystem crossing is the presence of a torque tending to rotate the spin vector and arising from a change in orbital angular momentum inherent in the reaction. A picture of dioxetan ring-cleavage is proposed[31] (Scheme 2) which is expected to provide such a torque[32] and to make singlet–triplet conversion a normal accompaniment of this reaction.



Scheme 1



Scheme 2

Neither of these mechanisms of dioxetan cleavage leaves much room for catalytic effects by ordinary polar solvents. When, therefore, it was observed[33] that in methanol the decomposition of tetramethyldioxetan was as much as 100 times as fast as in benzene, competing mechanisms were suspected. Richardson[34] noted that the chelating agent ethylenediaminetetra-acetic acid (edta) in many cases greatly reduced the rate of dioxetan decomposition; by following this lead

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[30] H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, 1970, **92**, 6553.

[31] N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, 1973, **95**, 264.

[32] L. Salem and C. Rowland, *Angew. Chem. Internat. Edn.*, 1972, **11**, 92.

[33] N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, 1973, **95**, 264; *Pure Appl. Chem.*, 1973, **33**, 363.

[34] W H. Richardson, private communication, 1973.

it was possible to show[29] that (i) the uncatalysed rate is much the same in benzene, ethanol, and methanol; (ii) only this uncatalysed reaction gives rise to chemiluminescence and to reactions of excited ketone triplets; and that (iii) the catalysis can be simulated by addition of a number of metal salts, whether in benzene or in an alcohol.

Table 3 *Catalysis of tetramethyldioxetan decomposition in methanol at* 57 °C[36]

Additive		10^5 k_1 s^{-1}		
	mol l^{-1} ($\times$ 10^5)	*without*	*with*	k_2(apparent) l mol^{-1} s^{-1}
$CuCl_2,2H_2O$	0.83	52—88	1150	1280
	1.64	12—17	2200	1290
CuCl	0.83	52—88	150	75 ?
	4.77	52—88	1050	200 ?
$FeCl_3$	3.6	52—88	140	14
$SnCl_2,2H_2O$	1.07	52—88	85	none
	5.1	12—17	9	none
Dipped aluminium foil		40	250	+
Dipped copper wire		8.3	200	+

It appeared, moreover, that small traces of catalysts in common solvents affected the rate of tetramethyldioxetan decomposition to an important extent. In subsequent experiments all hydroxylic solvents were treated with 5×10^{-4} mol l^{-1} edta to obtain the uncatalysed rate of tetramethyldioxetan ring opening. Even so, the uncatalysed rates varied with the history of the sample. In the experiments reported in Table 3 the uncatalysed rate was determined each time before adding the catalyst, and the catalytic rate constant was determined by difference. Cupric, cuprous, and ferric chlorides appear in descending order of catalytic power, with stannous chloride appearing to react little, if at all, faster than the uncatalysed ring opening. The sensitivity of the dioxetan to trace contaminants is dramatized by the fact that dipping a piece of clean aluminium foil, or stirring the sample with copper wire, increased the rate of decomposition by factors of 5—24. All catalysts, added intentionally or unintentionally, were rendered ineffective by a sufficient amount of edta.

The cupric salts of acetic acid, tropolone, and citric acid in methanol form a series in which the catalysis decreases, approaching the inactivity of the fully chelated edta complex (Table 4).

In view of the importance of orbital-symmetry considerations in the previous thinking about the formation and cleavage of dioxetans, it is natural to ask whether the catalysis of dioxetan ring opening is a matter of insertion of a metal ion between the oxygen atoms to produce a metallocycle whose fragmentation is symmetry-allowed. Indeed, complexes of rhodium and iridium, known for their ability to undergo oxidative additions with hydrogen chloride and with hydrogen, rank high among the catalysts for ring opening of tetramethyl-

Table 4 *Effect of added anions on catalysis of dioxetan destruction at* 57 °C *in* MeOH[a] (*ref.* 37)

Anion	$\frac{[Anion]}{[Cu^{2+}]^b}$	$10^4 (k_1^{cat} - k_1^{uncat})\ s^{-1}$
—	—	860
Acetate	2.1	260
Troponoxy	2.0	14
Citrate	2.0	4
Edta	1.2	0

[a]Treated with dry Chelex 100 and vacuum distilled at 0 °C; [b]$[CuCl_2] = 7 \times 10^{-5}\ mol\ l^{-1}$.

dioxetan.[35] Table 5 provides some examples of the effect of changes of metal, and of one component at a time of the complex, upon the rate of this catalysed reaction. These changes are not inconsistent with an oxidative addition mechanism for the rhodium and iridium complexes.

Table 5 *Cleavage of tetramethyldioxetan in benzene*[a]

Complex	*Relative rate*
$Rh(Ph_3P)_3Cl$	1.0
$Rh(CO)(Ph_3P)_2Cl$	1.5
$Rh(CO)(Ph_3P)_2I$	2.9
$Rh(CO)(Ph_3As)_2Cl$	6.2
$[Rh(CO)_2Cl]_2$	31
$Ir(CO)(Ph_3P)_2Cl$	62
$[Rh(nbd)Cl]_2$	185
Ir/Rh	41
I/Cl	2
Ph_3As/Ph_3P	4.1
CO/Ph_3P	1.5

[a]Reference 35.

Nevertheless, oxidative addition—implying a ready change of valence on the part of the metal ion from x to $x+2$—cannot be a general mechanism by which metal salts catalyse the opening of tetramethyldioxetan. The series of effective metal salts for this reaction includes some which are oxidized with difficulty and some that are not oxidized at all. Cupric ion, with no available higher oxidation state, is a much better catalyst than cuprous ion. The property of this series of metal ions that correlates well with their catalytic power is, instead, their Lewis acidity. The Figure shows the catalytic rate constants for dioxetan ring opening plotted, on a log scale, against their association equilibrium constants with malonate ion, one of the few series of such associations for which measurements are available.[36,37] It would appear that this ring opening

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[35] J. McKennis, unpublished work at T.C.U.

[36] J. E. Prue, *J. Chem. Soc.*, 1952, 2337; M. L. Bender, 'Mechanisms of Homogeneous Catalysis from Protons to Proteins', John Wiley, New York, 1971, p. 218.

[37] P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *J. Amer. Chem. Soc.*, 1974, **96**, 5557.

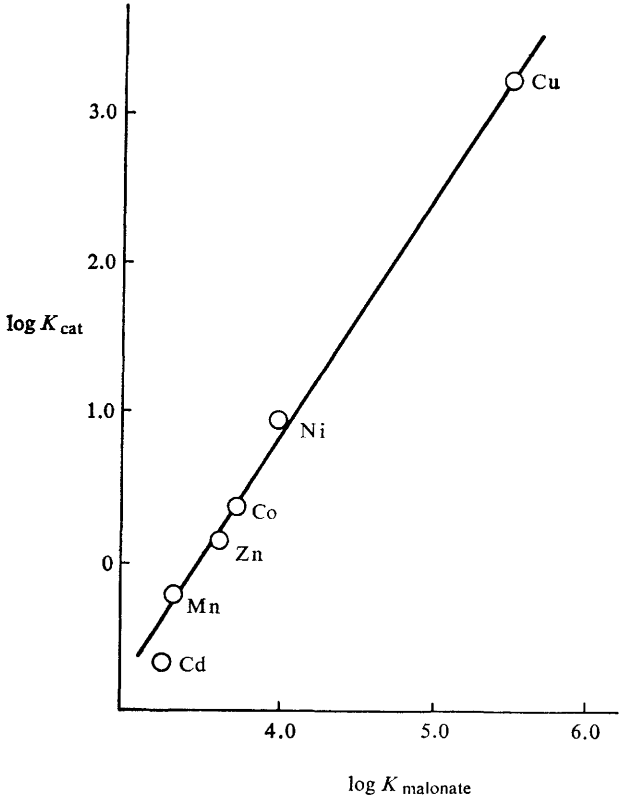
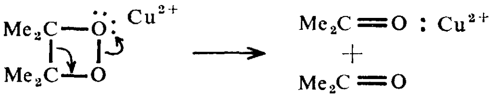


Figure *Relation between association equilibrium constants of bivalent metal ions with malonate ion*[36] *and their catalytic constants for cleavage of tetramethyldioxetan to acetone*[37]

must be initiated by an unsymmetrical electrophilic attack of the catalyst ion upon one of the oxygens of the O—O bond. In the dioxetan complexed with the Lewis acid, (11), fission of the ring by a polar process takes precedence over apparent homolytic cleavage in the uncatalysed reaction.



(11)

If this is so, tetramethyldioxetan should be subject to attack by simple, non-reducing Lewis acids like boron fluoride. Table 6 shows that indeed boron fluoride etherate cleaves the dioxetan in four halogenated or aromatic solvents.

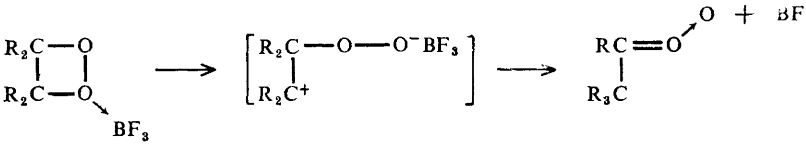
Competing with the cleavage, however, is a molecular rearrangement of which the isolated product is pinacolone. In $CFCl_3$ as solvent, a four-fold excess of boron fluoride etherate causes the entire product to be pinacolone, with no cleavage detected.

Table 6 *Tetramethyldioxetan and* BF_3 *etherate*[39]

$\frac{[BF_3]}{[TMD]}$	*Solvent*	*% Pinacolone*[a]	*% Acetone*
0.8	$CFCl_3$	41	59
4	$CFCl_3$	100	—
1	CCl_4	90	10
1	PhH	36	64
1	PhBr	40	52

[a] No t-butyl acetate formed.

The formation of pinacolone from tetramethyldioxetan represents a net reduction, with loss of one oxygen atom, and is reminiscent of the problem of the missing oxygen in photo-epoxidation with molecular oxygen. A careful check revealed no oxidized solvent molecules, and no tertiary butyl acetate formed by Baeyer–Villiger attack of an oxidizing intermediate upon pinacolone. The most likely alternative to cleavage in the co-ordinated intermediate (12) might be a 'perpinacol rearrangement' yielding the carbonyl oxide of pinacolone, (13). Such intermediates, in the absence of methanol, which converts them into methoxyhydroperoxides, are known to dimerize to cyclic bis-peroxides,[38] which are thermally unstable.

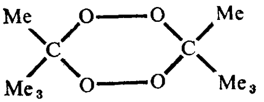


(12)

(13)

In an experiment carried out at −78 °C, gaseous boron fluoride was bubbled into a methylene chloride solution of tetramethyldioxetan for 10 s and methanol was added after the mixture had been allowed to stand for 30 minutes. In addition to 28 % recovered dioxetan the main product was still pinacolone (47 %), along with 5 % of acetone. There was found, however, 22 % of (14), the dimeric peroxide of pinacolone, and the mother liquor showed a peroxide titre corresponding to a further 60—80 % of the pinacolone. This result is consistent

[38] R. Criegee, A. Kerckow, and H. Zinke, *Chem. Ber.*, 1955, **88**, 122.



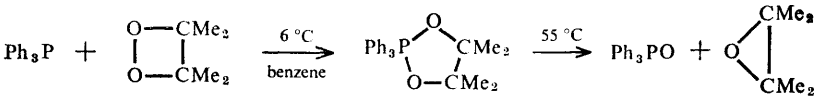
(14)

with rapid hydrolysis of the dimeric pinacolone peroxide by traces of water present in the solvents, powerfully catalysed by the boron fluoride.

Stannic chloride in deuteriomethanol or deuterioacetonitrile, followed by n.m.r., brought about complete cleavage of tetramethyldioxetan to acetone.[39]

Thus Lewis acids that are not insertion reagents produce dioxetan cleavage. What happens with insertion reagents that are not Lewis acids?

Triphenylphosphine in benzene at 6 °C reacts with tetramethyldioxetan to yield the insertion product (15), which at 55 °C undergoes cleavage to triphenylphosphine oxide and tetramethyloxiran, (16).[40]



(15) (16)

The relative reactivities shown in the insertion of several phosphorus compounds into tetramethyldioxetan can be correlated with the preference of phosphoranes to be formed with the most electron-attracting groups situated at the apical positions of the trigonal bipyramid.[41]

In the case of the stannous ion we have a reagent that is both a Lewis acid and capable of a two-unit valence increase, hence a candidate for oxidative addition. As shown in Table 7 stannous chloride in various solvents shows competitive cleavage of dioxetan and reduction to pinacol. The pinacol formation involves hydrolysis of stannic pinacolate, but is totally prevented only in solutions of the complex material diphenyltin in dry benzene. Stannic pinacolate, once formed, neither fragments to acetone and stannous tin nor rearranges to pinacolone. Evidently therefore the cleavage seen is the result of the stannous compound acting in the Lewis acid mode, like boron fluoride, in competition with oxidative addition.

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[39] A. L. Baumstark, Thesis, Harvard University, 1974.

[40] P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *J. Amer. Chem. Soc.*, 1973, **95**, 6486.

[41] P. D. Bartlett, A. L. Baumstark, M. E. Landis, and C. L. Lerman, *J. Amer. Chem. Soc.*, 1974, **96**, 5267.

Table 7 *Tetramethyldioxetan and stannous catalysts: fragmentation* vs. *reduction, room temperature*[39]

Reagent	*Solvent*	*% pinacol*	*% acetone*
$SnCl_2$	CD_3OD 'wet'	37	63
$SnCl_2$	$CD_3OD:D_2O$ (1:8, v:v)	68	32
$SnCl_2$	CD_3CN 'dry'	21	79
$SnCl_2$	$CD_3CN:D_2O$ (1:8, v:v)	68	32
$SnCl_2$	$[^2H_6]$DMSO 'wet'	31	69
'Ph_2Sn'	PhH, dry	0	100
$Sn(OAc)_2$	CD_3OD 'wet'	33	67

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