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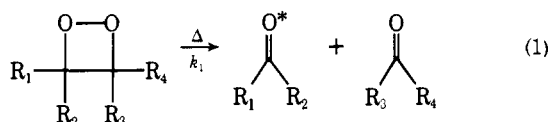(32) J. I. Brauman, J. Schwartz, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **90**, 5328 (1968).

Thermolysis of Tetramethoxy- and p-Dioxenedioxetanes. Kinetic Parameters, Chemiluminescence, and Yields of Excited Products

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Abstract: The kinetic parameters of the first-order thermal decompositions of tetramethoxy- (**1**) and p-dioxenedioxetanes (**2**) were determined (in benzene or xylene solutions) and compared, using the same experimental methods, with those of tetramethyl- (**3**) and cis-diethoxydioxetanes (**4**). **1** is much more stable than **3**. The activation energies of these two thermolyses are nearly the same; hence the greater stability of **1** is largely due to a smaller A factor ($E_a = 28.6$ kcal, $\log A = 12.9$ for **1**; $E_a = 27.6$ kcal, $\log A = 14.1$ for **3**). **2** is slightly more stable than **4** although their activation energies are the same, $E_a \simeq 24.5$ kcal ($\log A = 13.0$ for **2**; 13.6 for **4**). The last result indicates that the 3–4 kcal strain of the ester ring of **2** is released *after* the transition state is attained, suggesting that the decomposition proceeds via a diradical pathway. Quantum yields of excited singlet and triplet products ($^1\phi$ and $^3\phi$) were determined on the basis of chemiluminescence intensities with 9,10-diphenyl- or 9,10-dibromoanthracene. The yields from **2** ($^1\phi = 0.0001$ and $^3\phi = 0.3$) are very similar to those obtained with **3** and **4**. With **1**, in contrast, $^1\phi = 0.01$ and $^3\phi = 0.1$, showing a lower total yield of excited products, but a higher production of singlets. Quenching experiments with dienes, from which excited carbonyl lifetimes are derived, support these results.

The thermal cleavage (eq 1) of all isolated dioxetanes has been shown to generate excited carbonyl products,[1] generally favoring triplet over singlet states.

$$R_1 \overset{O-O}{\underset{R_2 \quad R_3}{\rule{0pt}{0pt}}} R_4 \xrightarrow[k_1]{\Delta} \overset{O^*}{\underset{R_1 \quad R_2}{\rule{0pt}{0pt}}} + \overset{O}{\underset{R_3 \quad R_4}{\rule{0pt}{0pt}}} \quad (1)$$

The nature of the substituents on the ring has relatively little effect on the dioxetane's properties. Whether the dioxetane is substituted by one or by several methyl or phenyl groups, for example, its stability remains much the same ($E_a \simeq 25 \pm 2$ kcal, $\log A = 13 \pm 1$),[2] although bulky rigid groups (as in adamantylideneadamantanedioxetane, $E_a \simeq 37$ kcal) render the dioxetane considerably more stable.[3]

On the other hand, the hypothetical dioxetanes, assumed to be the precursors of excited products in many classic cases of intense chemiluminescence,[4] must be considerably less stable and capable of generating more singlet excited products. Thus it is clear that appropriate substitution should not only decrease the stability of the dioxetane, but might also upset the balance of excited products in favor of singlets rather than triplets.

The effect of well-chosen substituents should also throw light on the much debated mechanism of reaction 1, concerted vs. diradical, and on excitation pathways. Two previously synthesized dioxetanes, tetramethoxydioxetane[5] (**1**) and p-dioxenedioxetane[1g,6] (**2**), were investigated and their properties compared with those of tetramethyldioxetane (**3**)
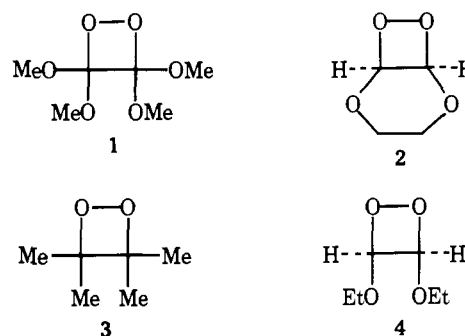
and cis-diethoxydioxetane (**4**); the same experimental methods were used in all cases. **2** is of interest because, while similar to **4**, its second ring has an appreciable strain. In **1** the effect of alkoxy substituents can be compared with that of the methyl groups of **3**. The results are interpreted as favoring a diradical mechanism; they emphasize the importance of entropy effects on the stability of the dioxetanes.

Experimental Section

Tetramethoxydioxetane was prepared by low-temperature photooxygenation of tetramethoxyethylene essentially as described by Mazur.[7] The dioxetane was recrystalized at $-78°$ from pentane to yield a light-yellow solid. The pure dioxetane, a liquid at room temperature, was rapidly dissolved in either benzene-d_6 or acetone-d_6 for storage at $-20°$. The dioxetane concentration was de-

termined by iodometric titration. Solutions (1 M) of tetramethoxy-dioxetane in benzene-d_6 could be stored at $-20°$ (in the dark) for months with no decomposition. The NMR spectrum (benzene-d_6) of the dioxetane was in agreement with the reported spectrum.[7] Decomposition of the dioxetane in acetone-d_6 in a NMR tube produced dimethyl carbonate as the only observable product.

p-Dioxenedioxetane was prepared by low-temperature photooxygenation of p-dioxene in Freon 11 according to the procedure described by Schaap for the preparation of 4.[8] The photooxygenation of p-dioxene is slower than that of cis-diethoxyethylene.[9] Therefore, the reaction was not carried out to completion but terminated after ~2 h in order to avoid complications arising from photolysis and catalyzed decomposition. The dioxetane crystallized from Freon 11 during the course of the photooxygenation at $-78°$. The light-yellow solid was dissolved in acetone-d_6 or benzene-d_6 for storage at $-20°$. (Caution: a small sample of solid p-dioxenedioxetane exploded upon warming to room temperature.) The concentration of dioxetane was determined by iodometric titration. The NMR spectra (acetone-d_6) of the dioxetane and its only thermal decomposition product (ethylene diformate) were in agreement with the reported spectra.[8]

Tetramethyldioxetane was prepared by the bromohydroperoxide method of Kopecky and Mumford and crystallized from pentane at $-78°$.[1a,10] The resulting pale-yellow needles were stored in approximately 30-mg quantities at $-20°$. Determinations of concentrations of solutions of tetramethyldioxetane by iodometric titration were in good agreement with the calculated values (based on weight). The NMR spectra in benzene of the dioxetane and its sole thermal decomposition product (acetone) were in agreement with reported spectra.[11]

cis-Diethoxydioxetane was prepared as described by Bartlett and Schaap.[8] Samples in benzene could be stored at $-20°$ for several months with little decomposition.

Solvents (Fisher) were of reagent grade except acetonitrile (Eastman spectrograde). cis-1,3-Pentadiene (Columbia Organic) was used without further purification; VPC analysis showed no impurities. 2,5-Dimethyl-2,4-hexadiene and a cis-trans mixture of 1,3-octadiene (both from Chemical Samples) were shaken with saturated aqueous Na_2EDTA to remove apparent catalytic (metal ion) impurities. 9,10-Dibromoanthracene (DBA) (Aldrich) was recrystallized from xylenes. 9,10-Diphenylanthracene (DPA) (Aldrich) was used without further purification. The concentration of DPA or DBA solutions was occasionally checked photometrically; there was no indication of decomposition during the course of experiments in the presence of dioxetanes. Iodometric titrations were performed as described by Wilson and Schaap.[13]

NMR spectra were obtained with a Varian T-60 spectrometer, absorption spectra with a Cary 15 spectrophotometer, and fluorescence spectra with an Aminco Bowman spectrofluorimeter. VPC analyses were performed on a Varian Aerograph Model 920.

The chemiluminescence monitoring system, calibrated against the Hastings–Weber light standard,[12] has been described previously.[13] The temperature-drop experiments for the determination of activation energies, as discussed previously,[13,14] were performed in a jacketed cell. Disposable Pyrex tubes (5 mm i.d. $\times$ 10 cm) were used for rate determinations and quenching studies to avoid contamination problems (solution volume generally ~0.6 ml). The "random" error on the first-order rate constants determined by the decay of chemiluminescence is estimated at $\pm15\%$ in each measurement. The solution temperature was determined by means of a glass-encased copper–constantan thermocouple ($\pm0.2°$).

The diene quenching experiments were performed as follows: a small volume (usually 10 μl) of concentrated diene solution was added to known concentrations of fluorescer and dioxetane in the appropriate solvent (usually ~0.6 ml). The intensities were recorded before and after diene quenching, taking into account a small correction for dilution. The intensity vs. fluorescer concentration experiments were customarily done as follows: a series of disposable tubes were filled with 0.300 ml of a dioxetane stock solution, and to each tube was added a known volume of concentrated fluorescer solution and the appropriate volume of solvent such that all tubes had a final volume of 0.600 ml. Care was taken to perform these experiments under conditions where the rate of thermolysis of the dioxetanes was negligible during the time scale of the experiments. Generally, the temperature of the solutions was monitored before and after each set of experiments.
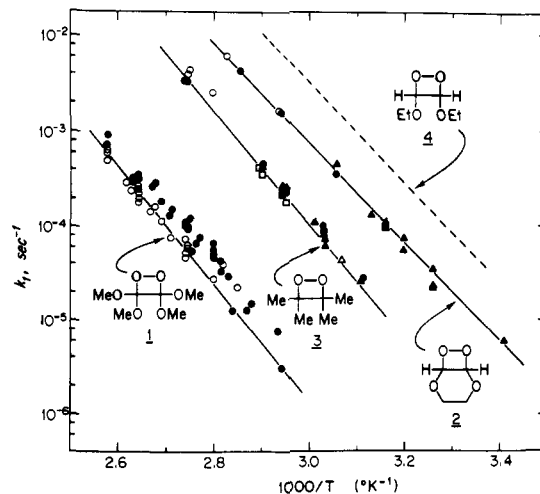

Figure 1. Arrhenius plot of the first-order rate constants (k_1) of dioxetane thermolyses, monitored by the decay of the chemiluminescence in the presence of DPA (empty symbols) or DBA (filled symbols) or with no added fluorescer (crossed symbols). The solvents were either benzene (triangles) xylenes (circles), or acetonitrile (squares). For each dioxetane, the slope of solid line corresponds to the value of the activation energy determined by the temperature-drop method (see text). The dashed line for 4 is taken from the literature (see ref 13 and 14). (Range of dioxetane concentrations, 3×10^{-4}-4×10^{-2} M, and of fluorescer concentrations, 2×10^{-4}-4×10^{-2} M).

Results

Kinetics. The rates of dioxetane decomposition were monitored by the decay of chemiluminescence, either with or without an added fluorescer, 9,10-diphenylanthracene (DPA) or 9,10-dibromoanthracene (DBA), in aerated solutions. In all cases, the decomposition was first order, and the products were only those expected from ring cleavage.

Figure 1 shows the Arrhenius plots for the thermal decomposition of 1–4. The dashed line for 4 is taken from published data.[13,14] The method employed to determine the best line for 1–3 deserves comment. The lines in Figure 1 are drawn such that their *slopes* correspond to the values of E_a obtained independently by the temperature-drop method in the presence of DPA. In positioning the lines, the low-rate values were systematically favored over the high rates because of the known sensitivity of dioxetanes 1–4 to impurities such as traces of transition metal ions,[15] amines,[14,16] and electron-rich olefins,[14,16] as well as to autocatalysis induced by excited products or fluorescers.[13,17] These alternate "dark" pathways of decomposition, competitive with the uncatalyzed unimolecular thermal decomposition, can result in abnormally high rates; these effects become relatively more important in the low-temperature range. In contrast, the results obtained by the temperature-drop method are not affected by catalytic complications and therefore reflect the true activation energy of the chemiluminescent cleavage.[2]

The "forced" lines drawn with the aid of the temperature-drop method for 2 and 3 are in good agreement with rate data (Figure 1). With these dioxetanes, the rates were found to be independent of fluorescer (DPA and DBA) and dioxetane concentrations. In the case of 1, the scatter of the data is larger and seems due, at least in part, to a dependence of the rates on dioxetane concentration. In spite of the presence of oxygen, induced decomposition appears to play a significant role.[2] Two lines of evidence support this conclusion: (a) at concentrations of 1 above 10^{-2} M, the rates are as much as two times faster than at concentrations below 5×10^{-3} M; (b) addition of triplet quenchers such as 1,3-pentadiene or 1,3-octadiene decreases the "high" rates

Table I. Kinetic Parameters for Thermolysis of 1–4

Dioxetane	Decomposition product	Log A^a	$E_a,^{a,b}$ kcal/mol
1	Methyl carbonate	12.9	28.6 ± 1
2	Ethylene diformate	13.0	24.6 ± 1
3	Acetone	14.1	27.6^c ± 1
4	Ethyl formate	13.6	24.4^d ± 1

^{a} Calculated from rates corresponding to lines shown in Figure 1 (see text). ^{b} From temperature-drop experiments with DPA as fluorescer (see text). ^{c} This value is in satisfactory agreement with the literature (see ref 2). ^{d} Data from ref 13.
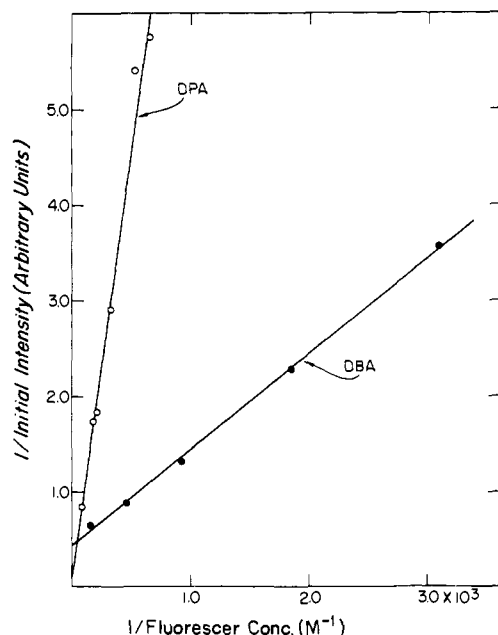

Figure 2. Effect of fluorescer concentration on the initial intensity of chemiluminescence from tetramethoxydioxetane (1): O, DPA; ●, DBA. Dioxetane concentration, 5 × 10⁻³ M in xylene at 64°.
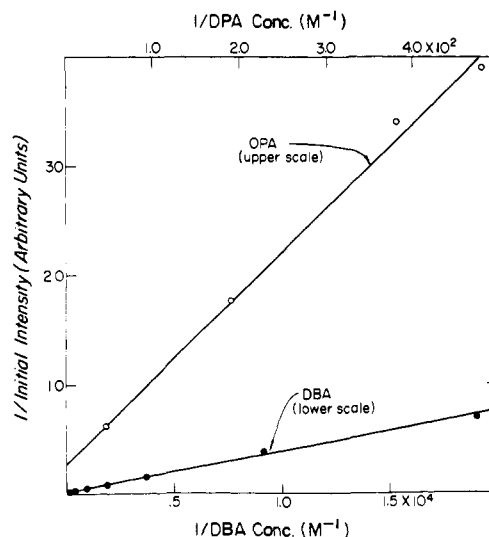

Figure 3. Effect of fluorescer concentration on the initial intensity of chemiluminescence from p-dioxenedioxetane (2): O, DPA, upper scale; ●, DBA, lower scale.

obtained at high concentration of 1. In addition, it seems that the rates obtained with DPA are slower than with DBA or with no added fluorescer,[19] although this difference becomes less marked at low-dioxetane concentration (<5 × 10⁻³ M). It is not yet clear whether induced decomposition is the only cause of this difference.

Table I lists the kinetic parameters for the thermal decomposition of 1–4. The activation energies of the most and the least stable of these four dioxetanes differ by ~5 kcal.

The data for 1 were not anticipated. The greater stability of 1 compared with that of 3 is surprising;[20] at 80° the lifetime of 1 is ~14 h while that of 3 is ~14 min. The activation energies of 2 and 4 were found to be the same, as anticipated from the preliminary findings of Schaap.[1g]

Yields and Multiplicity of Excited Products. The yields and multiplicities of excited products from 1–3 were determined from the intensities of chemiluminescence at constant dioxetane concentration in the presence of varying concentrations of DPA or DBA, which monitor singlet or triplet products, respectively.[1c,2,13] Double reciprocal plots of chemiluminescence intensity, I_{chl}, vs. fluorescer concentration are linear, as shown in Figures 2 and 3 for 1 and 2, respectively. The values of y-axis intercept (i.e., $1/I_{chl}$ at infinite concentration of fluorescer) and those of intercept/ slopes are presented in Table II. Also listed in this table are the corresponding chemiluminescence yields, ϕ^{DPA}_{obsd} and ϕ^{DBA}_{obsd}, which were calculated from the data by the expression

$$\phi_{obsd} = [(y \text{ intercept})k_1[D]]^{-1}$$

k_1 is the rate constant for dioxetane thermolysis at the temperature of the experiment (taken from Figure 1), and [D] is the dioxetane concentration. These observed yields are, in turn, converted into primary excitation yields, $^1\phi$ and $^3\phi$, which represent the yields of production of excited singlet or triplet carbonyl fragments per dioxetane molecule decomposed. It is assumed that energy transfer from the excited carbonyls to DPA or DBA is exothermic in all cases (see Discussion).

In the singlet case, $^1\phi = \phi^{DPA}_{obsd}$, since the fluorescence yield of DPA is unity and temperature independent,[21] and since all singlet carbonyls should be intercepted by DPA (at infinite concentration) via a spin-allowed energy-transfer step. In the case of DBA,

$$^3\phi = \phi^{DBA}_{obsd}/\phi_F^{DBA}\phi_{TS}$$

where ϕ_F^{DBA} is the fluorescence yield of DBA at the temperature of the experiment,[22] and $\phi_{TS} = k_{TS}/(k_{TT} + k_{TS})$ is the efficiency of triplet-singlet energy transfer from the carbonyl product to DBA. (k_{TT} and k_{TS} are the rate constants for energy transfer from triplet carbonyl to ^{1}DBA* and ^{3}DBA*, respectively.) ϕ_{TS} is unfortunately not known with certainty. In experiments with triplet acetophenone as donor and DBA as acceptor, ϕ_{TS} was found to be ~0.2.[23] Although not as high as the value of 0.3 reported by Berenfel'd et al.[24] for the same energy transfer step, this result casts doubts on the much lower value reported earlier by Belyakov and Vassil'ev.[25] In the present calculations of $^3\phi$, a value of $\phi_{TS} = 0.2$ is used throughout.

The results of Table II show that 2 generates excited products in about 30% yield, and that these are mostly in triplet rather than singlet states (ratio 3 × 10³); similar results are found for 3 and 4. On the other hand, the total yield of excited products from 1 appears significantly smaller (~11%), but the proportion of singlet excited products is much higher (~1%), and the absolute yield of singlets is higher than with 2–4.[26]

Quenching by Conjugated Dienes. Lifetime of Excited Products. Experiments with 1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene, and 1,3-octadiene support the product multiplicity assignments of Table II. These dienes effectively suppress the chemiluminescence from DBA by quenching the triplet carbonyl donors involved, as previously shown by Steinmetzer et al.[27] in the case of 3. Linear Stern–Volmer

Table II. Yields of Excited Products

Dioxetane	y intercept[a] $\times 10^{-11}$ $h\nu^{-1}$ ml s DBA	DPA	y intercept/slope,[a] M^{-1} DBA	DPA	ϕ_{obsd}^{DBA} [b]	ϕ_{obsd}^{DPA} [b] = $^1\phi c$	$^3\phi c$
1	14[d]	1.7[d]	430[d]	5.5[d]	7.7×10^{-4}	0.01[e]	0.1
2	0.83[f]	29[f]	270[f]	46[f]	3.3×10^{-3}	0.0001	0.3
3	0.17[g]	3.3[h]	380[g]	67[h]	3.3×10^{-3}	0.0015	0.3
4						Low	~0.2[i]

[a] From plots of $1/I_{chl}$ vs. $1/Fl$. Intensity calibration based on standard of Hastings and Weber.[12] The maximum error on the intercepts is ~50%; this error is carried over in the yields. [b] Observed quantum yields of chemiluminescence, in $h\nu$ per dioxetane molecule decomposed. [c] Calculated yields (see text) of excited carbonyl fragments, i.e., number of excited products per dioxetane molecule decomposed. [d] [D] = 5.0×10^{-3} M, solvent = xylenes, temperature = 64°. [e] After correcting for fraction of DBA excited by singlet–singlet transfer from singlet excited carbonate. [f] [D] = 6.3×10^{-4} M; solvent, benzene; temperature, 43.5°. [g] [D] = 5.0×10^{-3} M; solvent, benzene; temperature, 57°. [h] [D] = 1.0×10^{-3} M; solvent, benzene; temperature, 54.3°. [i] An estimate based on a recalculation of data from Wilson and Schaap,[13] using ϕ_{TS} = 0.2 (instead of 0.01, the literature value[25] at the time), the chemiluminescence intensity at infinite concentration of DBA (instead of [DBA] = 0.02 M), and the lowest observed rate of thermolysis at 50°.

Table III. Quenching by Dienes of Chemiluminescence Sensitized by DBA

Dioxetane	[D] $\times 10^{-4}$ M	[DBA] $\times 10^{-4}$ M	Temp, °C	Slope,[a] M^{-1}
1[b]	160	3.2	73	110
2[c]	6	1.0	42	130
3[c]	100	5.0	38	200
4[c]	10	0.5	30	120

[a] Slope of Stern–Volmer plots I_0/I vs. diene concentration. [b] Solvent, xylenes; quencher, 2,5-dimethyl-2,4-hexadiene. [c] Solvent, benzene; quencher, cis-1,3-pentadiene.

Table IV. Estimated Heats of Reaction ΔH_r and Energies Available $(E_a - \Delta H_r)$ for Excitation of Carbonyl Products (all in kcal M^{-1})

Dioxetane	ΔH_r(calcd)[a]	$E_a - \Delta H_r$ [b]
1	-120[c]	148
2	-92	116
3	-69[d]	97
4	-89[e]	113

[a] Reference 30a. [b] Values of E_a obtained by temperature-drop method with DPA; see Table I. [c] One unknown group was assigned as follows: [C–(O)$_3$(C)] ≡ [C–(O)$_2$(C)$_2$] = -18.1 kcal M^{-1}. [d] H. E. O'Neal and W. H. Richardson, *J. Am. Chem. Soc.*, **92**, 6553 (1970), and correction, *ibid*, **93**, 1828 (1971). [e] Compared to -80 kcal[13] previously calculated on the basis of earlier table of groups.[30b]

Figure 4. Quenching effect of cis-1,3-pentadiene on the intensity of chemiluminescence from p-dioxenedioxetane (**2**) in the presence of DPA (O) or of DBA (●). I_0 is the intensity without diene, I is the intensity with diene (dioxetane concentration, 6.3×10^{-3} M in benzene at 42°).

quenching plots were obtained for dioxetanes 2-4 up to quenching factors of ~200 at diene concentration ~1.5 M (Figure 4 and Table III). In the case of 1, the Stern–Volmer plot has a similar steep slope, but curves at higher diene concentrations, so that a maximum quenching factor of only ~20 is attained. The Stern–Volmer slopes for diene quenching correspond to $k_q\tau$, where τ is the lifetime of the excited carbonyl donor to DBA, and k_q is the quenching rate constant. Steady-state treatment shows that the values of y intercept/slope for the DBA plots (Table III, column 3) represents $\tau(k_{TT} + k_{TS})$. If $k_q = k_{TT} + k_{TS} \simeq 5 \times 10^9$ M^{-1} s^{-1} (for exothermic "diffusion-controlled" energy transfer), then the diene slopes of Table III and y intercept/slope of Table II should be equal if the lifetime of the donors is the same in the two sets of experiments. The agreement is fairly good, which confirms that the donor is indeed a triplet state with lifetime limited by oxygen quenching in aerated solutions ($\simeq 4 \times 10^{-8}$ s, from data above).[28]

When the sensitizer is DPA, these dienes have very little effect on the chemiluminescence intensity. The Stern–Volmer plots (Figure 4) are not linear (the slope is steeper at low diene concentration) and the maximum quenching is of the order of 2 to 5 at diene concentration ~1.5 M. Here, thus, singlet excited states are involved; this conclusion is
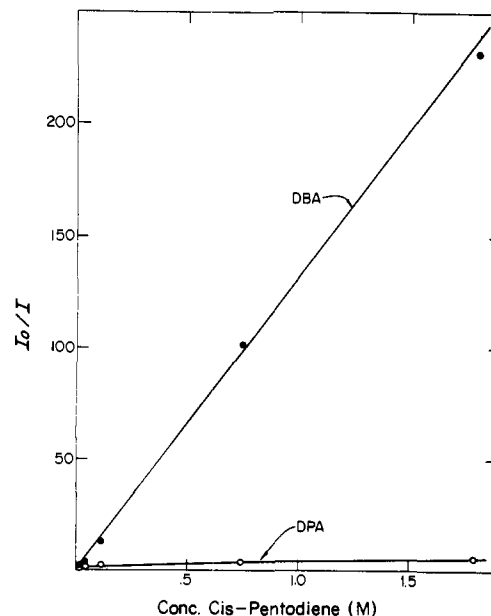
supported by the low values of y intercept/slope) = $\tau' k_{SS}$, with DPA[29] (Table II, column 4), where k_{SS} is the rate of energy transfer from singlet excited carbonyl to singlet excited DPA.

Discussion

Energetics and Yields of Excitation. Insufficient exoergicity of dioxetane cleavage is unlikely to be the cause of the significantly lower *overall* yield of excited products from 1 than from 2, 3, or 4, since, of these four dioxetanes, 1 actually generates the highest yield of excited *singlet* carbonyls. An estimate of the heat of thermolysis of 1, based on Benson's group additivity method,[30] indicates that the energy available for product excitation, $E_a - \Delta H_r$, may be as high as 150 kcal (Table IV).[31] Methyl carbonate begins to absorb at ~220 nm; hence the first excited singlet state may be located ~130 kcal above ground state. However, because of Franck–Condon factors, the 0th vibrational level of this state may be considerably lower. Thus it is indeed likely that sufficient energy is available to generate singlet excited carbonate and thereafter ^{1}DPA* (E_S = 70.1 kcal).[21] No information relative to the level of methyl carbonate first triplet is available. Unless the S–T interval is unusually large in this molecule (>45–50 kcal), the observed transfer of ener-

gy from methyl carbonate to ^{1}DBA* (E_S = 70.2 kcal)[21] should also be exothermic.

The levels of the excited states of the diester product of **2** are not known either. In rough approximation, this diester and ethyl formate may be assumed to have similar spectroscopic properties. Johnson et al.[32] reported a very weak phosphorescence from ethyl formate, which they tentatively assigned to triplet–singlet emission from the carboxyl group. The λ_{max} of this emission is ~400 nm, corresponding to ~70 kcal. As the geometry of the π,π^* triplet state involved and that of the ground state are predicted to be very different, these authors suggest that the true (not Franck–Condon) triplet is at least ~90 kcal above ground state. Consequently, there is no reason to doubt that the energy transfer to either DPA or DBA is exothermic, which is the basic assumption for the calculations of yields[33] (see Results, section 2).

In the case of dioxetanes **2–4**, where the ratio of triplet to singlet products is 100 or higher (i.e., at infinite concentration of DPA or DBA, *more* luminescence is emitted from DBA than DPA, as in Figure 3), most of the carbonyls are certainly formed *directly* in the triplet state, rather than via intersystem crossing from the singlet state. The situation is not as clear-cut in the case of **1**. Nevertheless, within the limits of error[34] in the determination of the y intercept in Figure 2, it is reasonably certain here again that the crossing over from singlet to triplet cannot alone account for all the triplet carbonyls observed, hence these must be primary products of the cleavage of **1**.

The accuracy of the excitation yields deserves comment. As the rates of dioxetane thermolyses enter in the calculations (Table II), it is important that these rates represent the true, chemiluminescent, uncatalyzed cleavage. For example, the presence of 10^{-7} M Cu^{2+} would be enough to increase the rate of decomposition of **3** in benzene at 57° by at least 50%, via a "dark" pathway, thus decreasing the apparent yields $^1\phi$ and $^3\phi$ by the same percentage. In addition, systematic errors may evidently result from the values chosen for ϕ_{TS} and for the intensity calibration factor.[35]

Kinetics of Cleavage and Stability of the Dioxetanes. Considering first dioxetanes **2** and **4**, their nearly identical activation energies imply that the release of the 3–4-kcal strain of the ester ring in **2** occurs *after* the transition state is reached, suggesting that the cleavage of **2** is not a concerted reaction. Richardson et al.[36] have argued against concertedness; one of their arguments is based on the observation that potential conjugation between a dioxetane ring substituent and a developing carbonyl does not lower the activation energy of cleavage.[37] In terms of a diradical mechanism, one could speculate that as long as the C–C bond of the dioxetane is unbroken, the diradical, still in its singlet state, will tend to recombine. This rebonding of the oxygens should be favored by the ester ring of **2**, which prevents rotation around the C–C bond of the dioxetane. As soon as this C–C bond breaks, however, the ester ring opens, the dioxetane oxygens separate, and the two carbonyl bonds begin to form.

Turning now to the pair of dioxetanes **1** and **3**, the greater stability of **1** seems to be mainly the consequence of entropy rather than energy factors. Here, a structural model of **1** does not suggest a ready explanation. **1** has more degrees of freedom than **3** and many possible conformations, often leading to crowding of the methoxy groups. The need for a specific geometry in the transition state may perhaps explain the low A factor, in terms of a small transmission coefficient.

The factors influencing the partition of excited products between singlets and triplets are not accessible yet. Two papers[38] have recently discussed hypothetical energy-level

patterns for dioxetane decomposition, particularly with respect to the crossing of the ground state and triplet excited levels near the transition state. With the aid of these postulated patterns, it is possible to rationalize the occurrence of high yields of excited products and their triplet character.[38b] Unfortunately, these patterns of potential energy surfaces are hypothetical and likely to remain so since they pertain to transition states, until reliable quantum-mechanical calculations are available. These discussions have so far not touched on the effect of substituents.

With respect to **1**, it is noteworthy that Darling and Foote[1h] reported relatively low and nearly equal yields (~3–5%) of singlet and triplet excited 2-hexanone from **5**. Thus, here also, substituents with a larger number of degrees of

5
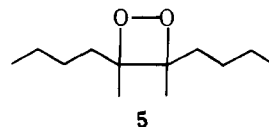
freedom than the methyl groups of **3** appear to reduce the total yield of excited products while increasing the yield of singlets. This suggests that it may be the flexibility of the methoxy groups which is responsible for the higher relative yield of singlet fragments from **1**. In this context it would be interesting to compare the properties of **3** with that of tetraethyldioxetane, yet unknown.

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(18) Turro et al.[17] report a rate constant of ~10^9 M^{-1} S^{-1} for the reaction of

triplet acetone with **3**, i.e., not so much slower than the rate of quenching of triplet acetone by oxygen.

(19) The emitter has not yet been identified in this case in the absence of fluorescer or in the case of **2**.

(20) Induced decomposition is the likely cause of the erroneously high rate ($t_{1/2}$ = 102 min at 56°, two orders of magnitude faster than observed here) reported by Mazur and Foote,[5] since their experiment was done with pure **1** by NMR.

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(29) In the case of **3**, the present value of $\tau' k_{ss}$ = 67 M^{-1} (Table II, column 4) is about five times smaller than reported by Steinmetzer et al.[27] Here, if τ = 2 × 10^{-9} s^{-1} (for singlet excited acetone), then $k_{ss} \simeq$ 3 × 10^{10} M^{-1} s^{-1}.

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(31) Note, however, that the energies of one of the groups entering the calculation is unknown and had to be assigned (see footnote c, Table IV). Nevertheless, this reaction can be expected to have a large exothermicity in view of the stabilization energy of methyl carbonate (~25 kcal).

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(34) A factor of ~2, because of the steepness of the slope of this 1/[DPA] plot.

(35) Most other methods for determining yields of excited products suffer from similar difficulties; see ref 2. In any case, the yields of excited products obtained here from **3** are not significantly different from the literature values.[1c,10b]

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The Measurement and Interpretation of Hydrogen–Tritium Kinetic Isotope Effects in Borane and Borohydride Reductions of Ketones. Implications on Steric Approach Control vs. Product Development Control[1]

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Abstract: Hydrogen–tritium isotope effects have been measured for the reduction of a series of ketones with borane and sodium borohydride. The isotope effects for the reductions are contrasted with those in the hydroboration of alkenes and are discussed in terms of the thermodynamics and kinetics of the reactions. It is concluded that both the reduction and hydroboration reactions involve four-center transition states leading to product formation; however, the extent of bonding between the various atoms in the four-center transition states differs significantly. These differences are discussed in terms of the relative strengths of the bonds being formed and broken in the transition states. The implications of the isotope effects on steric approach control and product development control are discussed.

Introduction

The concepts of steric approach control (SAC) and product development control (PDC), initially introduced by Dauben in 1956,[2] have been subjected to considerable scrutiny, particularly in their application to the reduction of substituted cyclohexanones to which the concepts were originally applied. The presence of SAC has been accepted in these and many other reactions; the presence of PDC, however, has proved more elusive to demonstrate, and considerable effort has been expended to either support or refute its operation. Although a number of slightly different definitions have been advanced to replace the original definitions of SAC and PDC,[3-5] the basic difference between SAC and PDC centers on the position of the transition state along the reaction coordinate,[5] i.e., whether the steric interactions in the transition state are of the long-range type between the

attacking reagent and the substrate molecule, which is in its ground-state geometry (an early transition state), or steric interactions present in the product (a late transition state). Several authors have suggested that the sodium borohydride reduction of ketones proceeds via an early transition state (no PDC),[5-9] Eliel and Senda have suggested "PDC plays at best a minor role",[4] while others have suggested that late transition states are involved[10-13] (PDC operative).

One of the techniques used to gain information concerning the extent of bond formation (or cleavage), i.e., the position of the transition state along the reaction coordinate, makes use of the measurement and interpretation of kinetic isotope effects (KIE). Even here, however, controversy reigns. Geneste and Lamaty[13a] have measured the secondary H–D KIE in the sodium borohydride reduction of α-deuterated ketones and interpreted the data in terms of