The Chemiluminescence from *cis*-Diethoxy-1,2-dioxetane. An Unexpected Effect of Oxygen

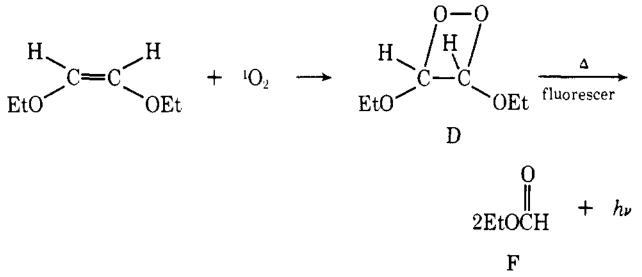
Thérèse Wilson* and A. Paul Schaap[1]

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received September 26, 1970*

Abstract: The first-order decomposition of *cis*-diethoxy-1,2-dioxetane generates excited ethyl formate; energy transfer to fluorescers causes chemiluminescence. With 9,10-diphenylanthracene (DPA) or perylene, the activation energies of the overall luminescent process and of the dioxetane cleavage are the same (24 kcal/mol). Intensity measurements before and after quick changes of solution temperature establish that there is no alternate, low activation energy, dark path of dioxetane decomposition. The efficiency is highest with 9,10-dibromoanthracene (DBA): 5×10^{-4} $h\nu$ per dioxetane molecule, about two orders of magnitude larger than with DPA. The dependence on fluorescer concentration shows that both DPA and DBA are excited *via* triplet–singlet collisional energy transfer from triplet formate. Given the literature value of 3×10^{8} M^{-1} sec^{-1} for the rate of this process in the case of DBA, the actual rate of decay of triplet formate in these solutions is $\sim 10^{8}$ sec^{-1}. The fluorescence efficiency of DBA at 55° being only ~ 0.05 $h\nu$/molecule, the chemiluminescence yield corresponds to the generation of one triplet formate per dioxetane decomposing. This supports the view that here electronic excitation of the product is a necessary consequence of the thermal cleavage of the dioxetane, as predicted by orbital symmetry rules. Degassing the solution of dioxetane and DBA (or DPA) increases both the rate of decay of the chemiluminescence and the rate of dioxetane decomposition. It is suggested that triplet anthracene, excited *via* t–t transfer from triplet formates, sensitizes the decomposition of the dioxetane, when not first quenched by oxygen. This hypothesis is supported by photochemical experiments with DBA as sensitizer; with DPA, the effect of oxygen and fluorescence quenching data indicate that most or all of the photosensitization takes place from the singlet state of the anthracene. Mechanistic implications are discussed.

The mechanism of the many intense chemiluminescent reactions in solution involving oxygen or peroxides is currently a topic of lively interest.[2] On the basis of circumstantial evidence supported by orbital symmetry considerations, it has been proposed[3] that the concerted cleavage of transient four-membered ring peroxides, 1,2-dioxetanes, is the common critical step in which an electronically excited carbonyl fragment is generated. The thermal instability of the proposed dioxetanes prevented a quantitative test of this hypothesis, until Kopecky and Mumford developed a synthetic route to the relatively stable dioxetane of trimethylethylene[4] and reported that its decomposition is indeed chemiluminescent.[5]

The recent isolation of similarly simple and stable dioxetanes, as the direct and often only product of the 1,2-addition of singlet oxygen to an activated olefinic double bond, adds considerably to the interest of such peroxides.[6] The present paper is concerned with the decomposition of *cis*-diethoxy-1,2-dioxetane (hereafter D) into ethyl formate (F), as the only reaction product.[6a] Chemiluminescence is readily observed in the presence of a fluorescer. Thus here is what appears to be an ideally simple chemiluminescent system: the thermal cleavage of a relatively stable molecule into two molecules of the same stable product, one in the ground state and one in an excited state, followed by transfer of this electronic energy to the fluorescer and emission of its fluorescence.



The study of the decomposition of D in aerated solutions with fluorescers such as 9,10-diphenylanthracene (DPA) or 9,10-dibromoanthracene (DBA) shows that the intensity of chemiluminescence and the concentration of dioxetane do indeed decay along the same expected first-order course; the rate of decomposition of D is thus unaffected by the presence of the fluorescer. The chemiluminescence yield is markedly greater with DBA than with DPA, in spite of the much higher fluorescence efficiency of the latter. This is evidence for the involvement of triplet excited formates, whose energy DBA is more capable of converting into singlet energy than is DPA, because of the increased spin–orbit coupling and mixing of singlet and triplet states due to the heavy atoms.[7] Thus, although most of the energy of the triplet formates will be converted into triplet energy of the anthracenes, evidently in the case of DBA (and actually also in the case of DPA) the energy transfer step leading to chemiluminescence is of the triplet–singlet type. Therefore it was expected that removing the dissolved oxygen, likely to compete with

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(1) Department of Chemistry, Wayne State University, Detroit, Michigan 48202.

(2) (a) K. D. Gundermann, *Angew. Chem., Int. Ed. Engl.*, 4, 566 (1965); (b) F. McCapra, *Quart. Rev., Chem. Soc.*, 20, 485 (1966); (c) M. M. Rauhaut, *Accounts Chem. Res.*, 2, 80 (1969); (d) E. H. White and D. F. Roswell, *ibid.*, 3, 54 (1970).

(3) F. McCapra, *Chem. Commun.*, 155 (1968).

(4) K. R. Kopecky and C. Mumford, Abstracts, 51st Annual Conference of the Chemical Institute of Canada, Vancouver, B. C., June 1968, p 41.

(5) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, 47, 709 (1969).

(6) (a) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, 92, 3223 (1970); (b) S. Mazur and C. S. Foote, *ibid.*, 92, 3225 (1970); (c) A. P. Schaap, *Tetrahedron Lett.*, 1757 (1971).

(7) For other examples and a discussion of this effect, see V. A. Belyakov and R. F. Vassil'ev, *Photochem. Photobiol.*, 11, 179 (1970).

DBA for the quenching of triplet formates, should increase the chemiluminescence yield.

However, a routine degassing of the solutions revealed an unexpected and very interesting complication. Surprisingly, the intensity of chemiluminescence is not markedly enhanced, but its rate of decay is considerably increased. This effect appears to be due to a "photo"-decomposition of the dioxetane, sensitized by the triplet excited anthracene formed in the reaction and normally quenched by oxygen in aerated solutions. Thus here oxygen appears to play a protective role against a damaging effect of "photochemistry without light."[8]

Experimental Section

Reagents. *cis*-Diethoxy-1,2-dioxetane was prepared at −78° by photooxygenation of vpc purified *cis*-diethoxyethylene in fluorotrichloromethane (Freon 11) with tetraphenylporphine as sensitizer, as described earlier.[6a] The dioxetane was recrystallized from Freon 11, dried under vacuum at −78°, and immediately thereafter dissolved in a known volume of the appropriate solvent. Benzene was the solvent used for the chemiluminescence experiments; stock solutions usually about 1.6 *M* in dioxetane were stored in the freezer, where they were stable. Working with solid *cis*-diethoxydioxetane was avoided because of its tendency to decompose explosively; nmr data on *cis*-diethoxydioxetane have been reported earlier.[6a] In order to prepare a solution of the dioxetane which was uncontaminated by any trace of the photosensitizer, and thus suitable for absorption spectroscopy, a sample of *cis*-diethoxyethylene in Freon 11 was treated at Dry Ice temperature with singlet oxygen generated by an electrodeless radiofrequency discharge.[9] The resulting solution was then diluted with cyclohexane (Eastman, Spectrograde). Nmr analysis showed no starting material; an appreciable amount of ethyl formate[10] (36%) was present besides the dioxetane (64%).

9,10-Dibromoanthracene (Aldrich) was recrystallized from xylene. 9,10-Diphenylanthracene, perylene, and rubrene (all from Aldrich) were used without further purification. Appropriate volumes of the solutions of the fluorescers and of the dioxetane, kept on ice when about to be used, were mixed immediately before a run.

Analytical Procedures. A sample of pure *cis*-diethoxydioxetane in Freon 11, prepared photochemically as described above from 2.39 mmol of *cis*-diethoxyethylene, was analyzed for its dioxetane content by nmr with methylene chloride as an internal standard. The total volume of the dioxetane solution was 9.0 ml to which 0.984 mmol of CH_2Cl_2 was added. The ratio of dioxetane to CH_2Cl_2 peaks, averaged over three scans on the Varian A-60 spectrometer, was 1.51 ± 0.05, corresponding to a dioxetane concentration of 0.166 ± 0.06 *M* and therefore to a yield of 62% of isolated pure dioxetane from the starting olefin.[11]

The concentration of dioxetane in a given solution was also determined by iodometric titration in acetic anhydride.[12] Typically 1 ml of a freshly prepared solution of 10% sodium iodide in acetic anhydride (Mallinckrodt, Analytic Reagent) was added to 5 ml of cold acetic anhydride, followed quickly by the addition of a pipetted sample (usually 0.2 ml) of the dioxetane solution to be titrated (usually ~0.08 *M* in benzene). The iodine color appears immediately. The solution in a stoppered erlenmeyer flask was left to stand at 0° in the dark for 15 min with occasional stirring. Water (5 ml) was then added and the iodine present was titrated with $Na_2S_2O_3$ (0.01 *N*) with vigorous swirling.

For comparison, this method was used on the solution of dioxetane in Freon 11 whose concentration had been independently determined by the calibrated nmr method described above. Four successive iodometric titrations gave an average D concentration of 0.145 ± 0.010 *M*, *i.e.*, 87.5 ± 5% of the nmr result; the inaccuracy in these particular iodometric titrations resulted largely from the difficulty of syringing out exact volumes of a solvent as volatile as Freon 11. The agreement between the two analytical methods is satisfactory.

Absorption spectra were obtained with a Cary 14 spectrophotometer and fluorescence spectra with an Aminco-Bowman spectrofluorimeter. The concentration of DPA and DBA were occasionally monitored photometrically with a Beckman DU2.

Chemiluminescence Measurements. Apparatus and Methods. The light intensity measuring system consisted of a Dry Ice cooled EMI 9558B photomultiplier tube (S-20 response) with a Northeast high-voltage power supply, a Keithley electrometer, and a Texas Instrument strip chart recorder.[13]

The photomultiplier, in a Pacific photometer housing, was rigidly mounted to a 9 × 9 in. metal box housing the reaction cell and its temperature control system. A photographic-type shutter permitted access to the reaction cell without exposing the photomultiplier tube to room light; either of two wide band interference filters[14] could be slid in the light path in order to obtain information on the spectral distribution of the chemiluminescence.

The volume of the solution samples was 0.6 ml. For degassed solutions, the reaction cells consisted of sealed sections of Pyrex tubing (5 mm i.d., 11 cm long) fastened in a reproducible position inside a Pyrex dewar with an unsilvered window facing the photomultiplier tube. Clear Dow-Corning silicone oil, circulated from a Tamson thermostat bath, filled the dewar to a constant level. Degassing the solution was achieved by three successive freeze–thaw cycles to better than 10^{-4} Torr, prior to the sealing of the tubes at liquid nitrogen temperatures. The tubes were allowed to warm up to about 10° before a run. They were then inserted into the oil-filled dewar; the box was closed and the shutter opened, all of which could be achieved in less than 20 sec.

In the case of aerated solutions, the dewar and sealed tube arrangement was replaced by a Pyrex reaction cell made of a similar length of Pyrex tubing (5 mm i.d.) with a fused outer jacket (20 mm o.d.) for temperature control. This reaction cell occupied exactly the same position in the housing as the sealed tubes used for degassed solutions. The dioxetane–fluorescer solutions were syringed directly into the reaction cell through a serum cap on an opening of the housing cover directly above the cell. Silicone oil from either of two thermostat baths (the Tamson bath or a Lauda K-2/R bath), maintained at different temperatures, could be circulated in the reaction cell jacket *via* a set of appropriate toggle valves. This setup permitted a quick and reproducible change of temperature of the reaction cell. The solution temperature was determined by means of a stainless-steel-encased copper–constantan thermocouple monitored by a Leeds and Northrup potentiometer or strip chart recorder.

Quantum Yields Determinations. An absolute calibration of the luminescence intensity readings was obtained through a sample of a radioactive liquid light standard,[15] kindly supplied by Professor J. W. Hastings. This standard (^{131}I in toluene with PPO and POPOP as fluorescers) emitted a light flux of 3 × 10^{10} quanta sec^{-1} ml^{-1} with peak intensity at 416 nm. This maximum is close enough to the maxima of fluorescence of DPA and DBA to make any correction regarding the spectral sensitivity of the S-20 photocathode unnecessary. Thus the procedure consisted simply in replacing the 0.6 ml of a chemiluminescent solution by an equal volume of light standard and comparing the intensity readings, all geometrical and electrical conditions remaining unchanged.

Photochemical Experiments. Samples (5 ml) of benzene solutions of *cis*-diethoxydioxetane with DPA or DBA, aerated or degassed, were irradiated in a Pyrex reaction cell with "monochromatic" light at 400 nm from a Bausch and Lomb monochromator, while magnetically stirred at 5.5°.

Results

1. Absorption Spectrum of *cis*-Diethoxydioxetane. Figure 1 shows the absorption spectrum, after correction

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[8] E. H. White, J. Wiecko, and D. F. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969).

[9] For this technique, see E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964); also C. Ouannès and T. Wilson, *ibid.*, **90**, 6527 (1968), footnote 1.

[10] Believed to result from a competitive reaction of *cis*-diethoxyethylene with ozone present in the stream of singlet oxygen.

[11] Such a low yield is to be expected, considering the high solubility of the dioxetane in Freon 11 with which it was washed. The nmr spectrum showed no starting material and no other product.

[12] K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

[13] The results of some of the runs with the more intense chemiluminescence were cross-checked by replacing this EMI photomultiplier tube system with the RCA 1P28 in its Aminco housing fed to the Aminco photometer.

[14] From Baird-Atomic, transmitting between 410 and 490 nm and 530 and 650 nm, respectively.

[15] J. W. Hastings and G. Weber, *Photochem. Photobiol.*, **4**, 1049 (1965).

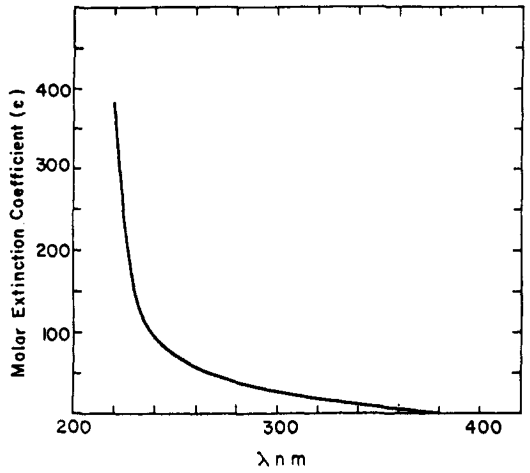

Figure 1. Absorption spectrum of *cis*-diethoxydioxetane in mixed cyclohexane–Freon 11.

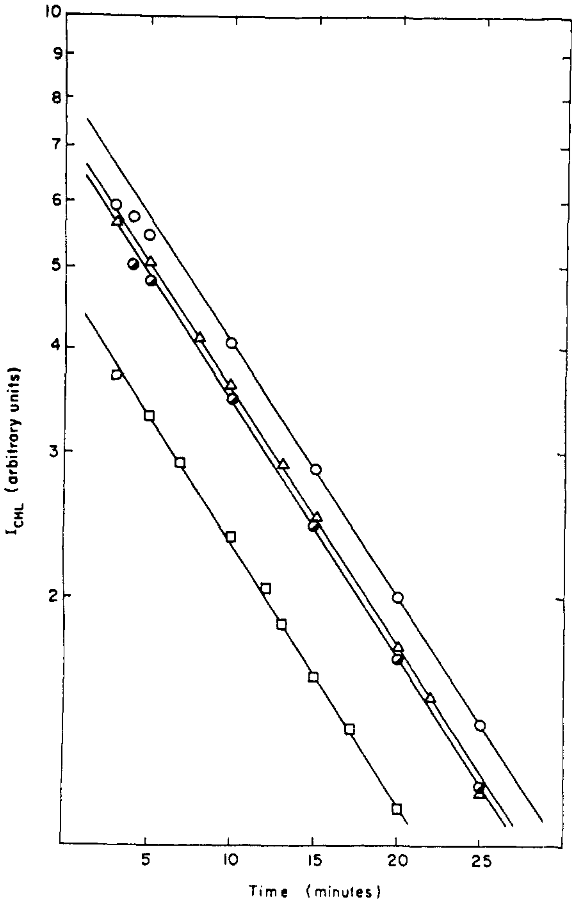

Figure 2. Effect of DBA concentration on the rate of chemiluminescence decay at 55° (DBA concentration × $10^{-4}M$): ○, 181; △, 90; ◐, 45; □, 3.6; initial D concentration = 0.015 *M*.

for the absorption by the ethyl formate present in the dioxetane solution (see Experimental Section) in mixed cyclohexane–Freon 11. Absorption extends to the edge of the visible in a structureless tail.

2. First-Order Course of the Dioxetane Decomposition in Aerated Solutions. Activation Energy. Heating a solution of *cis*-diethoxydioxetane in benzene ($\sim$0.08 *M*) to 60° produces no detectable chemiluminescence, although a bluish flash accompanied the

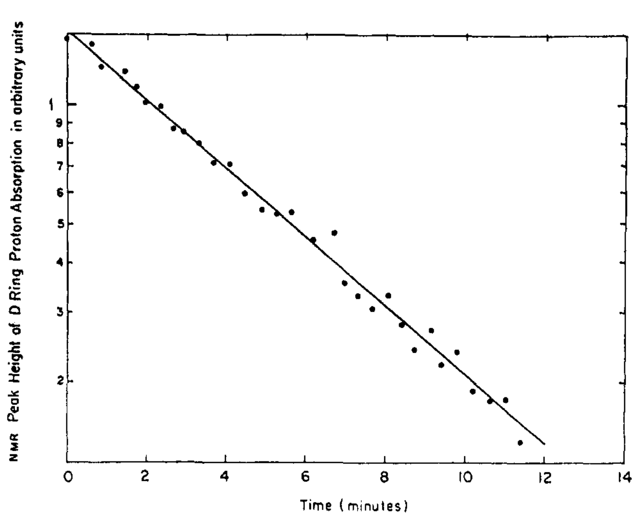

Figure 3. First-order plot of the decomposition of *cis*-diethoxydioxetane in benzene at 54°, by nmr; $k = 3.17 \times 10^{-3}$ sec^{-1}.

explosive decomposition of a sample of solid dioxetane on warming to room temperature.[16]

Addition of fluorescers such as DPA, DBA, perylene, rubrene, or rose bengal induces the heated dioxetane solutions to emit a visible chemiluminescence of a color matching the fluorescence of the aromatic hydrocarbon or dye added. As mentioned earlier, the intensity of the luminescence is considerably higher with DBA than with any of the other fluorescers tried: it can be readily observed in a dimly lit room.

After a cold solution of fluorescer and dioxetane in benzene (concentration 0.1–0.01 *M*) reaches the temperature of the preheated cell (40–70°), the intensity of the chemiluminescence decays with first-order kinetics. The peak intensity is roughly proportional to the initial concentration of dioxetane; the dependence on the fluorescer concentration will be discussed later. Figure 2 shows that the rate of chemiluminescence decay is independent of the fluorescer concentration.[17]

The same first-order kinetics govern indeed the decomposition of the dioxetane in benzene. Figure 3 shows a first-order plot of the decrease of the nmr signal (δ 5.91) of the ring protons of the dioxetane in the Varian HA-100 spectrometer probe at 54°. Iodometric titrations confirmed this result and showed that the presence of DBA does not modify the first-order rate of decomposition of the dioxetane in benzene (Figure 4).

Figure 5 is an Arrhenius plot of the rate constant for the chemiluminescence decay with different sensitizers; the data are scattered but correspond to an activation energy ($E_{(1)}$) of approximately 23.6 kcal/mol. This

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(16) As the reaction cells were made of Pyrex, no emission corresponding to the possible fluorescence of ethyl formate would have been observed. However, as no fluorescence from ethyl formate was observed from quartz cells, it is very unlikely that any chemiluminescence was missed in our setup.

(17) However, at high concentration of D ($\sim$0.08 *M*) and low concentration of fluorescer (5×10^{-4} *M*), the observed rates are faster than expected, as if the fluorescer was consumed (probably by photooxidation). A photometric check of the concentration of DBA in a pair of solutions, one 0.06 *M* in dioxetane, the other containing no dioxetane, did confirm this hypothesis: whereas after 20 min at 55.7°, the final concentration of DBA was unchanged in the latter solution (1.4×10^{-4} *M*), it was only 0.6×10^{-4} *M* in the solution containing the dioxetane. However, as this complication does not affect the main results and conclusions of this work, it was not further investigated at this point.

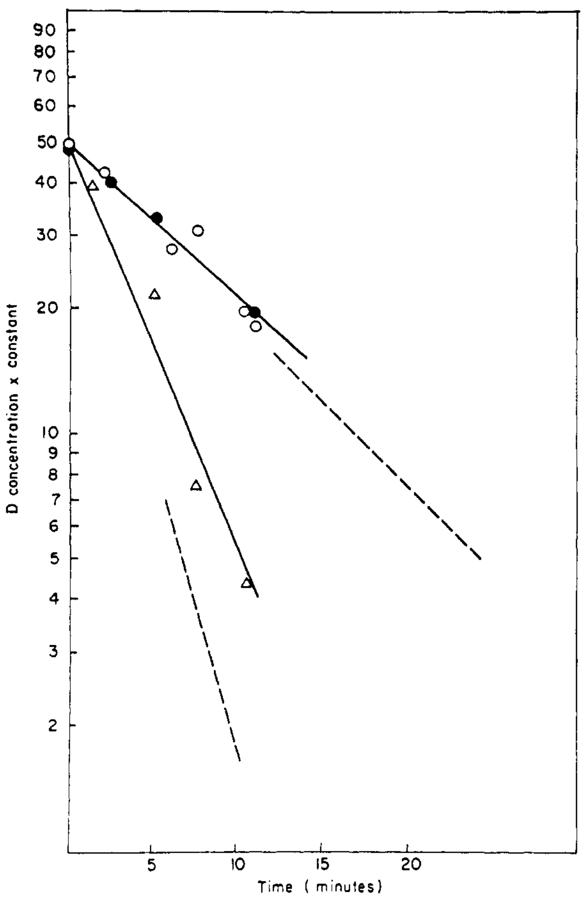

Figure 4. Rate of decomposition of *cis*-diethoxydioxetane in benzene at 55°, by iodometry. Initial D concentration = 0.08 *M*; ○ = aerated solutions with DBA (0.018 *M*); ● = aerated solutions without DBA; △ = degassed solutions with DBA (0.018 *M*). Broken lines represent slopes of chemiluminescence decay in a similar pair of experiments with and without O_2.

value is consistent with the results of three experiments in which the rate of decomposition of the dioxetane in Freon 11 was determined in the absence of any fluorescer by nmr at different temperatures.[18] Thus the first-order rate of decomposition of the dioxetane is not altered by the presence of a fluorescer, nor does it seem to depend on the solvent.

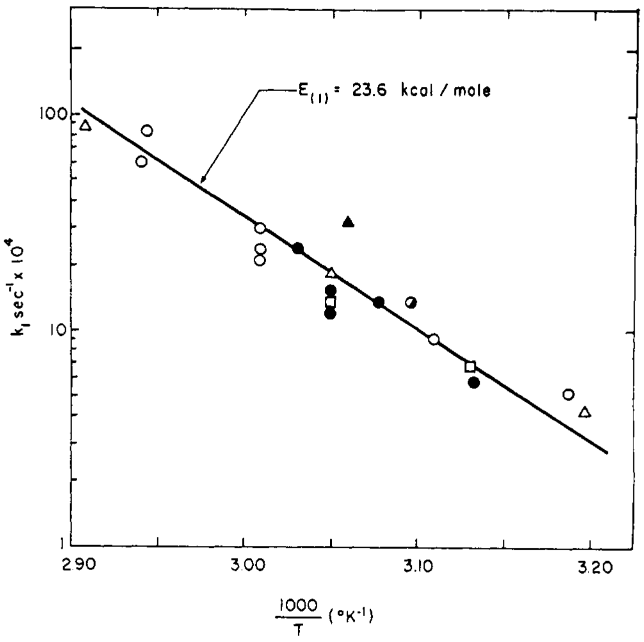

Figure 5. Temperature dependence of the first-order rate constant k_1 for the *cis*-diethoxydioxetane decomposition. The circles correspond to chemiluminescence decay rates (○ with DPA, ● with DBA, ◐ with perylene). The triangles correspond to nmr measurements of the rate of decay of the dioxetane, without fluorescer (△ in Freon 11, ▲ in benzene). The squares correspond to iodometric determination of the rate of decay of the dioxetane, in benzene. The initial concentration of D was ~0.08 *M*.

3. Activation Energy from the Effect of Quick Temperature Changes. These results are consistent with the kinetic scheme shown by eq 1–5 where electronic levels are purposely left unspecified at this time (A is the fluorescer, at constant concentration).

$$D \xrightarrow{k_1} F^* + F \tag{1}$$

$$F^* + A \xrightarrow{k_2} A^* + F \tag{2}$$

$$F^* \xrightarrow{k_3} F \tag{3}$$

$$A^* \xrightarrow{k_4} A \tag{4}$$

$$A^* \xrightarrow{k_5} A + h\nu \tag{5}$$

Equations 3 and 4 show first-order or pseudo-first-order decay (such as quenching by O_2 or by other quenchers at constant concentration), and eq 5 shows chemiluminescence. Steady state approximations give

$$I_{\text{chl}} = k_1[\text{D}]\Phi_{\text{F}}\frac{k_2[\text{A}]}{k_2[\text{A}] + k_3}$$

where $I_{\text{chl}} = k_5[\text{A}^*]$ is the intensity of the chemiluminescence and $\Phi_{\text{F}} = k_5/(k_4 + k_5)$ is the fluorescence efficiency of A. If, as one should expect, the energy transfer step (2) and the deactivation process (3) are fast compared to (1) and have negligible activation energies compared to $E_{(1)}$, then

$$E_{(1)} = E_{\text{chl}} - E_{\Phi_{\text{F}}}$$

where $E_{(1)}$ is the activation energy for the unimolecular decomposition of the dioxetane, E_{chl} is the activation energy for the chemiluminescence, and $E_{\Phi_{\text{F}}}$ is the activation energy for the fluorescence of A. Therefore, if the temperature of a solution of dioxetane and fluorescer is rapidly changed from T_1 to T_2 and the chemiluminescence intensities I_1 and I_2 are measured immediately before and after the quick change, the activation energy of reaction 1 is given by

$$E_{(1)} = \frac{R \ln (I_1/I_2)}{\dfrac{1}{T_2} - \dfrac{1}{T_1}} - E_{\Phi_{\text{F}}}$$

In our experimental conditions, temperature equilibration for a 20° drop is achieved only after about 60 sec. However, 80% of the temperature change occurs within the first 30 sec and the light intensity change is fastest at first (Figure 6, with perylene as sensitizer). Therefore, the assumption that the reaction proceeds at

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[18] To this effect, samples of a solution of D (0.16 *M*) in Freon 11 without fluorescer but with methylene chloride as an internal standard were heated in nmr tubes in a constant-temperature bath for selected periods of time, cooled in Dry Ice immediately thereafter, then analyzed by nmr at room temperature for the peak ratio of dioxetane/methylene chloride (δ 5.91 and 5.29, respectively). An activation energy of 22 ± 2 kcal/mol was calculated from these data.

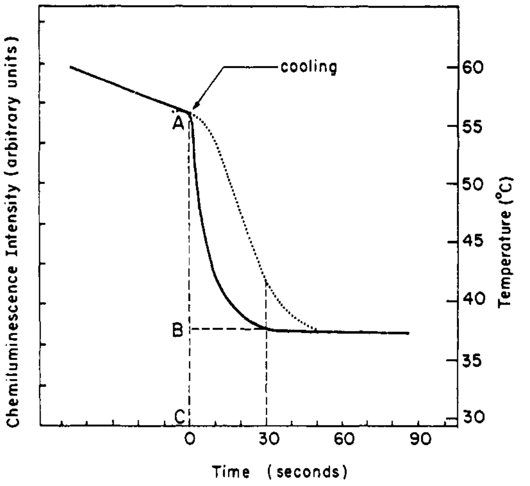

Figure 6. Effect of a quick change of temperature on the chemiluminescence of a solution of *cis*-diethoxydioxetane with perylene as fluorescer: initial temperature = 55.8°, finial temperature = 37.5°. The full line corresponds to the chemiluminescence intensity (left-hand scale). The dotted line corresponds to the temperature of the solution (right-hand scale).

the low temperature rate during the intermediate region (*i.e.*, I_1 = AC, I_2 = BC, on Figure 6) leads to values of E_{chl} greater than the true value by ~0.5 kcal only. The method applies also to quick rises in temperature; here it is assumed that the reaction proceeds at the high temperature rate throughout the equilibration period. In both cases, heating or cooling, the concentration of D is assumed to be constant during the measurements; only the reaction rate differs. Table I lists the results with different sensitizers. The fluorescence efficiency of DPA is temperature independent, within the limits of these experiments. Thus

Table I. Activation Energy of Chemiluminescence from Quick Temperature Changes[a]

Fluorescer	Fluorescer concn, M	E_{chl}, kcal mol^{-1}	E_{Φ_F}, kcal mol^{-1}	$E_{(1)}$, kcal mol^{-1}
DPA	0.1	24.4 ± 0.6 (4 expts)	~0	24.4 ± 0.6
Perylene	0.1	24.1 ± 1.8 (2 expts)	0[b]?	24.1 ± 1.8
Rubrene	0.01	21.8 ± 1.5 (3 expts)	0[b]?	21.8 ± 1.5
DBA	0.02	18.9 ± 0.2 (2 expts)	~−4	~23

[a] Concentration of *cis*-diethoxydioxetane in benzene = 0.075 *M*.
[b] The fluorescence yield of rubrene and perylene is about unity, like that of DPA. Therefore, an important temperature coefficient is unlikely.

$$E_{(1)} = E_{\text{chl}} = 24 \text{ kcal}$$

in excellent agreement with the activation energy from the Arrhenius plot (Figure 5). This point is important, because it establishes that there is no alternate, low activation energy path of decomposition of D competing with reaction 1. If there were, the values of $E_{(1)}$ listed in Table I would be higher than the activation energy obtained from the Arrhenius plot. The values of E_{chl} obtained with perylene and with rubrene are quite close to the value obtained with DPA, and also to $E_{(1)}$ from Figure 5. With DBA, the value for E_{chl} is markedly lower. But the fluorescence efficiency of DBA, as also that of 9,10-dichloroanthracene (DClA), has a large negative temperature coefficient.[19] For DClA, E_{Φ_F} is ~−4 kcal which seems a reasonable approximation for DBA also. This correction term removes the discrepancy between the results with DBA and with the other fluorescers (Table I).

One more point deserves mention. The behavior of a given solution of dioxetane and fluorescer submitted to alternate periods of cooling and heating is always consistent with the simple kinetic scheme shown in eq 1-5; namely, the rates of chemiluminescence quickly reach their expected values at the new temperatures. This is in sharp contrast with the behavior of a chemiluminescent system where the production of an unstable intermediate is involved. The same method of quick temperature changes had previously been applied to the decomposition of the endoperoxide of 1,4-dimethoxy-9,10-diphenylanthracene:[20] upon reheating quickly a previously cooled solution, the chemiluminescence intensity first reached abnormally high peaks (decomposition of the accumulated intermediate) before realigning on a "normal" course for that temperature.

4. Quantum Yields. The quantum yield of the relatively weak chemiluminescence of a dioxetane solution containing DPA was obtained by direct comparison with the still weaker emission of the light standard and integration of the curve of intensity *vs.* time for a given run. The efficiency of luminescence with DBA was calculated by comparison with a run with DPA. The results are given in Table II. The efficiency is 50–100 times greater with DBA than with DPA.

Table II. Quantum Yield of Chemiluminescence[a]

Fluorescer	Concn, M	Temp, °C	$\Phi = h\nu$/mol of D decomposed
DPA	0.10	59.6	7×10^{-6}
DBA	0.008–0.02	50.2–52.4	$5 \pm 2 \times 10^{-4}$

[a] Initial concentration of D = 0.07 *M*.

5. Effect of the Fluorescer Concentration on the Quantum Yield. A mechanism such as eq 1-5 leads to an expression of the form

$$\frac{1}{\Phi} = \frac{1}{\Phi_F} + \frac{k_3}{k_2\Phi_F}\frac{1}{[A]}$$

where $\Phi = I_{\text{chl}}/(\text{d}[\text{D}]/\text{d}t)$ is the chemiluminescence quantum yield. Figure 7 is a plot of the reciprocal of the relative values of Φ *vs.* the reciprocal of the concentration of DBA and DPA. Although scattered, the results fit the linear equation above, with $k_3/k_2 \approx 10^{-2}$ *M* (ratio of slope to intercept). The meaning of this ratio will be discussed later. The important point is that it has the same value within the limits of error (a factor of ~2) for DPA and DBA; thus, except for an un-

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(19) The rate of intersystem crossing increases with temperature, because of the position of the second triplet state in these molecules: (a) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectrosc.*, **19**, 412 (1966); (b) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964); (c) R. G. Bennett and P. J. McCartin, *ibid.*, **44**, 1969 (1966).

(20) T. Wilson, *Photochem. Photobiol.*, **10**, 441 (1969).

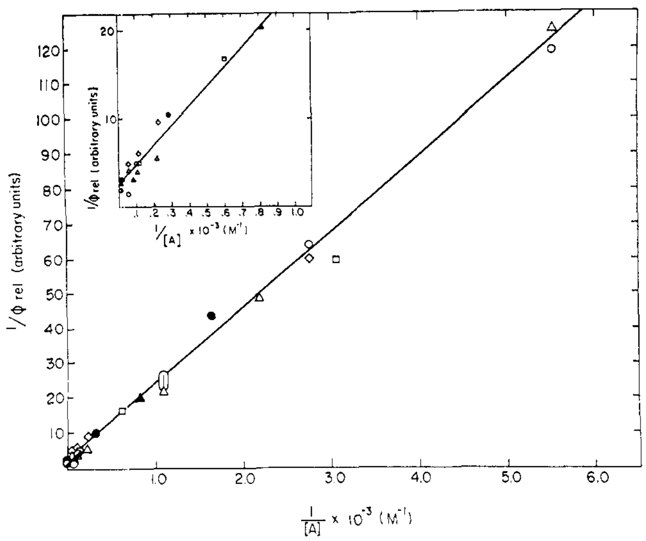

Figure 7. Effect of the concentration of fluorescer on the relative quantum yield Φ_{rel}. Full symbols = DPA; empty symbols = DBA. Initial concentration in $M \times 10^2$ of *cis*-diethoxydioxetane in each series: with DPA, ◑, 7.5; ●, 4; ▲, 4; with DBA, ○, 8; △, 6; □, 3; ◇, 1.5.

likely coincidence, these fluorescers must intercept the same electronically excited state of the energy donor (ethyl formate). As mentioned briefly but discussed later, there can be no doubt that the electronic state of F involved is a triplet of short actual lifetime.

6. Effect of Oxygen. The same type of experiments with degassed instead of aerated solutions of dioxetane and DBA led to an unanticipated result. Although the initial and peak light intensities were not markedly changed,[21] the luminescence decay was considerably faster and consequently the quantum yield was smaller (Figure 8). The same effect of degassing was observed with DPA and also with biacetyl, in one experiment where it was tried as sensitizer. Rubrene and perylene were not used in oxygen-free solutions.

In order to establish that such acceleration of the rate was truly the result of the removal of oxygen and of no other unknown cause, a sealed ampoule of a degassed solution of D and DBA was first heated at 52° until the chemiluminescence had reached its peak and had started on its fast decline. The ampoule was then removed, quickly cooled in an ice bath, opened and swirled to hasten the saturation with air, and then reheated to 52°; its chemiluminescence now followed a slow course with a rate befitting that of a "normal" aerated solution, although with a lower intensity, as if less dioxetane were present (Figure 9). Thus the effect of oxygen removal is "reversible" only insofar as the rate constant is concerned, but not the intensity.

The effect of oxygen is so marked that it can readily be observed visually in a dimly lit room by comparing the luminescence of an aerated and of a degassed solution.

To test the assumption that the dioxetane is decomposing faster in the absence of oxygen, a series of am-

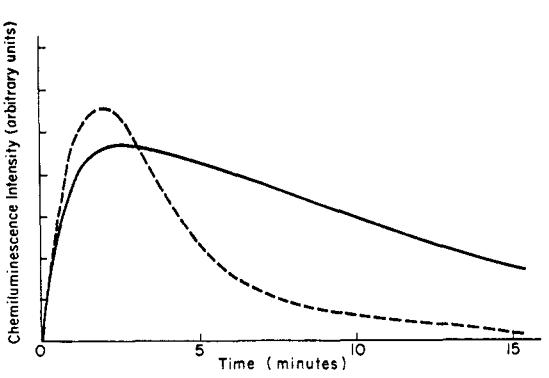

Figure 8. Effect of oxygen on the chemiluminescence. Initial concentrations: dioxetane D = 0.08 *M*, DBA = 0.018 *M*. Full line = aerated solution; broken line = degassed solution.

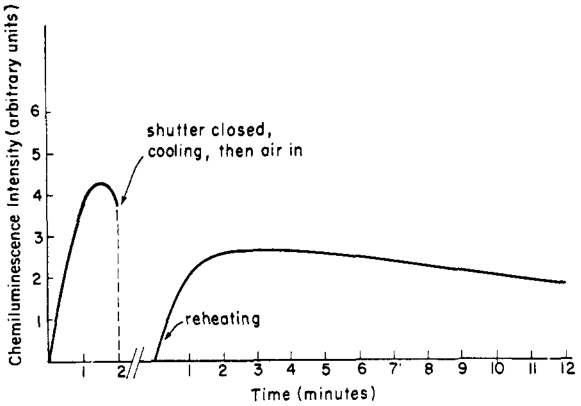

Figure 9. Effect on the chemiluminescence of admitting air into a degassed solution of dioxetane and DBA.

poules containing the same solution of dioxetane and DBA was prepared; then some of them were degassed. They were heated simultaneously at 55° for given periods of time, prior to titrating their dioxetane content iodometrically. The results are plotted in Figure 4; the broken lines indicate the slopes of the decay of luminescence intensity in a similar pair of experiments with or without O_2 at the same concentrations and temperature (from the data of Figure 8). Thus the faster decay of chemiluminescence matches indeed a faster decomposition of the dioxetane. In this particular set, the rate is increased by a factor of about 3. Comparable results were obtained at 46 and 52°.

Since the presence or absence of O_2 has no detectable influence on the rate of decomposition of pure dioxetane in benzene without sensitizer (Figures 4 and 10),[22] the effect of oxygen described above is clearly associated with the presence of the anthracene. It seems that oxygen prevents a decomposition of the dioxetane induced by the fluorescer.

Dye-sensitized photodecomposition of the dioxetane into ethyl formate had been detected, as an undesirable complication, during the final stages of the preparative photooxidation of *cis*-diethoxyethylene, if the photooxidation was carried too far. Furthermore, it had also been observed qualitatively that stopping the oxygen flow induced considerably faster decomposition of the dioxetane.[23]

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[21] That is, at least at the high concentrations of fluorescers (≥ 0.02 *M*) at which these degassed experiments were performed. One would expect a pronounced intensity enhancement at much lower concentrations of fluorescers (<0.001 *M*, the oxygen concentration in aerated solutions) because then quenching of $^3F^*$ by O_2 would prevail over energy transfer to A.

[22] This is also true for the rate in Freon 11, as monitored by nmr.

[23] P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N. Y. Acad. Sci.*, 171, 79 (1970).

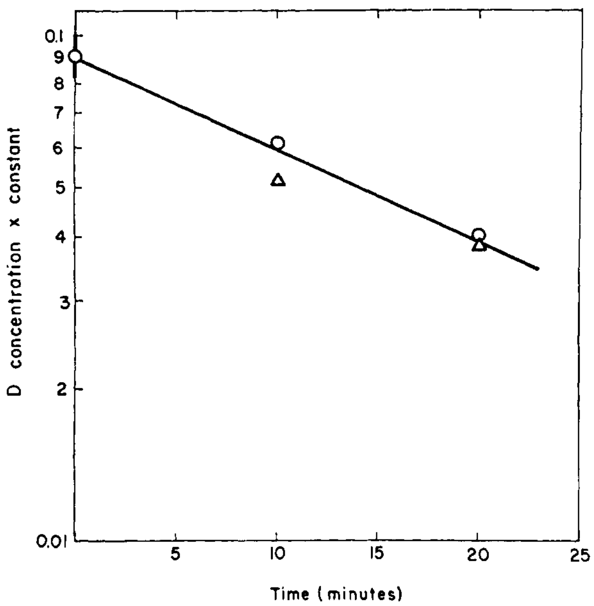

Figure 10. Effect of oxygen on the rate of decomposition of *cis*-diethoxydioxetane in benzene at 46°, by iodometry. No sensitizer present; initial D concentration = 0.09 *M*; ○ = aerated solutions; △ = degassed solutions.

These observations, and the results presented in this section, have very likely the same origin: the decomposition of the dioxetane sensitized by triplet excited dye or, here, by triplet excited anthracene, if these are not rapidly quenched by oxygen first.

The generation of a large amount of *triplet* anthracene is to be expected; excited singlet DBA was attributed to triplet-singlet energy transfer (see Discussion), but by and large energy transfer from $^3F^*$ to DBA (or DPA) can be expected to produce triplet DBA (or $^3DPA^*$). A kinetic scheme improving on reactions 1-5 should therefore include the following reactions.

$$^3F^* + A \xrightarrow{k_2} {}^1A^* + F \quad (2)$$

$$^3F^* + A \xrightarrow{k_2'} {}^3A^* + F \quad (2')$$

$$^1A^* \xrightarrow{k_4} A \quad (4)$$

$$^1A^* \xrightarrow{k_5} A + h\nu \quad (5)$$

$$^3A^* \xrightarrow{k_6} A \quad (6)$$

$$^3A^* + O_2 \xrightarrow{k_7} A + O_2 \quad (7)$$

$$^3A^* + D \xrightarrow{k_8} A + F + F \quad (8)^{24}$$

7. Photodecomposition of *cis*-Diethoxydioxetane Sensitized by Anthracenes. This mechanism is supported by exploratory experiments which showed that DPA or DBA can sensitize the decomposition of the dioxetane.

Stirred solutions of D and DPA or DBA in benzene at 5.5° were irradiated at 400 nm and the concentrations of dioxetane iodometrically titrated before and after. Without sensitizer the dioxetane is stable. Rapid decomposition took place with both sensitizers, even in the case of aerated solutions. While removing O_2 had little effect (20% or less) on the rate with DPA, it resulted in a 60-70% increase in the rate of the decomposition photosensitized by DBA (Table III).

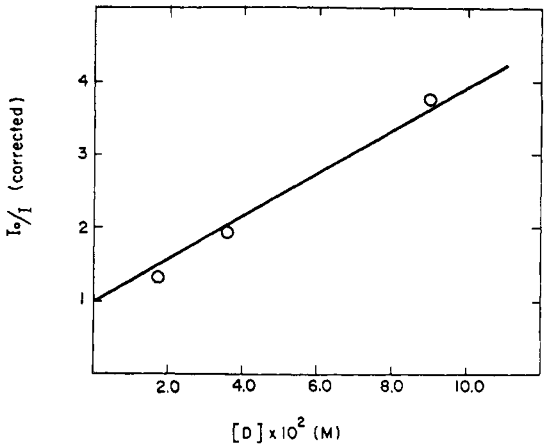

Figure 11. Quenching of 9,10-diphenylanthracene fluorescence by *cis*-diethoxydioxetane; exciting wavelength = 363 nm; concentration of DPA = 3 × 10^{-5} *M*; slope = 29.2.

Table III. Photodecomposition of *cis*-Diethoxydioxetane Sensitized by DBA or DPA at 400 nm and 5.5°

Initial concn, D × 10^2 *M*	Sens	Sens concn × 10^3 *M*	O_2	Mol of D decomposed/ min (× 10^3)
4.63	DBA	7.7	No O_2	2.5
4.63	DBA	7.7	With O_2	1.6
4.37	DBA	7.7	No O_2	2.7
4.37	DBA	7.7	With O_2	1.6
5.63	DPA	1.5	No O_2	1.82
5.63	DPA	1.5	With O_2	1.51
2.87	DPA	1.5	With O_2	0.93
2.87	DPA	1.5	With O_2	0.91
1.50	DPA	1.5	No O_2	0.70
3.17	None		With O_2	0.04

This difference in behavior of DBA and DPA as sensitizers can be rationalized. Both act efficiently as *singlet* sensitizers of the dioxetane decomposition. The fluorescence yield of DPA is near unity (0.89);[25] its yield of intersystem crossing is only 0.03.[25] Practically no triplet DPA is formed so that the small inhibitory effect of oxygen corresponds to the inefficient deactivation of the singlet state. Therefore triplet DPA probably plays no role in the photosensitized decomposition of the dioxetane. On the other hand, the fluorescence yield of DBA is only 0.1;[26,27] *i.e.*, its rate of intersystem crossing is faster. The resulting singlet lifetime (1.8 nsec)[27] is five times shorter than that of singlet DPA.[28] Therefore an appreciable part of the quanta absorbed by DBA serves to populate the triplet state. $^3DBA^*$, like $^1DBA^*$, is able to sensitize the decomposition of the dioxetane, although perhaps less efficiently. The longer lived triplet of DBA is more efficiently quenched by oxygen than the short-lived singlet state.

8. Quenching of the Fluorescence of DPA by *cis*-Diethoxydioxetane and by Oxygen. If singlet energy

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(24) The question of the electronic states of the formates produced by (8) will be discussed later.

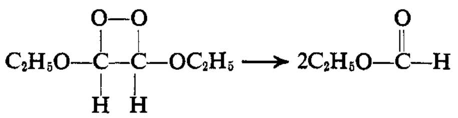
(25) C. A. Parker and T. A. Joyce, *Chem. Commun.*, 744 (1967).

(26) W. H. Melhuish, *J. Sci. Technol.*, **37B**, 142 (1955).

(27) R. S. H. Liu and D. M. Gale, *J. Amer. Chem. Soc.*, **90**, 1897 (1968).

(28) I. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, London, 1965.

Table IV. Estimates of the Heat of Reaction[a]



$$C_2H_5O-\underset{H}{\overset{O-}{C}}-\underset{H}{\overset{-O}{C}}-OC_2H_5 \longrightarrow 2C_2H_5O-\overset{O}{\overset{\|}{C}}-H$$

ΔH_f°(dioxetane D)		a. From Benson's Group Additivity Method[b] ΔH_f°(ethyl formate F)		Balance
Group contribution	−128	Group contribution	−90	
Cis and gauche				
Corrections	~2			
Ring strain[c]	~26			$\Delta H = 2\Delta H_f$°(F) − ΔH_f°(D)
ΔH_f°(D)	−100	ΔH_f°(F)	−90	$\Delta H = -80$
Energy spent		**b. From Bond Energies[d] Energy gained**		**Balance**
C—C	83	2C═O[e]	181	
O—O	35	Ring strain[c]	~26	
		Resonance energy[f]	~10	
	118		217	$\Delta H = -99$

[a] All data in kcal mol^{-1}. [b] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [c] Ring strain in cyclobutane. [d] From J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965. [e] The second bond in C═O is taken as the difference between C═O = 176 kcal and C—O = 85.5 kcal. [f] The resonance stabilization energy in methyl acetate is 15 kcal;[d] from the same table, we calculate this to be about 10 kcal for methyl formate.

transfer is responsible for the photodecomposition of the dioxetane sensitized by DPA, the dioxetane should quench the fluorescence of DPA. Figure 11 shows a Stern–Volmer plot of this quenching. Because of the weak but nonnegligible absorption by the dioxetane at the exciting wavelength ($\epsilon_{363\ \mathrm{nm}} \approx 5$, see Figure 1), a small correction based on the geometry of the instrument was applied to the observed I_0/I ratio. The slope of 29.2 corresponds to a k_Q of $2.92 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ (with τ_s DPA = 10^{-8} sec). Thus the dioxetane quenches singlet DPA at a nearly diffusion-controlled rate.

Last, the small effect of oxygen on the rate of decomposition of the dioxetane sensitized by DPA is compatible with the amount of quenching of DPA fluorescence by O_2. The fluorescence of an aerated solution of DPA was found to be about 20% weaker than that of a degassed sample, a result which is in agreement with the literature as well as with the extent of the observed effect of O_2 on the dioxetane decomposition (Table III).

Discussion

Our results support the hypothesis that thermal cleavage of the dioxetane can yield one excited molecule of the ethyl formate, which subsequently transfers its energy to a fluorescer.

Two different methods of estimating the heat of reaction are listed in Table IV. A major uncertainty is attached to the "strain" of the dioxetane ring, which is assumed in both calculations to be the same as in cyclobutane. In any event, Figure 12 shows that a total energy of 104–123 kcal is available to excite one molecule of ethyl formate either to its singlet excited state or to its first triplet state. The singlet state may be estimated at 118 kcal above ground state;[29] the energy of the first triplet state is unfortunately not known.

Our attempts at observing any luminescence—fluorescence or phosphorescence—from ethyl formate have been unsuccessful. The singlet–triplet splitting is unlikely to be large in this type of carbonyl compound and therefore E_T is probably >90 kcal. Thus decomposition of D should not give *two* ethyl formate molecules in the triplet state.

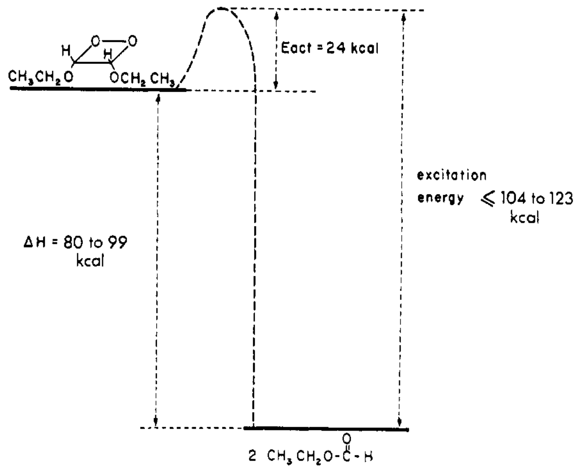


Figure 12. Energy available for excitation of ethyl formate from the thermal decomposition of *cis*-diethoxydioxetane.

The appreciably higher chemiluminescence yield with DBA compared to DPA[30] (in spite of a fluorescence yield ten times smaller) is an effect that Vassil'ev[7,31] was the first to observe in other chemiluminescent systems. He attributed it to a decrease in the forbiddenness of the exchange energy transfer[32] from a triplet donor to a singlet acceptor (DBA), where the bromine substituents induce a mixing of triplet and singlet states because of

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(29) Based on our guess of 240 nm for the 0–0 band in the absorption spectrum of ethyl formate published by J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 429. However, one of the referees points out that this 240-nm band may correspond to a Franck–Condon singlet, if the geometry of ethyl formate is very different in the excited state from that in the ground state, and thus that the true 0–0 singlet state could be appreciably lower in energy.

(30) Similarly observed with trimethyldioxetane, see ref 8.

(31) R. F. Vassil'ev, *Nature (London)*, **196**, 668 (1962); see also, *Opt. Spectrosc. (USSR)*, **18**, 234 (1965).

(32) Not to be confused with a triplet–singlet resonance transfer, such as in the examples studied by R. E. Kellogg, *J. Chem. Phys.*, **47**, 3403 (1967), and references therein.

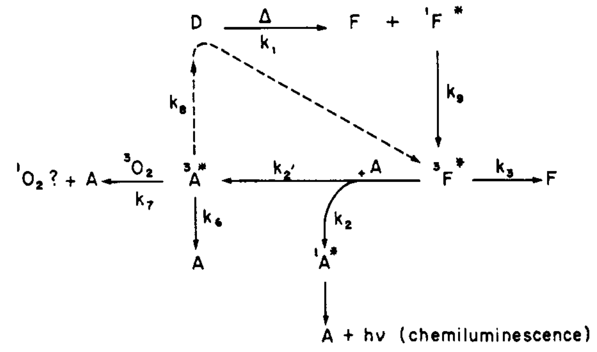

Figure 13. Reaction scheme illustrating the thermal decomposition of *cis*-diethoxydioxetane (D) to ethyl formate (F) and its chemiluminescence in the presence of an anthracene derivative (A) as fluorescer. The broken line is one possible path of decomposition of D induced by ^{3}A* (reaction 8) in oxygen-free solutions.

enhanced spin–orbit coupling of the electrons. According to Vassil'ev's latest experimental figures,[7] the rate constant for energy transfer from a triplet carbonyl (acetophenone or cyclohexanone) to singlet DBA is $\sim 3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, *i.e.*, about 100 times slower than the allowed, diffusion-controlled triplet–triplet transfer between these two molecules, whereas for DPA the rate of triplet–singlet transfer is only about $10^6\ M^{-1}\ \text{sec}^{-1}$.

Direct formation of triplet formate from the dioxetane cleavage would not conserve the spins. It is therefore likely that ethyl formate is formed first in its singlet excited state, and then undergoes very rapid and efficient intersystem crossing to the triplet state.[33] However, there is no experimental evidence for singlet formate, considering that even DPA at a concentration of 0.1 M acquires its singlet energy from triplet formate (see below). Neglecting internal conversion and quenching of ^{1}A*, the various reaction steps so far discussed can be visualized as shown in Figure 13. In the presence of oxygen, the fate of ^{3}A* can be disregarded ($k_7[\text{O}_2] \gg k_8[\text{D}]$). With $k_2 \ll k_{2'}$, the expression for the quantum yield now becomes

$$\Phi = \Phi_\text{F} \frac{k_2[\text{A}]}{k_{2'}[\text{A}] + k_3}$$

and therefore the experimental ratio of rate constants derived from Figure 7 is $k_3/k_{2'} \approx 10^{-2}\ M$. As $k_{2'} \approx 3 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ (diffusion controlled), $k_3 = 3 \times 10^8\ \text{sec}^{-1}$ is the total rate of decay of ^{3}F* by modes other than energy transfer to DBA; taking $[\text{A}] = [\text{DBA}] = 2 \times 10^{-2}\ M$ gives $(k_{2'}[\text{A}] + k_3) = 6 \times 10^8\ \text{sec}^{-1}$. Using Vassil'ev's value for $k_2 \approx 3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, $k_2[\text{A}] = 6 \times 10^6\ \text{sec}^{-1}$ yields $k_2[\text{A}]/(k_{2'}[\text{A}] + k_3) \approx 10^{-2}$.

At 20°, the quantum yield of fluorescence of DBA is 0.1. However, the fluorescence of DBA probably has a negative activation energy as large as that of 9,10-dichloroanthracene ($\Delta H = -4$ kcal)[19a] which would bring the Φ_F for DBA down to 0.05 at 55°. Consequently, the value for the quantum yield of chemiluminescence calculated from the proposed mechanism is $\Phi_\text{DBA} \approx 0.05 \times 10^{-2} \approx 5 \times 10^{-4}\ h\nu\ \text{molecule}^{-1}$, in striking agreement with experimental results (Table II).

This is important, because it shows that the *primary yield of triplet excited formates must be unity or near unity; that is, one molecule of triplet formate is formed per molecule of dioxetane decomposing*, a result that strongly supports McCapra's view of the cleavage of a dioxetane as requiring excited products.[3,34]

It is evidently difficult to estimate the limits of accuracy for the various rate constants entering in the above calculation. That the primary yield of triplet excited formates ($\Phi_{^3\text{F}^*}$) has to be very high is, however, intuitively obvious. Indeed, if is is accepted that ^{1}DBA* is produced from ^{3}F*, which seems ineluctable in view of the higher yield with DBA than with DPA, then one has to expect this energy transfer process to be inefficient compared to the competing triplet–triplet transfer. In other words, the yield of ^{1}DBA* produced by collisions between ^{3}F* and DBA can only be but a fraction of that of ^{3}DBA* produced; thus a value of 0.01 for this transfer yield $\Phi_{\text{t-s}}$ does not appear excessive. Now

$$\Phi_\text{DBA} = \Phi_{^3\text{F}^*}\Phi_{\text{t-s}}\Phi_\text{F}$$

with the fluorescence yield $\Phi_\text{F} \approx 0.05$ as above. Thus, here again one sees that the experimental value for the chemiluminescence yield $\Phi_\text{DBA} = 5 \times 10^{-4}$ corresponds to a primary yield of excited formates $\Phi_{^3\text{F}^*} \approx 1$.

It should be recalled here that the experiments with quick temperature changes also ruled out the existence of an alternate, low activation path for the thermal decomposition of the dioxetane.

When DPA is the sensitizer, the same calculation (with $k_2 \approx 10^6\ M^{-1}\ \text{sec}^{-1}$, $\Phi_\text{F} \approx 1$ and $[\text{A}] = [\text{DPA}] = 0.1\ M$, see Table II) gives $\Phi_\text{DPA} \approx 3 \times 10^{-5}\ h\nu\ \text{molecule}^{-1}$ which can also be considered in satisfactory agreement with the experimental result, and thus strongly supports the conclusion that DPA, like DBA, is excited by a triplet–singlet energy transfer.[35]

It may be worth pointing out that a triplet–triplet annihilation, which could in principle account for the generation of singlet excited fluorescers from triplet excited formates,

$$^3\text{A}^* + {}^3\text{A}^* \longrightarrow {}^1\text{A}^* + \text{A}$$

cited formates, is not compatible with the experimental data. Besides the fact that T–T annihilation is exceedingly unlikely in aerated solutions,[36] such a process would lead to a higher chemiluminescence yield with DPA than with DBA (because of the higher fluorescence yield and the longer triplet lifetime of DPA). Moreover, the rate of decay of the chemiluminescence intensity would then depend on the square of the dioxetane concentration instead of its first power, as it does.

The efficiency of DBA as a triplet to singlet energy converter was particularly well illustrated by one experiment. Drops of a DBA solution were added to a heated solution of dioxetane with rubrene as fluorescer. The low intensity of chemiluminescence immediately increased tenfold, yet its spectral distribu-

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(33) An alternative description can be given in terms of stationary states which necessarily have mixed singlet–triplet character.

(34) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

(35) If DPA acquired its excitation energy from intercepting singlet excited formates, then $k_{2'} = k_2 \approx 3 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ (for a diffusion-controlled s–s energy transfer). At the high concentration of DPA used, the experimentally observed $k_3/k_2 = 10^{-2}\ M$ would correspond to a quantum yield of about 1. The 10^5-fold discrepancy with the experimental value of Φ cannot be explained, for instance, by efficient excimer deactivation of ^{1}F* within the primary solvent cage, for the yield of ^{3}F* is very high in spite of ^{3}F* being formed *via* ^{1}F*. Without a knowledge of the electronic states and properties of simple esters like ethyl formates, it is inappropriate to try and ascertain why there is no evidence of s–s transfer to fluorescers; extremely fast intersystem crossing seems inescapable.

(36) C. A. Parker, "Photoluminescence of Solutions," Elsevier Publishing Co., New York, N. Y., 1968.

tion remained unchanged, still corresponding to the rubrene fluorescence. Evidently the DBA was more efficient than rubrene in the triplet–singlet energy transfer from the formate, but the singlet DBA thus formed was in turn deactivated at a diffusion-controlled rate by rubrene, thereby resulting in singlet excited rubrene which fluoresced with efficiency of unity.

The near-theoretical primary yield of triplet formates implied by the chemiluminescence efficiency with DBA contrasts with the results of White, *et al.*[37] These authors attempted to titrate chemically the triplet molecules produced by the decomposition of trimethyldioxetane: their best "primary" quantum yields are only of the order of 10^{-2}. However, there is direct evidence that trimethyldioxetane first generates singlet excited carbonyl fragments which have a tendency to form exciplexes;[5] this may well account for deactivation before intersystem crossing and triplet counting take place. A competing, nonchemiluminescent, biradical pathway of dioxetane decomposition is another possibility.

The major surprise of this work was, of course, the striking acceleration of the luminescence decay rate when the solutions are degassed. There is no doubt that this effect reflects the faster decomposition of the dioxetane itself. Furthermore, the photochemical evidence presented here strongly supports, in our view, an unusual type of "autosensitized" reaction whereby the electronic energy generated in the primary thermal cleavage of the dioxetane finally serves to "photo"-decompose another molecule of the peroxide.

The photosensitized decomposition of some peroxides has been shown to present unusual aspects.[38] Benzoyl peroxide, for instance, is decomposed by triplet sensitizers such as β-acetonaphthone (E_T = 59.3 kcal) and benzophenone (E_T = 69 kcal),[38b] although when benzophenone is the sensitizer complications due to hydrogen abstraction have to be taken into account.[39] Wagner and Hammond[40] pointed out that a "nonvertical" type of energy transfer is probably involved in these sensitized decompositions, as no low-lying triplet states are known for benzoyl peroxide. Aromatic hydrocarbons such as anthracene (E_T = 42 kcal) are also efficient as sensitizers of the decomposition of benzoyl peroxide,[38] but it is very likely that they act as singlet sensitizers (E_s(anthracene) = 75 kcal) in this case.[41]

The photochemical experiments presented in this paper clearly demonstrate that DPA is an efficient singlet sensitizer of the decomposition of *cis*-diethoxydioxetane: the dioxetane quenches the fluorescence of DPA at near-diffusion-controlled rate, whereas oxygen quenches equally poorly both DPA fluorescence and its sensitized decomposition of the dioxetane. Again with DBA, there is no doubt that singlet sensitization of the decomposition of D also takes place; however, now the larger inhibiting effect of oxygen very likely reflects a more important contribution from triplet DBA sensitization.

These results illustrate the special power of chemiluminescence as a photochemical tool. In our system, it is evident that in the case of DPA and to a lesser extent also with DBA, the singlet state of these sensitizers is nearly completely by-passed, thus reversing the photochemical conditions where singlet sensitization dominates.

As *cis*-diethoxydioxetane is very unlikely to possess any spectroscopic level as low as 40.2 kcal (E_T of DBA),[19b] again some type of nonvertical energy transfer or exciplex between the excited antracene and dioxetane must be invoked. Obvious experimental difficulties probably account for the dearth of spectroscopic data on triplet exciplexes,[42] but photochemical observations begin to suggest that such cases must occur.[43]

Whatever the intimate mechanism whereby the triplet anthracene induces the cleavage of the dioxetane, the ~40 kcal of triplet energy available more than covers the 24 kcal of activation energy for the thermal cleavage. In addition, the large exothermicity of the process may conceivably permit spin conservation as in eq 8 followed immediately by energy transfer to the

$$^3A^* + D \longrightarrow A + {}^3F^* + F \qquad (8)$$

anthracene present in the solvent cage. Reaction 8 would thus lead to autocatalytic decomposition of the dioxetane. Whether or not the transfer of energy of the $^3F^*$ to the anthracene within the cage would lead to the same proportion of triplet–singlet transfer *vs.* triplet–triplet transfer as in the bulk of the solvent is a matter of conjecture. If also in the cage about one transfer in 10^2 yielded $^1A^*$, degassing would have the following consequences: (a) an increase in the rate of decay of light intensity (and of dioxetane decomposition) by a factor depending on the length of the autocatalytic chain (2, 3, 4, or more), (b) an increase in the initial luminescence intensities such that the chemiluminescence quantum yield was not affected by the removal of oxygen, and (c) non-first-order plots of I_{chl} or D *vs.* time because of a second-order contribution in the rate equation.

On the other hand, reaction 8 followed by exclusive triplet–triplet energy transfer to generate $^3A^*$ and no $^1A^*$ would be accompanied by consequences (a) and (c) above. But there would be no increase in light intensity and thus an altogether smaller luminescence output would be observed.

Alternatively, instead of reaction 8 the induced decomposition of D may yield only ground-state products (reaction 8′) with the following experimental

$$^3A^* + D \longrightarrow A + F + F \qquad (8')$$

effects: (a) at most, if every $^3F^*$ formed *via* the thermal reaction (1) ultimately gave $^3A^*$, and every $^3A^*$ reacted with D *via* (8′), then the rate of decomposition of D in degassed solution would still be first order in D, but twice that of an aerated solution; (b) the chemiluminescence would only be generated by the fraction of dioxetane molecules that decomposes thermally; *i.e.*, the luminescence intensity and the quantum yield would be reduced by a factor of 2, at best.

The experimental data presented in the Results do not permit a positive decision between these alter-

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(37) E. H. White, J. Wiecko, and C. C. Wei, *J. Amer. Chem. Soc.*, **92**, 2167 (1970).

(38) (a) C. Luner and M. Zwarc, *J. Chem. Phys.*, **23**, 1978 (1955); (b) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3413 (1965).

(39) W. F. Smith, Jr., *Tetrahedron*, **25**, 2071 (1969).

(40) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(41) R. F. Vassil'ev and V. A. Krongauz, *Kinet. Katal.*, **4**, 55, 177 (1963).

(42) See Th. Förster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969).

(43) A. M. Braun, W. B. Hammond, and H. G. Cassidy, *J. Amer. Chem. Soc.*, **91**, 6196 (1969).

natives. Degassing increases the rate of decay of I_{chl} and of D by a factor larger than 2 (usually about 3), yet the data fit a first-order plot. The intensity is at first increased, but the total quantum yield is definitely reduced by degassing. To fit best the present data would seem to require some measure of involvement from both reactions 8 and 8′, which may be a possibility. Further experiments, including a study of the dependence of intensity and rate on concentration and temperature, as well as a determination of photochemical quantum yield, are clearly needed to permit a detailed analysis of the observed effect of oxygen.

A crude upper limit for k_8 or $k_{8'}$ can be derived from the experimental data, if oxygen and the dioxetane are considered as competing for the triplet anthracene (reaction 7 and 8). At the concentration of dissolved oxygen in aerated benzene solutions ($\sim 2 \times 10^{-3}$ *M*), oxygen suppresses reaction 8. Thus $k_7[O_2] > k_8[D]$, $[D] \approx 8 \times 10^{-2}$ *M*, and $k_7 = 10^{10}$ M^{-1} sec^{-1}; therefore $k_8 < 2.5 \times 10^8$ M^{-1} sec^{-1}. On the other hand, the observed cleavage of the dioxetane in the final stages of its synthesis *via* the photosensitized oxidation of *cis*-diethoxyethylene (E) (see Results, section 6) yields another very rough estimate for the rate constant of the similar reaction 10 (here S is tetraphenylporphin or rose bengal). Indeed ethyl formate from reaction 10 begins to

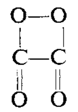
$$^3S^* + D \longrightarrow S + F + F \qquad (10)$$

$$^3S^* + O_2 \longrightarrow {}^1O_2 + S \qquad (11)$$

$$E + {}^1O_2 \longrightarrow D \qquad (12)$$

appear as a side product only toward the end of the synthesis of D, *i.e.*, when the concentration of D is ~ 0.2 *M*. Assuming that the concentration of O_2 in Freon 11 at $-78°$ is also $\sim 10^{-3}$ *M* and that then $k_{10}[D] \approx k_{11}[O_2]$, one gets $k_{10} \approx 5 \times 10^7$ M^{-1} sec^{-1}. It seems quite reasonable to consider that k_8 is of the order of 10^8 M^{-1} sec^{-1}.

In their recent communication on the dioxetane of tetramethoxyethylene, Mazur and Foote note that its decomposition appears to be catalyzed by zinc tetraphenylporphin.[6b] This observation recalls the most interesting results of Rauhut and coworkers on the chemiluminescence of oxalate esters. These authors found that the fluorescers they used act as catalysts for the decomposition of the intermediate,[2c,44] presumed to be



They suggested that the presence of an electronic energy sink (the fluorescer) accelerates the exothermic decomposition of C_2O_4. Definitely no such effect was observed with *cis*-diethoxydioxetane, which decomposes at the same rate with or without added fluorescer.[45] It is true that the induced decomposition of the dioxetane in the absence of oxygen superficially mimics a fluorescer catalysis. But Rauhut's observation and the "photo"-induced decomposition described here are two different phenomena. This points out the need for a deeper understanding of the alternate paths of decomposition of such energy-rich molecules as dioxetanes.

Several other interesting questions remain unanswered at this point. If oxygen quenching of triplet anthracene (reaction 7) produces singlet oxygen, as one would expect, what is its fate? Could it be identified through the use of suitably reactive acceptors?[46] Where is the triplet state of ethyl formate located? If it is higher than the triplet state of benzene ($E_T = 84$ kcal), the solvent benzene should intervene in the sequence of energy transfer from formate down to anthracene. Actually, there does not seem to be any evidence of benzene involvement; at any rate, triplet benzene, if formed from triplet formates, does not sensitize the decomposition of the dioxetane in degassed solutions (Figure 5). Is it meaningful that no photolysis products of ethyl formate (ethyl alcohol, in particular[47]) are observed among the products of the dioxetane thermal decomposition? Does it indicate that the excited ethyl formate is formed in an electronic level lower than that leading to photodecomposition?[29]

Conclusions

The important result of this study is undoubtedly the yield of chemiluminescence with DBA, which implies that one triplet formate is eventually produced per dioxetane molecule. Thus the Woodward–Hoffmann rules of orbital symmetry conservation may indeed be determinative in the chemiluminescent cleavage of dioxetanes.[3,34] The bright chemiluminescent reactions for which McCapra suggested mechanisms *via* intermediate (not isolated) dioxetanes very likely have high efficiencies also. However, the cleavage of these assumed dioxetanes yields products which are themselves good fluorescers, by contrast with ethyl formate: no energy transfer is then required.

The role of dissolved oxygen as a "protecting" agent was unexpected. The decomposition of the dioxetane sensitized by triplet anthracene thus brought to view deserves further and thorough study. The possibility that it may be autocatalytic and involve short excited-molecule reaction chains is particularly intriguing.

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[44] M. M. Rauhut, L. J. Bollyky, B. G. Roberts, M. Loy, R. H. Whitman, A. V. Iannotta, A. M. Semsel, and R. A. Clarke, *J. Amer. Chem. Soc.*, **89**, 6515 (1967).

[45] The same is true of trimethyldioxetane.[5]

[46] It was established, in an experiment with singlet oxygen generated by a discharge, that $^1O_2$ does not induce the decomposition of the dioxetane.

[47] (a) P. Ausloos, *J. Amer. Chem. Soc.*, **80**, 1310 (1958); (b) P. Ausloos, *Can. J. Chem.*, **36**, 383 (1958).