Adamantylideneadamantane-1,2-dioxetane. An Investigation of the Chemiluminescence and Decomposition Kinetics of an Unusually Stable 1,2-Dioxetane

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Abstract: The thermolysis of adamantylideneadamantane dioxetane **1** was investigated. The activation energy for cleavage of **1** was found to be ca. 37 kcal/mol and essentially solvent independent. The thermal decomposition of **1** is chemiluminescent. The yield and nature of the chemically produced excited states were determined by chemical titration and found to be ca. 2% singlet and ca. 15% triplet. Photolysis of **1** leads to the adiabatic formation of singlet and triplet adamantanone with yields of 8 and 40%, respectively. A detailed kinetic analysis of the photochemical reactions of adamantanone with *trans*-dicyanoethylene was carried out.

Chemiluminescence from the thermolysis of 1,2-dioxetanes is a recently discovered phenomenon.[2] Interest in this reaction stems not only from the experimental observation of the "cold light" phenomenon but also from a theoretical problem of understanding a mechanism for the conversion of *ground state* reactants into *excited state* products. An understanding of these reactions may lead to the ability to predict the design of chemiluminescent reactions and to establish a more complete picture of potential energy surfaces near crossing points.[3]

Several interesting observations have been made on the reactions of dioxetanes.[4] Perhaps the most outstanding of these was that tetramethyldioxetane yields *triplet* acetone with an efficiency nearly 50 times that for singlet production (eq 1).[5] Recent investigations have shown that both the

$$\text{(eq 1)} \qquad (1)$$
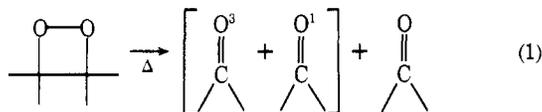
total yield of excited states and the ratio of triplet to singlet product may be dependent on the substituents on the dioxetane ring.[6]

Two general mechanisms have been advanced to explain the chemiluminescence of dioxetanes. Richardson has proposed an initial reversible cleavage of the oxygen-oxygen bond to yield a biradical intermediate (eq 2). Subsequent

$$\text{(eq 2)} \qquad (2)$$
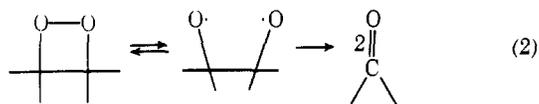
fragmentation of the biradical leads to the observed carbonyl compound products.[7] Thermochemical calculations based upon the proposed mechanism predict the observed activation energy for a number of different dioxetanes.[8] However, a standard biradical mechanism offers little insight as to the reason for the high efficiency of excited state production or to the high spin selectivity of the reaction.

A second proposal for the mechanism of the chemiluminescent decomposition of dioxetanes has been advanced by several workers. This mechanism postulates concerted bond cleavage leading directly to excited state products. A key concept in this mechanism was advanced by us to explain a correlation of electron motion and electron spin. In this case, intersystem crossing (singlet dioxetane to triplet ke-

tone or biradical) occurs along a concerted reaction coordinate.[4b] The rationalization for this special process involves the formal conversion of one of the σ electrons of the oxygen-oxygen bond to the π electron of the excited carbonyl group at the transition state.[9] The transition state for the thermolysis is thought to be at or near the potential energy surface for the triplet thereby facilitating surface crossing. Recent calculations by Dewar and elementary considerations of surface symmetries in forbidden pericyclic reactions[3d] tend to support this view.[3c]

Bis(adamantylidene)dioxetane (**1**) is of special interest because of its remarkable thermal stability.[10] It was our

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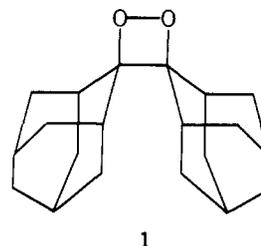
purpose to study the thermolysis of **1** with the hope of understanding what features of this structure contribute to this stability and how these structural features affect the course of the chemiluminescent reaction.

Results and Discussion

1. Preparation and Identification of 1. The preparation of **1** is readily accomplished (eq 3) by the dye sensitized addi-

$$\xrightarrow{^1O_2} \mathbf{1} \qquad (3)$$

2
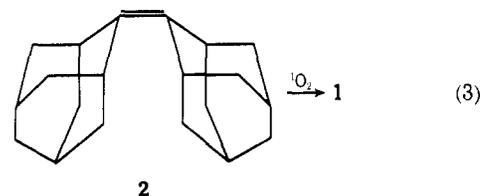
tion[10,11] of singlet oxygen to biadamantylidene (**2**). Since the stability of **1** is so much greater than that of other dioxetanes investigated, it is appropriate to consider the evidence that **1** is, indeed, a 1,2-dioxetane.
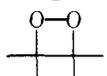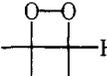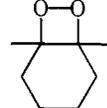
We find that the dioxetane structure of **1** is strongly supported by both chemical and spectroscopic evidence. Thermolysis of **1** yields adamantanone (**3**) as the only detected product (eq 4). The reduction of **1** with zinc in acetic acid

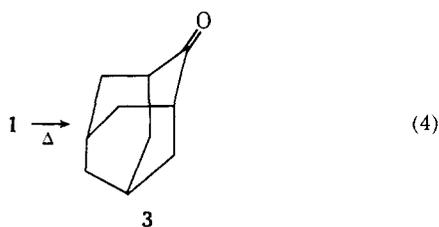Table I. ^{13}C NMR Chemical Shifts of Dioxetane 1 and Model Compounds

| Compd^a	δ ppm^b
1	95.0
Tetramethyl-1,2-dioxetane	89.4
Adamantylideneadamantane epoxide	72.7
Adamantylideneadmantane	133.5
Adamantanone	213.5

^{a} In benzene solution. ^{b} Relative to Me$_4$Si.

Table II. Position of O–O Stretch in Ir Absorption Spectrum in Various Dioxetanes

Compd^a	ν, cm^{-1} ^{b}
1	885 915
O–O	870
O–O —H	885
O–O	882 895

^{a} 0.1 M solutions in CCl$_4$. ^{b} Position of the O–O stretching absorption.

Figure 1. Ir absorption spectrum of 1 in CCl$_4$ solution. Note complete absence of carbonyl absorption.
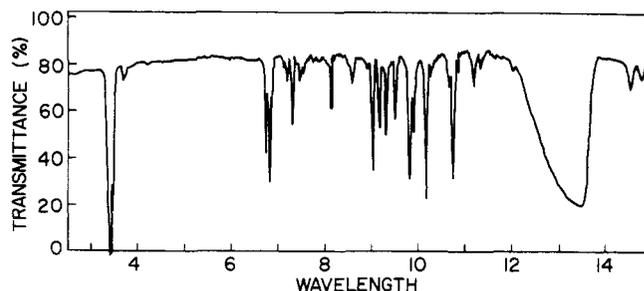
$$1 \xrightarrow{\Delta} 3 \qquad (4)$$

gives diol 4 in high yield (eq 5).[10] These reactions establish, beyond a reasonable doubt, the carbon framework of the molecule.

$$1 \xrightarrow{Zn-HOAc} 4 \qquad (5)$$
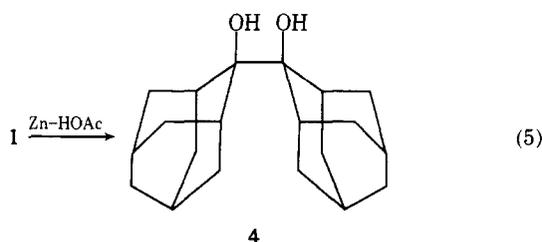
Spectroscopic investigation of 1 is also completely consistent with a 1,2-dioxetane structure for this compound. The ^{13}C NMR spectrum of 1 shows only one type of carbon bonded to oxygen.[12] The chemical shift of that carbon is consistent with the dioxetane structure (see Table I). The ir spectrum of 1 (Figure 1) shows an absorption assignable to oxygen–oxygen[13] deformation. This absorption is similar in position and intensity to the oxygen–oxygen stretch in other 1,2-dioxetanes (see Table II).

The mass spectrum of 1 shows a strong peak at m/e 300, corresponding to the molecular ion of the structure proposed for 1. No peaks at m/e value higher than 300 are observed. Fragmentation peaks in the mass spectrum of 1 are observed at m/e values corresponding to loss of one and two oxygen atoms. The base peak in the mass spectrum occurs at m/e 150 corresponding to the adamantanone molecular

weight. The Experimental Section should be consulted for further details of the mass spectrum of 1.

The uv absorption spectrum of 1 shows a maximum at 265 nm with extinction coefficient of 21.5 l./mol cm. The absorption shows no fine structure and exhibits a long wavelength tail which extends to ca. 420 nm (extinction coefficient of ca. 1.5 l./mol cm at 400 nm). The uv absorption spectrum of tetramethyldioxetane is very similar to that observed for 1.[13]

Of the various conceivable structures possible for the product of addition of singlet oxygen to olefin 2 (1, 5, 6), we
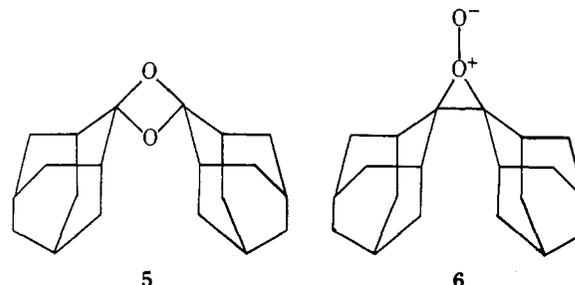
conclude that the considerable weight of the above chemical and spectroscopic evidence effectively rules out all plausible structures other than 1. Thus the inference that is drawn is that the thermal behavior of 1 must be understood in terms of other dioxetanes studied.

2. Chemiluminescence from the Thermolysis of 1. Thermolysis of 1 in a variety of solvents results in a readily detectable luminescence. The spectrum of the emitted light in acetonitrile at 82° shows a maximum at 420 ± 5 nm. This spectrum is virtually identical with the photoexcited fluorescence of adamantanone under comparable conditions. The emission and chemiluminescence spectra are shown in Figure 2. The observation of adamantanone fluorescence from the thermolysis of 1 suggests that a moderately high yield of singlet adamantanone was produced.

The formation of triplet adamantanone from the thermolysis of 1 is more difficult to establish because adamantanone phosphorescence cannot be observed in fluid solution near room temperature. However, the detection of triplet adamantanone by an indirect method is possible. It is well known that 9,10-dibromoanthracene (DBA) is capable of accepting the excitation energy from a triplet excited carbonyl group via *triplet to singlet* energy transfer. This energy transfer results in the formation of the fluorescent singlet state of DBA.[15] 9,10-Diphenylanthracene (DPA) is ca. 1000 times less efficient an acceptor of triplet energy via triplet to singlet energy transfer.[16] Significantly, we find that thermolysis of 1 in CH$_3$CN containing either DBA or DPA results in the chemi-excited emission of the added dyes. Comparison of the intensity of the chemi-excited dye emission (corrected for the difference in fluorescence effi-
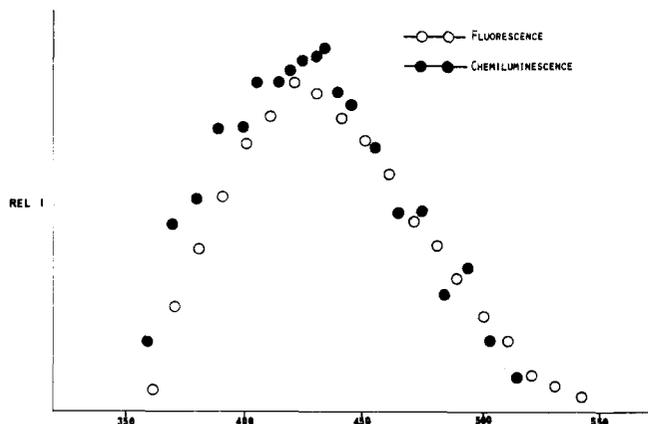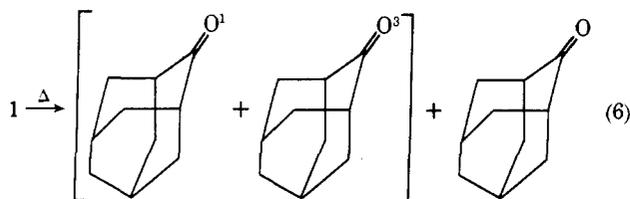
Figure 2. Fluorescence of adamantanone and chemiluminescence of 1 in CH_3CN at 82°.

ciency of the dyes at the appropriate temperature) indicates that a considerable yield of adamantanone triplet was formed on thermolysis of 1. Thus the preliminary indication was that both singlet and triplet adamantanone results upon thermolysis of 1 (eq 6).

An estimate of the ratio of the triplet to singlet excited adamantanone yields from the thermolysis of 1 can be obtained from the intensity of DBA and DPA chemi-excited emission intensity. This method of analysis has been described elsewhere.[16] The observed intensities of DPA and DBA emission were compared at extrapolated infinite dye concentration. Corrections were applied for differences in (a) energy transfer efficiency, (b) fluorescence efficiency of the dyes, and (c) cross activation (singlet–singlet energy transfer to DBA). The ratio of the corrected limiting intensities yields an approximate value for the ratio of the yields of excited states. A ratio of the yield of triplet to singlet excited adamantanone from 1 of ca. 10 was observed. This limiting intensity method was not capable of easily giving actual yields of excited states. Chemical titration[5] proved to be a more satisfactory method for the determination of the actual yields of the excited states produced from thermolysis of 1.

3. Chemical Titration of Excited States from Thermolysis of 1. Chemical titration[5] is a technique for determining the nature and the yields of chemically produced electronically excited states. A basic requirement of this procedure is that a specific and reliable reaction be available from both the singlet and triplet excited states of the species of interest. Simply by analyzing the types and yields of products formed, information on the primary yields of excited states can be evaluated. In the choice of a titrant, we were guided by the previous use of *trans*-dicyanoethylene (*t*-DCE) in the chemical titration of acetone excited states from the thermolysis of tetramethyldioxetane.[5]
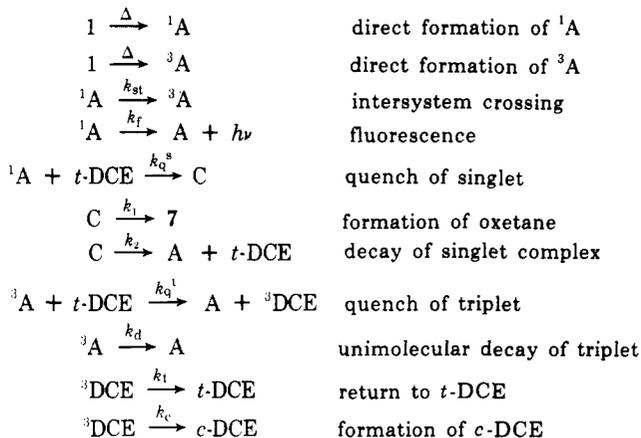
Adamantanone has previously been observed to form both an oxetane (7) and *cis*-dicyanoethylene (*c*-DCE) upon photolysis in the presence of *t*-DCE in acetonitrile solution.[17] In order that this reaction be of use as a chemical titration, it must first be determined if the different observed products result from different excited states of adamantanone, as is the case with acetone.[18] Furthermore, the *limit-*
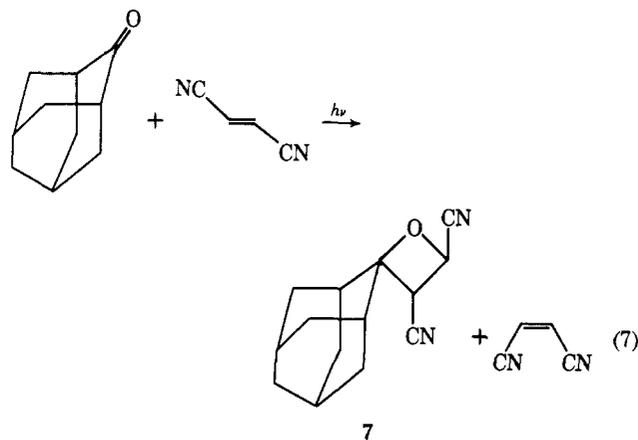
ing quantum yields for the formation of 7 and *c*-DCE must be determined. Finally, the effect of temperature on the limiting quantum yields must be measured. These parameters were determined by a detailed study of the photochemical reaction mechanism. A discussion of the photochemistry of this system is deferred to a later section of this paper.

With the knowledge of the photochemical parameters in hand, it was possible to proceed with the determination of the yields of excited states from the thermolysis of 1. Scheme I represents the series of reactions leading to the

Scheme I

$1 \xrightarrow{\Delta} {}^1A$		direct formation of ${}^1A$
$1 \xrightarrow{\Delta} {}^3A$		direct formation of ${}^3A$
${}^1A \xrightarrow{k_{st}} {}^3A$		intersystem crossing
${}^1A \xrightarrow{k_f} A + h\nu$		fluorescence
${}^1A + t\text{-DCE} \xrightarrow{k_q{}^s} C$		quench of singlet
$C \xrightarrow{k_i} 7$		formation of oxetane
$C \xrightarrow{k_i} A + t\text{-DCE}$		decay of singlet complex
${}^3A + t\text{-DCE} \xrightarrow{k_q{}^t} A + {}^3DCE$		quench of triplet
${}^3A \xrightarrow{k_d} A$		unimolecular decay of triplet
${}^3DCE \xrightarrow{k_t} t\text{-DCE}$		return to *t*-DCE
${}^3DCE \xrightarrow{k_c} c\text{-DCE}$		formation of *c*-DCE

observed chemical titration products. This sequence of reactions represents a slight departure from the normal photochemical mechanism in that triplet adamantanone (${}^3A$) can be formed in two distinct ways: first, the normal mode, intersystem crossing from adamantanone singlet (${}^1A$); second, direct formation of ${}^3A$ from the decomposition of 1. As we are primarily interested in the determination of the primary yields of triplet and singlet adamantanone resulting directly from the thermolysis, some procedure for separating the two paths of triplet formation had to be devised.

We define $\phi_S{}^*$ to be the number of ${}^1A$ molecules per molecule of 1 that decomposes and $\phi_T{}^*$ as the number of *directly* formed ${}^3A$ molecules per molecule of 1 that decomposes. By inspection of Scheme I we can write expressions for the yield of oxetane 7 (ϕ_{OX}) and *c*-DCE (ϕ_C).

$$\phi_{OX} = \phi_S{}^* \left(\frac{k_q{}^s[t\text{-DCE}]}{k_q{}^s[t\text{-DCE}] + k_{st} + k_f} \right) \left(\frac{k_1}{k_1 + k_2} \right) \quad (8)$$

$$\phi_C = \left[\phi_t{}^* + \left(\frac{k_{st}}{k_{st} + k_f + k_q{}^s[t\text{-DCE}]} \right) \phi_S{}^* \right] \times$$
$$\left[\left(\frac{k_c}{k_c + k_t} \frac{k_q{}^t[t\text{-DCE}]}{k_q{}^t[t\text{-DCE}] + k_d} \right) \right] \quad (9)$$

Equations 8 and 9 can be simplified considerably by ex-

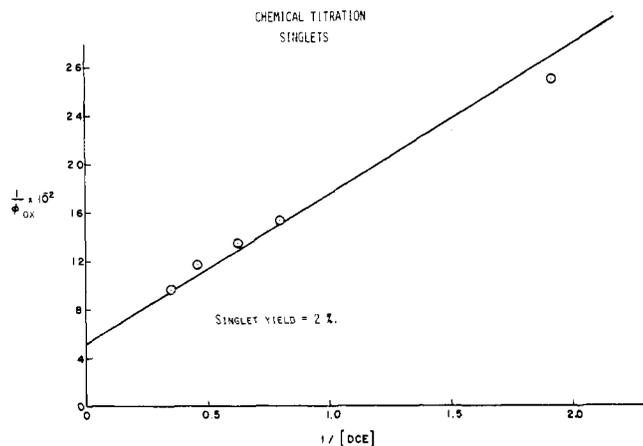Figure 3. Chemical titration of 1 with t-DCE in CH₃CN at 145°. Observation of singlet adamantanone.

Figure 4. Chemical titration of 1 with t-DCE in CH₃CN at 145°. Observation of triplet adamantanone.

trapolation to infinite t-DCE concentration. Rearrangement of eq 8 yields eq 10:

$$\frac{1}{\phi_{OX}} = \frac{1}{\phi_{S}^*}\left(\frac{k_1 + k_2}{k_1}\right)\left(1 + \frac{k_{st} + k_f}{k_q^s[t\text{-DCE}]}\right) \quad (10)$$

A plot of $1/\phi_{OX}$ against $1/(t\text{-DCE})$ according to eq 10 should give a line with intercept at infinite t-DCE concentration (ϕ_{OX}^∞) shown in eq 11.

$$\frac{1}{\phi_{OX}^\infty} = \frac{1}{\phi_{S}^*}\left(\frac{k_1 + k_2}{k_1}\right) \quad (11)$$

The value of the ratio $(k_1 + k_2)/k_1$ is the decay ratio determined by analysis of the photochemistry of the system (see below). Thus the value of ϕ_{S}^* can be calculated from eq 11.

The simplification of eq 9 is slightly more complex. In the region of high t-DCE concentration $(t\text{-DCE} > 2.0\ M)$, the term for the quantum yield of intersystem crossing of ^1A is less than 4% of the value in the absence of t-DCE. This estimate is based upon the measured rate of fluorescence quenching of ^1A by t-DCE (see below). The estimated value of ϕ_{S}^* is ca. 10% (see above) of the triplet yield. Thus in the high concentration region, eq 12 applies.

$$\phi_t^* \gg \left(\frac{k_{st}}{k_{st} + k_f + k_q^s[t\text{-DCE}]}\right)(\phi_s^*) \quad (12)$$

At the limit of infinite t-DCE concentration, the smaller term in eq. 12 can be neglected. With these modifications eq 9 can be rewritten as eq 13.

$$\frac{1}{\phi_C} = \frac{1}{\phi_t^*}\left(\frac{k_c + k_t}{k_c}\right)\left(1 + \frac{k_d}{k_q^t[t\text{-DCE}]}\right) \quad (13)$$

A plot of $1/\phi_C$ against $1/(t\text{-DCE})$ according to eq 13 is predicted to yield a straight line with an intercept at infinite concentration (ϕ_C^∞) shown in eq 14.

$$\frac{1}{\phi_C^\infty} = \frac{1}{\phi_t^*}\left(\frac{k_c + k_t}{k_c}\right) \quad (14)$$

Again the decay ratio of DCE triplet is identical with the photochemically determined value (see below), and a value for the triplet yields can be calculated from eq 14.

Solutions of 1 in CH₃CN containing from 0.5 to 2.79 M t-DCE were thermolyzed in sealed tubes at 145° for 2 days. Control experiments showed that oxetane 7 was stable under these conditions and that a very slow thermal isomerization of t-DCE to c-DCE occurred, which was easily corrected for. Figures 3 and 4 show plots of $1/\phi_{OX}$ and $1/\phi_C$ against $1/(t\text{-DCE})$ according to eq 10 and 13, respectively. Reasonable straight lines are observed in both plots. One final assumption was necessary before the singlet and triplet
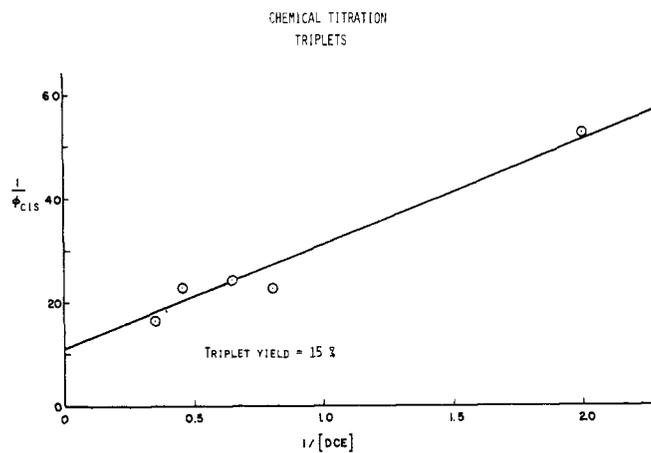
Table III. Rate Constants and Activation Parameters for Thermolysis of Dioxetane 1

T, K[a]	$k \times 10^5$[b]	$E_A{}^c$, kcal/mol
415.4	6.67 ± 0.25	
420.2	10.4 ± 0.7	
424.5	13.9 ± 0.34	34.6 ± 1.5
433.2	37.8 ± 0.32	
435.2	41.2 ± 0.61	

[a] o-Xylene solution 0.02 M in 1. [b] least-squares value, followed for at least 3 half-lives. [c] Eyring activation enthalpy, $\Delta H^\ddagger = 33.8$ kcal/mol; Activation entropy, $\Delta S^\ddagger = 2.9 \pm 2$ eu.

yields could be calculated, namely the temperature dependence of the decay ratios leading to 7 and c-DCE. Since no change in the measurable parameters leading to the decay ratios was observed over the temperature range from 25 to 90° (see below), the assumption was made that no change in these ratios occurs at 145°, the temperature of the chemical titration. With this consideration, the intercepts of Figures 3 and 4 yield values of ca. 2% for ϕ_S^* and ca. 15% for ϕ_T^*, respectively. The estimated error in these quantities is about 50% of the reported value.

The ratio of ϕ_T^*/ϕ_S^* from the chemical titration was ca. 7.5. This compares very favorably with the value for this ratio of ca. 10 calculated above from the limiting intensities of DBA and DPA activated emission. The fact that these numbers are within probable experimental error of each other tends to confirm the validity of the methods of analysis.

4. Activation Energy Analysis of Thermolysis of 1. The remarkable stability of 1 has been commented upon previously.[10] To gain a better understanding of the mechanistic implication of this stability, the activation parameters for the thermal decomposition of 1 were determined.

Conventional kinetic methods were used to determine the rate of reaction of 1 at several temperatures in xylene solvent. The disappearance of 1 was first order over the entire temperature range studied. The results of the analysis are shown in Table III. The calculated activation energy for the reaction by this method was 35 ± 2.0 kcal/mol. This activation is nearly 10 kcal/mol greater than that measured for any other dioxetane studied.[19] The activation entropy of this reaction was found to be 2.9 ± 2.0 eu. This value is typical of uncatalyzed unimolecular rearrangement of 1,2-dioxetanes.[4b,c]

Chemiluminescent reactions are somewhat unique in that a method is available for the determination of the activation energy for that fraction of the total reaction leading to
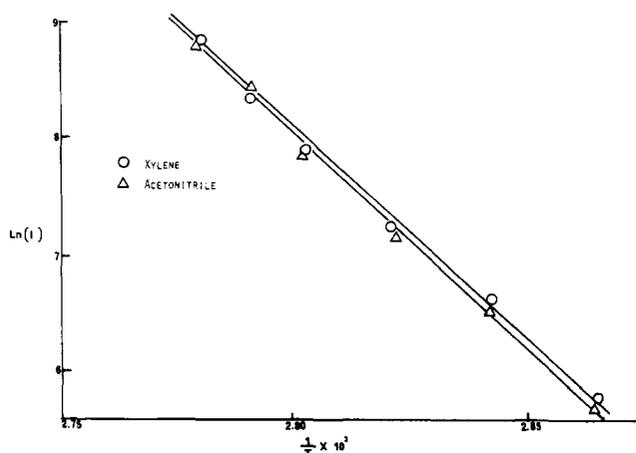
Figure 5. Step function activation energy of 1 in CH₃CN and xylene.

chemiluminescence.[20] An expression for the intensity of the chemiluminescence observed from **1** can be written as eq 15

$$I_{cl}{}^t = K\phi_s{}^*\phi_{fl}k_t[\mathbf{1}] \qquad (15)$$

where $I_{cl}{}^t$ is the observed chemiluminescent fluorescence intensity from thermolysis of **1** at temperature t, K is an instrument parameter containing spectral response, amplification, and light collection optics, $\phi_s{}^*$ is the previously defined singlet yield, ϕ_{fl} is the efficiency of fluorescence from singlet adamantanone, and k_t is the first-order rate constant for the reaction of **1** leading to singlet adamantanone at temperature t. At the highest temperature employed (86.6°) for this analysis, the concentration of **1** changes by less than 0.01% during the time the measurement is made. Thus the concentration of **1** may be treated as a constant in eq 15. The relative value of ϕ_{fl} was measured over the temperature range 25 to 92.1° and found to be invariant. With the further assumption that $\phi_s{}^*$ is also temperature independent, eq 15 can be rewritten as eq 16, where $K' = K\phi_s{}^*\phi_{fl}[\mathbf{1}]$. Substitution of the Arrhenius expression for k_t in eq 16 results in eq 17.

$$I_{cl}{}^t = K'k_t \qquad (16)$$

$$\ln I_{cl}{}^t = \ln (K' + A) + E_a/RT \qquad (17)$$

A plot of $\ln I_{cl}{}^t$ against $1/T$ gave a straight line, strengthening the above assumptions. From the slope of the line, a value for the activation energy E_a can be extracted. Unfortunately, the value of the constant K' is very difficult to obtain, and thus information from the intercept is lost.

When this "step" method of analysis was applied to thermolysis of **1**, values of the activation energy could be determined (see Figure 5). In xylene, the activation energy determined by the step method was 39.7 ± 3 kcal/mol and in acetonitrile, 38.3 ± 3 kcal/mol. These values are slightly higher than those measured by the total rate of reaction. We feel, however, that the difference is due to the considerable difference in the techniques rather than a mechanistic consequence. The important point we wish to emphasize is that the activation energy measured is again ca. 10 kcal/mol above the measured for any other known and measured dioxetane.

5. Photoexcitation of Bis(adamantyladamantane)dioxetane.

It has been previously observed that tetramethyldioxetane yields excited acetone by photoexcitation as well as by thermolysis.[21] The spectroscopy of **1** was investigated to determine if **1** also underwent an adiabatic photochemical reaction[22] (eq 18).

$$1 \xrightarrow{hv} 1^* \longrightarrow \qquad\qquad (18)$$
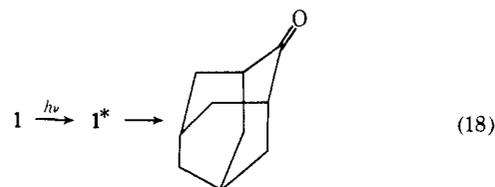
Photoexcitation of **1** in acetonitrile solution at room temperature with 280-nm light led to an easily detectable amount of adamantanone fluorescence. The emission was identified as fluorescence by both spectral overlap and the identical lifetimes of photoexcited and adamantanone fluorescence decay. The yield of singlet adamantanone from photolysis of **1** can be estimated by comparison to adamantanone fluorescence intensity. An expression for the intensity of photoexcited emission intensity $(I_{cl}{}^{Ph})$ is shown in eq 19

$$I_{cl}{}^{Ph} = K\phi_S{}^{Ph}\phi_{fl}P_{abs}{}^1 \qquad (19)$$

where K is an instrument constant, $\phi_S{}^{Ph}$ is the yield of adamantanone singlet from photolysis of **1**, ϕ_{fl} is the fluorescence quantum yield of adamantanone under these conditions, and $P_{abs}{}^1$ is the fraction of the incident light absorbed by dioxetane **1**. A similar expression can be derived for the intensity of fluorescence from photoexcited adamantanone (I_{Ad}) as shown in eq 20

$$I_{Ad} = K\phi_{fl}P_{abs}{}^{Ad} \qquad (20)$$

where K is the same instrument constant as in the previous expression, and $P_{abs}{}^{Ad}$ is the fraction of the light absorbed by adamantanone. Comparison of the intensity of fluorescent emission from photoexcited **1** and adamantanone allows the calculation of $\phi_S{}^{Ph}$; see eq 21.

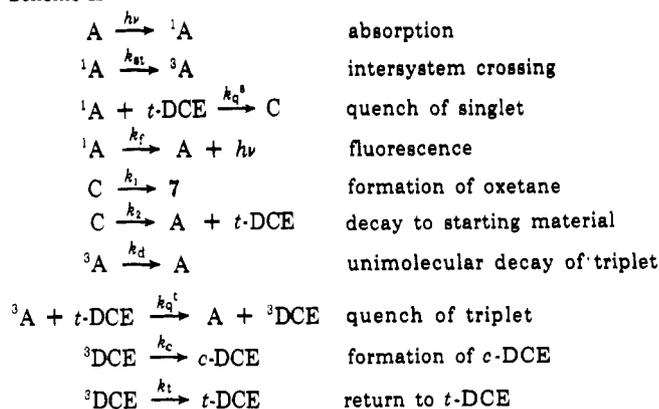$$\phi_S{}^{Ph} = (I_{cl}{}^{Ph}P_{abs}{}^{Ad})/(I_{Ad}P_{abs}{}^1) \qquad (21)$$

Application of this method yielded a value of about 8% for $\phi_S{}^{Ph}$. Thus the photoexcited singlet yield was ca. five times the singlet yield for thermolysis of **1**. A similar increase in singlet yield has also been observed for tetramethyldioxetane.[14]

The triplet yield from the photolysis of **1** ($\phi_T{}^{Ph}$) was determined by an entirely analogous procedure. The phosphorescence intensity from **1** and adamantanone in EPA at 77 K was determined and corrected for differences in optical density. In this case the assumption was made that, under these conditions, the intersystem crossing yield of adamantanone was unity. The calculated value of the yield of photoexcited triplets from dioxetane **1** ($\phi_T{}^{Ph}$) was ca. 40%.

6. Photochemistry of Adamantanone and *t*-DCE.

It was necessary to investigate the reaction between photoexcited adamantanone and *t*-DCE in considerable detail. As a working hypothesis the mechanism shown in Scheme II was proposed for the photoreactions in this system. The proposed mechanism postulates exclusive formation of **7** via singlet adamantanone and formation of *c*-DCE via triplet adamantanone only. One point that deserves comment at this time concerns the intermediate C. The exact nature of C is not known; it may be a charge-transfer complex, exciplex, or Schenck type one bond intermediate.[18,23] However, it is certain that an energy wasting intermediate proceeds formation of **7**.

Investigation of the mechanism proposed in Scheme II proceeded along three major paths. First, the effect of temperature on the quantum yields for product formation and the nature of the excited states leading to product were determined. Second, determination of the ratio of decay pathways for the intermediates C and ³DCE was made. Third,

Scheme II

$$A \xrightarrow{h\nu} {}^1A \qquad \text{absorption}$$

$${}^1A \xrightarrow{k_{st}} {}^3A \qquad \text{intersystem crossing}$$

$${}^1A + t\text{-DCE} \xrightarrow{k_q{}^s} C \qquad \text{quench of singlet}$$

$${}^1A \xrightarrow{k_f} A + h\nu \qquad \text{fluorescence}$$

$$C \xrightarrow{k_1} 7 \qquad \text{formation of oxetane}$$

$$C \xrightarrow{k_2} A + t\text{-DCE} \qquad \text{decay to starting material}$$

$${}^3A \xrightarrow{k_d} A \qquad \text{unimolecular decay of triplet}$$

$${}^3A + t\text{-DCE} \xrightarrow{k_q{}^t} A + {}^3DCE \qquad \text{quench of triplet}$$

$${}^3DCE \xrightarrow{k_c} c\text{-DCE} \qquad \text{formation of } c\text{-DCE}$$

$${}^3DCE \xrightarrow{k_t} t\text{-DCE} \qquad \text{return to } t\text{-DCE}$$

Figure 6. Determination of limiting quantum yield of singlet adamantanone and t-DCE.

identification of the excited state of adamantanone responsible for the observed reactions was carried out.

Two methods were employed for the determinamvof the limiting quantum yield for the formation of 7. The quantum yield for the formation of 7 (ϕ_{OX}) has been determined previously at room temperature in acetonitrile with t-DCE concentration at 0.1 M.[24] The room temperature reaction therefore proved to be the ideal actinometer for measuring the quantum efficiencies of the processes outlined in Scheme II. The value of ϕ_{OX} at 90° was determined by simultaneously irradiating identical solutions of adamantanone and t-DCE in acetonitrile in jacketed test tubes. Water at 25° was circulated through the jacket of the actinometer tubes while water at 90° was circulated through the jacket of the experimental tubes. The solutions were irradiated with light filtered so that only the adamantanone absorbed The amount of oxetane 7 in each tube after photolysis was determined by VPC. Comparison of the amount of 7 formed at 25 and 90° results in a value of ϕ_{OX} at 90° under these conditions of 0.12. This compares with the previously measured value of 0.14 at room temperature. We consider these values to be the same within the experimental error of the determination.

From inspection of the proposed mechanistic sequence shown in Scheme II, the analytic expression for ϕ_{ox} shown in eq 22 can be derived

$$\frac{1}{\phi_{ox}} = \frac{k_1 + k_2}{k_2}\left(1 + \frac{1}{k_q{}^s \tau_s[t\text{-DCE}]}\right) \qquad (22)$$

where $\tau_s = 1/(k_{st} + k_f)$

As previously mentioned, the key value for the chemical titration was the decay ratio $k_1/(k_1 + k_2)$. If the value of $k_q{}^s\tau_s$ were known, a value for this decay ratio could be obtained from eq 22. This necessary value for $k_q{}^s\tau_s$ could be obtained from the fluorescence quenching of singlet adamantanone by t-DCE at 90°. The normal Stern–Volmer treatment of fluorescence quenching gives eq 23, where $I°$ is the unquenched intensity and I the intensity at various t-DCE concentrations.

$$I°/I = 1 + k_q{}^s\tau_s[t\text{-DCE}] \qquad (23)$$

A plot of $I°/I$ against t-DCE concentration according to eq 23 was linear and gave the predicted intercept. From this plot, a value of $k_q{}^s\tau_s$ equal to 43 l./mol was extracted. By substituting this value in eq 22, a value for the decay ratio of 0.15 was obtained. The significance of this quantity was that only 15% of the adamantanone singlets that *were quenched* by t-DCE lead to 7. Thus the necessity for the energy wasting decay of C in the proposed mechanism was confirmed. The room temperature value for this decay ratio has been shown to be 0.16.[24] It appears therefore that there
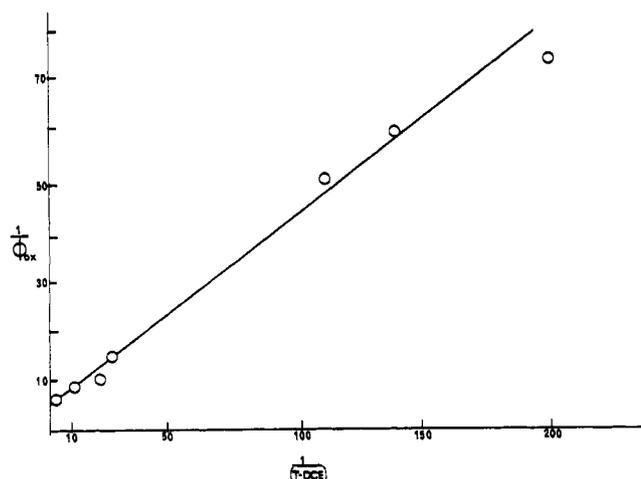
was no change in the decay ratio over the temperature range studied.

A second method for the determination of the efficiency at which C goes on to give 7 was investigated. This method has the added advantage of providing verification that adamantanone singlet is that state responsible for the formation of 7. Inspection of eq 22 reveals that a plot of $1/\phi_{ox}$ against $1/(t\text{-DCE})$ should yield a straight line. The intercept of the line at infinite t-DCE concentration should give a value for the ratio of decay paths for intermediate C. The ratio of the intercept to the slope should yield the same value of $k_q{}^s\tau_s$ as the study of fluorescence quenching of adamantanone by t-DCE. Figure 6 shows a plot of $1/\phi_{ox}$ against $1/(t\text{-DCE})$ according to eq 22. The photolysis was carried out at 90° in the same manner previously described. The intercept of Figure 6 yields a value of $k_1/(k_1 + k_2)$ equal to 0.17 and the ratio of slope to intercept a value for $k_q{}^s\tau_s$ equal to 27 l./mol. The remarkable agreement between the calculated values for the decay ratio obtained by the two methods was probably fortuitous. The agreement between the fluorescence quenching data and the reciprocal plot was sufficiently close to indicate that the excited state that leads to 7 is the same state that was responsible for the fluorescence, that is, the excited singlet of adamantanone.

The nature of the excited state leading to the isomerization of t-DCE was identified by an analogous procedure. An expression for the quantum yield for formation of c-DCE (ϕ_c) based upon the mechanism shown in Scheme II is seen in eq. 24. The middle term in eq 24 represents the fraction of the photoexcited adamantanone singlets that are not quenched by t-DCE.

$$\phi_c = \left(\frac{k_c}{k_c + k_t}\right)\left(\frac{1}{1 + k_q{}^s\tau_s[t\text{-DCE}]}\right)\left(\frac{k_q{}^t[t\text{-DCE}]}{k_q{}^t[t\text{-DCE}] + k_d}\right) \qquad (24)$$

With the assumption that, under these conditions, in the absence of t-DCE the quantum yield for triplet formation from singlet adamantanone is unity the middle term in eq 24 becomes the quantum yield for formation of triplet adamantanone in the presence of t-DCE (ϕ_t); see eq 25.

$$\phi_t = \frac{1}{1 + k_q{}^s\tau_s[t\text{-DCE}]} \qquad (25)$$

An important point is that all of the terms in eq 25 have known values. Thus a value for ϕ_t can be calculated at any given concentration of t-DCE. Substitution of eq 25 into eq 24 and rearrangement give eq 26.

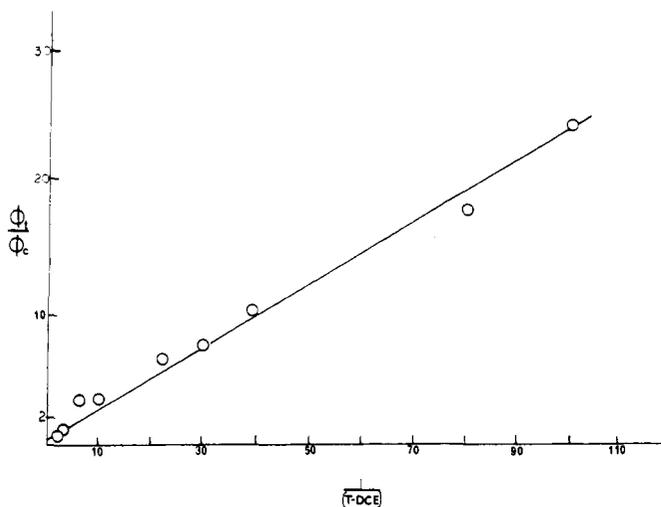*Turro, Schaap, et al. / Adamantylideneadamantane-1,2-dioxetane*

Figure 7. Determination of adamantanone excited state responsible for isomerization of t-DCE.

$$\frac{\phi_t}{\phi_c} = \frac{k_c}{k_c + k_t}\left(1 + \frac{k_d}{k_q{}^t[t\text{-DCE}]}\right) \qquad (26)$$

The mechanism shown in Scheme II predicts that, as the t-DCE concentration increased, the value of ϕ_c should decrease, due to singlet quenching, if isomerization occurs only via triplet adamantanone. Figure 7 shows a plot of ϕ_t/ϕ_c against $1/(t\text{-DCE})$. This photolysis was carried out at 90° under the conditions previously described. Within the experimental uncertainty, the behavior predicted by eq 26 is clearly observed. Thus the proposal that isomerization occurs only via triplet adamantanone was verified. It should be pointed out that this differential reactivity of singlet and triplet adamantanone was identical with that observed with acetone and t-DCE.[18]

Another parameter of interest in the proposed mechanism in Scheme II was the ratio of decay of ^{3}DCE to the cis and the trans isomers, $k_c/(k_c + k_t)$. The method chosen for the determination of this triplet decay ratio was the comparison of the quantum yield of trans to cis isomerization for c-DCE (ϕ_{tc}) with ϕ_c. The ratio of ϕ_{tc} to ϕ_c based upon the proposed mechanism is shown in eq 27.

$$\frac{\phi_{tc}}{\phi_c} = \frac{k_c}{k_t}\left(\frac{1 + k_{qc}{}^s[c\text{-DCE}]\tau_s}{1 + k_{qt}{}^s[t\text{-DCE}]\tau_s}\right)\left(\frac{1 + k_{qc}{}^t[c\text{-DCE}]\tau_t}{1 + k_{qt}{}^t[t\text{-DCE}]\tau_t}\right) \qquad (27)$$

The additional subscripts on the quenching rate constants represent interaction with c-DCE (c) or t-DCE (t). To apply eq 27 so that a value for k_c/k_t can be determined, it was necessary to determine values for the other terms of the equation. The value for $k_{qt}{}^s\tau_s$ has been discussed previously; the value for the fluorescence quenching by c-DCE, $k_{qc}{}^s\tau_s$, was determined in an analogous manner to be 61.3 l./mol at 90°. Unfortunately, it did not prove possible to determine the quenching parameters of adamantanone triplet with c-DCE and t-DCE.[25] A model for this process was devised using acetone triplet in the place of adamantanone. The rate constant for quenching of acetone triplet by t-DCE and c-DCE was determined by measuring the lifetime of acetone triplet at various c- and t-DCE concentrations. Values for the quenching rate constants for t-DCE and c-DCE of 7.2×10^9 and 9.3×10^9 l. mol^{-1} sec^{-1}, respectively, were determined. With the assumption that the ratio of quenching rates for c-DCE and t-DCE is the same for adamantanone and acetone triplet, a range of values for k_c/k_t can be calculated from eq 26. A value of the decay ratio for the isomerization of DCE in the range of 0.55 to 0.59 is found.

The investigation of the photoreactions of adamantanone and t-DCE shows that formation of oxetane 7 results only from interaction with singlet adamantanone. The limiting quantum yield for this reaction was essentially temperature independent over the range 25–90° with a value of 0.16. The trans to cis isomerization of t-DCE occurs exclusively through interaction with triplet adamantanone. The limiting quantum yield for this reaction was 0.57, and again it appears to be independent of temperature over the range studied.

One last point should be mentioned in regard to the photochemistry of adamantanone and that is the shortness of the triplet lifetime. From the value of the ratio of the slope to intercept of Figure 7 and the estimated value of $k_{qt}{}^t$ (see above), an estimate of the unimolecular decay rate constant (k_d) for adamantanone triplet can be obtained. The lifetime of adamantanone triplet was temperature dependent with a value of about 0.15 nsec at 25° (acetone triplet under comparable conditions has a lifetime of ca. 20 μsec), and about 0.06 nsec at 90°. It appears that adamantanone triplet lifetime may be limited by a very rapid cleavage process. Since no unimolecular photoproducts were observed when adamantanone alone was photolyzed, this cleavage is probably reversible giving ground state adamantanone as the only product.

Conclusion

The investigation of the formation of excited states from the thermolysis of dioxetane 1 reveals several important new aspects of this reaction that may have implications to the mechanism of 1,2-dioxetanes in general. Let us consider the intimate behavior of a 1,2-dioxetane along the reaction coordinate leading to excited state production.

There are three general classes of mechanisms that we would like to discuss. First is the concerted opening in which both the carbon–carbon and oxygen–oxygen bonds are lengthening simultaneously. In this case, as has been previously stated, there is a conceptual basis for the favored formation of triplet excited states over singlet excited states.[4b] The second general mechanism that has been proposed postulates the opening of the oxygen–oxygen bond to form a biradical intermediate. This intermediate can then approach the statistical three to one ratio of triplet to singlet states predicted. Subsequent partitioning of the triplet and singlet biradicals between ground and excited state products would then account for the greater than three to one ratio of excited states actually observed. Lastly, let us consider a third mechanism which is a hybrid of some of the features of the previous two. *Opening of the oxygen–oxygen bond of a 1,2-dioxetane may occur in concert with the spin inversion of an electron to form directly the triplet biradical.*[3d] In fact, the same factors previously invoked to favor the concerted formation of triplet excited states also apply to *the concerted formation of the triplet biradical.* If the biradical is formed to a great extent in the triplet state, then we need not invoke any special partitioning in the formation of the excited states to account for the observed triplet to singlet ratio.

The results obtained from the study of dioxetane 1 seem to favor ring-opening mechanisms that invoke compression of the alkyl substituents on the dioxetane ring. Thus the rigidity and steric bulk of the adamantyl ring systems make the compression energetically unfavorable and result in the greatly increased activation energy that is observed for this system. Certainly, this conclusion tends to favor the initial step as a leading breaking of the oxygen–oxygen bond, either in concert with the spin-flip or to form a singlet biradical. If both the oxygen–oxygen bond and the carbon–carbon

Table IV. Chemical Titration of Dioxetane 1 with t-DCE

1^a	$t\text{-DCE}^b$	Oxetane $7^g \times 10^5$	$c\text{-DCE} \times 10^{3\,i}$
0.533	2.79	1.80	1.05
0.511	2.32	1.40	0.725
0.33	1.86	0.91	0.516
0.478	1.39	1.19	0.725
0.533	0.50	0.636	0.329
0.478	0	0	0
c	2.79	0	0.03
d	2.79	0	0.07
e	2.79	$102\%^h$	0.04
0.00	f	0	$110\%^j$

^{a} Concentration of dioxetane 1 in mol/l. ^{b} Concentration of t-DCE in mol/l. ^{c} 0.889 M in adamantanone. ^{d} 0.867 M in adamantanone. ^{e} 0.030 M in oxetane 7. ^{f} 2.85 × 10^{-3} M in c-DCE. ^{g} In mmol × 10^{-3} of oxetane product formed. ^{h} Percent recovered oxetane. ^{i} In mmol of c-DCE product formed, corrected for thermal isomerization of t-DCE. ^{j} Percent recovered c-DCE.

Table V. Photoexcitation of Dioxetane 1. Detection of Excited Adamantanone

	$\text{OD}_1^{280\,a}$	$\text{OD}_{\text{adone}}^{280\,b}$	I_{cl}^c	I_{ad}^d
Singlets	0.180	0.124	14.8	124
Triplets	0.16	0.29	6.2	20.7

^{a} Optical density of solution of dioxetane 1. ^{b} Optical density of solution of adamantanone. ^{c} Intensity of emission from photoexcited dioxetane 1, arbitrary units. Identified as fluorescence in the case of singlets and phosphorescence for the measurement of triplets. ^{d} Intensity of adamantanone emission, arbitrary units.

bond of the dioxetane ring system were breaking simultaneously, one would not anticipate the great stabilization of dioxetane 1 that is observed unless the carbon–carbon bond cleavage requires motions which cause steric compression.

The key measurable parameters of the chemiluminescent reactions, yield of excited states, ratio of excited-state multiplicity, from dioxetane 1 and most of the other dioxetane investigated are qualitatively similar. Quantitatively, however, in the case of 1, the triplet–singlet ratio is considerably smaller than all but one previous reported value.[6] We imply from these observations that a common mechanism operates among all of the 1,2-dioxetanes studied, but that the extent of the oxygen–oxygen bond breaking may vary depending on the flexibility and the carbon–carbon bond strengths of the system.

Experimental Section

Instrumentation. Chemiluminescence, in general, was measured by the single photon-counting technique. Spectral resolution was obtained with a Jarrel Ash 0.25 M monochromator. Light signals were detected with an Amperex 56 AUP 14 stage photomultiplier tube. Fluorescence quenching studies were performed on a Perkin-Elmer MPF-3A spectrofluorimeter. Gas chromatographic analysis was carried out on a Hewlett-Packard 5750 Research Chromatograph equipped with dual flame detectors. The ^{13}C NMR spectra were taken on a Jeol 4H-100 spectrometer equipped with pulsed Fourier transform and an EC-100 data system. Mass spectral analysis was carried out on a Jeol JMS-07 mass spectrometer. Ir analysis was performed on a Perkin-Elmer 137 spectrometer. Uv absorption spectra were recorded on a Cary 14 spectrometer.

Dioxetane 1. Preparation of the olefin has been described previously.[11b,c] The preparation of the dioxetane is similar to the previously described procedure.[10] A solution of 0.20 g (0.75 mmol) of biadamantylidene (2), 8 mg of 2,6-di-tert-butyl-p-cresol, and Methylene Blue (10^{-4} M) in 10 ml of methylene chloride continuously saturated with oxygen was irradiated with a 500-W tungsten-iodide lamp through a uv-cutoff filter (Corning 3060). The photooxidation was monitored by thin layer chromatography on silica gel with 90:10 hexane–ethyl ether: R_f(2) 0.8, R_f(1) 0.3. Upon complete conversion of 2 to 1, the solvent was removed under vacuum and the residue chromatographed over silica gel with 90:10 hexane–ethyl ether to yield a pale yellow, crystalline material, mp 154–159° (lit.[10] mp 164–165°). Recrystallization from acetonitrile gave 0.15 g (66% yield) of off-white needles: mp 174–176°; ir (CCl$_4$), 1480, 1460, 1110, 1030, 985, 882, 895 cm^{-1}; mass spec (rel int) (12 V) m/e 300 (0.7), 284 (7), 268 (11), 150 (100), 134 (40), 80 (86), 72 (27).

Chemiluminescent Emission of 1. A 5.0 × 10^{-3} M solution of dioxetane 1 was prepared in MCB "spectroquality" acetonitrile. The emission spectrum of this air-saturated solution was determined at 89° by recording the intensity of emission at 5-nm intervals. The spectral resolution obtained by this procedure is not better than 10 nm.

Chemical Titration of Dioxetane 1. Solutions of dioxetane 1 and t-DCE in MCB "spectroquality" acetonitrile were prepared in 3-mm o.d. capillary test tubes. The tubes were sealed and heated at 145° for 2 days. Analysis for oxetane 7 and c-DCE was made by GLC, 3 ft × ⅛ in. SE-30 on Chrom W at 170° and 5 × ⅛ in. β,β,β on Chrom W at 175°, respectively. Typical results are shown in Table IV.

Determination of the Activation Parameters by Classical, Isothermal Techniques. A 0.02 M stock solution of 1 in o-xylene (analytical reagent) was distributed by means of a syringe over constricted Pyrex test tubes. Sets of ten of the constricted tubes were connected to a degassing manifold, cooled to Dry Ice temperature, degassed by three successive "freeze–pump–thaw" cycles, and sealed under vacuum. Ten bundles of three ampules each were preheated for ca. 5–10° above the constant bath temperature and quickly transferred to the constant temperature silicon oil bath, regulated within ±0.05° of the desired temperature by means of a Fisher Scientific Proportional Temperature Regulator. The ampules were allowed to equilibrate thermally for ca. 5 min, and the first bundle representing the initial point was removed and placed in an ice bath to quench the thermal decomposition. At regular time intervals, bundles were removed and stored for quantitative infrared analysis on a Perkin-Elmer Infracord 237B, using matched and calibrated 0.5 mm. NaCl cells and compensating solvent absorption with o-xylene in the reference cell. For each point the zero base line was readjusted to minimize scatter of the data. From the absorbance at 1710 cm^{-1} of the carbonyl band of adamantanone, the thermolysis product, the concentration of the product as a function of time was assessed by extrapolation from a Beer–Lambert plot, previously prepared from pure adamantanone.

Photoexcitation of Dioxetane 1. A 9.85 × 10^{-3} M solution of 1 in MCB "spectroquality" acetonitrile was prepared. Irradiation of this sample with 280-nm light resulted in an emission identified as adamantanone fluorescence. The intensity of the emission was compared with the fluorescence from a 9.0 × 10^{-3} M solution of adamantanone. The results are shown in Table V; the singlet yield was calculated according to eq 19.

Similarly the phosphorescence (chopped emission) emission of a 1.73 × 10^{-2} M adamantanone and a 9.2 × 10^{-3} M dioxetane 1 solution in EPA was compared. The results are shown in Table V.

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Directive Effects in Free Radical Oxidation by Fe(III). Reductive Decarboxylation of Peroxy Acids[1]

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Abstract: Treatment of peroxycyclohexanecarboxylic acid with ferrous perchlorate in acetonitrile has been found to afford a 25% yield of cyclohexanol. Similar treatment of *cis-* or *trans-*3-hydroxyperoxycyclohexanecarboxylic acid yields largely *cis-*1,3-cyclohexanediol, revealing a directive effect for free radical oxidation by iron(III) analogous to that observed for the stereospecific cis-1,3 hydroxylation of cyclohexanol by ferrous ion-hydrogen peroxide. Preference for cis diol formation is also observed for *cis-*4-hydroxyperoxycyclohexanecarboxylic acid, but the cis- and trans-1,2 isomers give a cis/trans diol ratio near unity. Analysis of the stereoisomeric mixture of 1,2-cyclohexanediols from the reaction of cyclohexene with ferrous ion-hydrogen peroxide leads to the conclusion that, in acetonitrile, the predominant mode of olefin hydroxylation does not proceed via addition of hydroxyl radical to the double bond.

Transition metal ions are known to catalyze the decomposition of peroxides by reductive cleavage of the peroxy linkage.[2] Thus, reductive decomposition of peroxy esters[3] leads predominantly to metal carboalkoxides and alkoxy radicals. Similarly, the reaction of diacyl peroxides with cuprous ion is known to afford carboalkoxy radicals.[4] Much less is known of the fate of peroxy acids upon reductive decomposition by variable valence metals.[5] The observed formation of carbon dioxide upon treatment of peracetic acid with ferrous ion in acetic acid is not definitive since substantial amounts of the decarboxylation results from reactions of the solvent. These results have been interpreted as the consequence of competing modes of one-electron cleavage of the peroxy bond leading either to acyloxy radicals or hydroxyl radicals.[6]

We have been interested in site-specific aliphatic hydroxylation mediated by metal-peroxide species both from the view of developing new stereospecific remote functionalization procedures and elaborating possible parallels between iron-peroxide chemistry in solution and intermediates involved in aliphatic hydroxylation by mixed function oxidases. Toward these ends we reported[7] recently the cis-1,3 hydroxylation of cyclohexanol with net retention at the oxidized carbon together with the proposal that this process proceeds by directed oxidation by a bound iron species, formally equivalent to a ferryl ion, and leading to discreet rad-

Scheme I
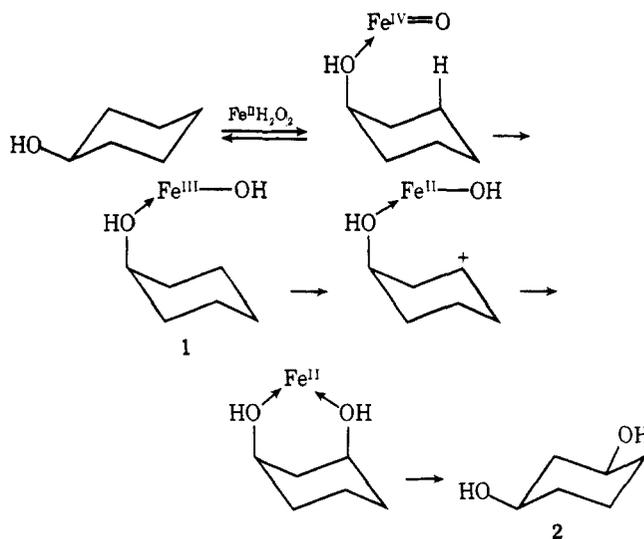
ical and carbonium ion intermediates (Scheme I). An important consequence of this conclusion is that aliphatic hydroxylation with retention of configuration, common among the steroid hydroxylases,[8] need not necessarily require an