Trimethyloxonium tetrafluoroborate was a commercial sample purchased from Cationics, Inc. Sulfolane was purified extensively as described previously.[3] Because purified sulfolane has a relatively inconvenient melting point, 30°C, 5.25 mol % dimethyl sulfone was added to lower the melting point and enhance the ease of handling of this solvent. The rare constant for the reaction of *p*-chlorophenyl methyl sulfide with methyl triflate was found to be independent of the presence of this amount of additive, within experimental error.

Kinetic Procedures. Methylation of aryl methyl sulfide was followed by the stopped-flow technique by using a Durrum 110 spectrophotometer. The absorption maximum of each substance in sulfolane was recorded by means of a Cary 14 or Cary 17 spectrophotometer. In all cases, methylation resulted in a large decrease in absorption at 258 nm. Concentrations employed were $\sim 1 \times 10^{-4}$ M for the sulfides, 0.8–0.2 M for methyl triflate, and 0.2 M for trimethyloxonium tetrafluoroborate.

The reactions of pyridine and dimethylanilines were also studied at 258 nm, at which wavelength methylation produced a decrease in absorption with the dimethylanilines and an increase with pyridine. Reactions with dimethyl sulfate were conveniently followed under pseudo-first-order conditions (excess dimethyl sulfate) by using a Cary 14 spectrophotometer with its cell compartment thermostated at 30 °C. With methyl triflate solutions, acidic contaminants in the reaction mixtures probably derived from the reaction of adventitious water with methyl triflate precluded the use of large excesses of methylating agents because the protonated form of the amines simulated spectroscopically the methylated form. These runs were therefore made using second-order conditions with concentrations in the range of 1×10^{-5} to 5×10^{-5} M for dimethylanilines and $\sim 1 \times 10^{-4}$ for pyridine.

Kinetic runs employing NMR measurements were done by using a Varian EM-390 spectrometer. Runs with trimethylanilinium ion in pyridine were conducted in tubes that were sealed under vacuum. The chemical shifts of the methyl group protons were: methyl triflate δ 4.17; phenyl methyl sulfide, 2.43; aryldimethylsulfonium salts, 3.24–3.36; pyridinium ion, 4.43; trimethylanilinium ion, 3.77; and dimethylaniline, 2.75.

Acknowledgment. We thank the National Science Foundation for a grant supporting this research. Carl D. Slater thanks Memphis State University for partial support in the form of a Faculty Development Leave for 1978–1979. Semyon Kukes acknowledges the award of a Robert A. Welch Foundation postdoctoral fellowship.

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(1) (a) Robert A. Welch Foundation Postdoctoral Fellow. (b) Permanent address: Department of Chemistry, Memphis State Univeristy, Memphis, Tenn.

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Chemiluminescence of Dimethyldioxetanone. Unimolecular Generation of Excited Singlet and Triplet Acetone. Chemically Initiated Electron-Exchange Luminescence, the Primary Light Generating Reaction[1]

Steven P. Schmidt[2a] **and Gary B. Schuster***[2b]

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801.

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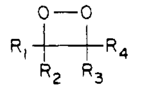
Abstract: Dimethyldioxetanone (**2a**) undergoes two distinct thermal reactions which generate electronically excited states. The unimolecular decomposition of **2a** at 30.0 °C produces excited singlet and triplet acetone, with efficiencies of 0.1 and 1.5%, respectively. The composite activation energy for formation of singlet acetone is 3-4 kcal mol^{-1} greater than the activation energy for the thermal disappearance of **2a**. This result is interpreted in terms of two parallel competitive pathways for dioxetanone decomposition, the more highly activated one of which leads to excited acetone. The addition of easily oxidized aromatic hydrocarbons or amines catalyzes the chemiluminescence of **2a**. The magnitude of the catalytic rate constant and the efficiency of light production are correlated with the one electron oxidation potential of the hydrocarbon. Under these conditions, the chemiluminescence results from a chemically initiated electron-exchange luminescence path.

Considerable insight into the mechanisms of chemiluminescence has been provided by the extensive investigation over the past decade of the chemistry of 1,2-dioxetanes (**1**).[3] To date nearly 100 of these molecules have been prepared and their properties scrutinized in order to elucidate the mechanistic details of their remarkable transformation to excited state carbonyl-containing products. Meanwhile, only a few of the closely related dioxetanones (**2**) have been reported.[4] Their study has been hindered by difficulties in synthetic entries[5] and by their thermal and catalytic lability.



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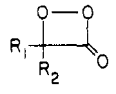
a, $R_1 - R_4 = CH_3$



2

a, $R_1, R_2 = CH_3$

The chemiluminescence of dioxetanones is of particular interest due to their postulated intermediacy in several bioluminescent reactions,[6] including that of the firefly.[7] Prior to their isolation, simple alkyl substituted dioxetanes such as **1a**

Table I. Activation Parameters for the Thermolysis of Dioxetanone **2a**[a]

solvent	kinetics E_a, kcal mol^{-1} [b]	kinetics (log A)	chemiluminescence intensity (E_{chl}), kcal mol^{-1} [c]
$C_2Cl_3F_3$	22.3 ± 0.3[d]	(12.9 ± 0.2)	25.6 ± 0.1
CCl_4	21.3 ± 0.3[e]	(12.6 ± 0.2)	24.5 ± 0.5
PhH	21.8 ± 0.1[e]	(13.0 ± 0.1)	24.9 ± 0.4
CH_2Cl_2	20.8 ± 0.1[e]	(12.2 ± 0.2)	24.8 ± 0.4
$CFCl_3$			25.5 ± 0.5

[a] Air-saturated solutions. All uncertainties are standard deviations. [b] Temperature range over which rate constants were determined was 15 to 40 °C. [c] For details, see Experimental Section. [d] Eyring activation enthalpy, $\Delta H^{\ddagger} = 21.7$ kcal mol^{-1}; activation entropy, $\Delta S^{\ddagger} = \pm 1$ eu. [e] Solutions contained Na_4EDTA.

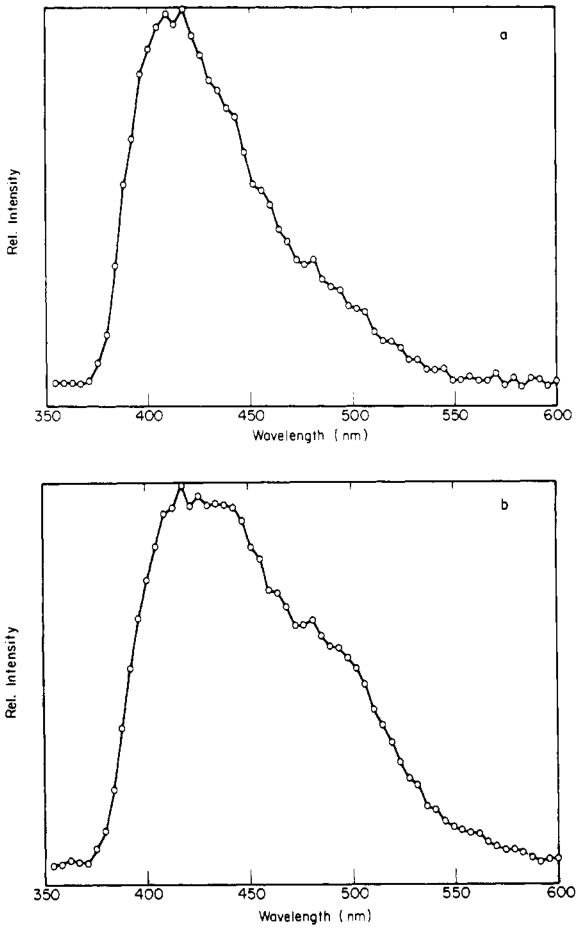


Figure 1. Chemiluminescence emission spectra from the unimolecular reaction of **2a** in $C_2Cl_3F_3$: (a) acetone fluorescence; (b) acetone phosphorescence.

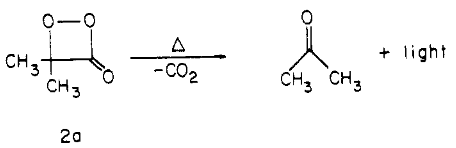
had been proposed as appropriate models for these bioluminescent reactions.[8] Upon careful study of the chemiluminescence of alkyl dioxetanes, however, a major incongruity with this suggestion soon became apparent. While all dioxetanes synthesized thus far do indeed generate excited states with fair efficiency, these are predominantly in the essentially nonluminescent triplet state.[3] Bioluminescent systems, on the other hand, form the emitting excited singlet state with high efficiency.[9]

An early report by Adam[10] noted that the addition of rubrene to solutions of **2a** gave a yield of light 20 times that when 9,10-diphenylanthracene was added. Only recently, however, was a satisfactory explanation advanced by us[1b] and later Adam.[11] Recently, Sawaki and Ogata[12] also observed, in the base catalyzed decomposition of α-hydroperoxy esters, for which a dioxetanone intermediate was proposed, an unusual dependence of the chemiluminescence yield on the identity of added fluorescer. The findings of Adam and those of Sawaki and Ogata lie in stark contrast to results on simple alkyl substituted dioxetanes.

With these ideas in mind, we initiated a detailed investigation of the chemiluminescent decomposition of **2a**. This study had two primary objectives. First, we wished to examine the direct chemiluminescence resulting from the unimolecular transformation of **2a** to carbonyl excited states, and to compare the activation parameters, the absolute yield of excited states, and the triplet to singlet excited state ratio with those of dioxetanes such as **1a**. Second, we wished to examine the chemiluminescence of **2a** in the presence of various fluorescers, and determine the nature of the apparently unconventional generation of excited states. It was anticipated that this study would engender new insight into the role of dioxetanones in other chemi- and bioluminescent reactions.

Results

I. Unimolecular Chemiluminescence. Chemiluminescence from Thermolysis of Dimethyldioxetanone. Thermolysis of dimethyldioxetanone (**2a**) in any of a number of solvents leads quantitatively to acetone and to readily detected chemiluminescence (eq 1). Excited singlet and triplet states of acetone



(1)

2a

are both generated, and are readily identified by their characteristic fluorescence and phosphorescence spectra. The chemiluminescence of air-saturated $C_2Cl_3F_3$ solutions of **2a** consists of acetone fluorescence (Figure 1a), while in argon-purged solutions the emission is predominantly phosphorescence (Figure 1b). These chemiluminescence spectra of **2a** are superimposable with those from tetramethyl-1,2-dioxetane (**1a**) obtained under comparable conditions.[1a,13] This finding confirms the generation of electronically excited acetone from **2a**. It also rules out the involvement of an emissive acetone excimer from **1a**.[14]

Activation Energy for the Thermolysis of 2a. Two techniques were used in analyzing the activation parameters for the unimolecular reaction of **2a**. In the first, the kinetics of decomposition were measured in the conventional manner by monitoring the decrease in [**2a**] by the change in chemiluminescence intensity (acetone fluorescence) with time. The activation energy, E_a (Table I), is obtained by standard Arrhenius analysis of the temperature dependence of the derived first-order rate constants. Measurements were made in four solvents.

In the second technique, the temperature dependence of the initial instantaneous chemiluminescence intensity was used to determine the activation energy for that fraction of reaction of **2a** which leads to chemiluminescence via the excited singlet of acetone.[15] This chemiluminescence intensity activation energy, E_{chl}, was measured in five solvents, as summarized in Table I. Critically, and in contrast to the activation parameters of simply substituted dioxetanes studied thus far, E_{chl} for **2a** is 3-4 kcal mol^{-1} greater than E_a. This difference is independent of solvent.

Dioxetanes are extremely susceptible to catalyzed decomposition by various trace impurities.[16] Such a parallel, non-light-generating path, if operative in the present system, could result in a lowering of the apparent kinetic activation energy, E_a. Several experimental observations address this possibility. Most significantly, E_a was determined in four solvents which

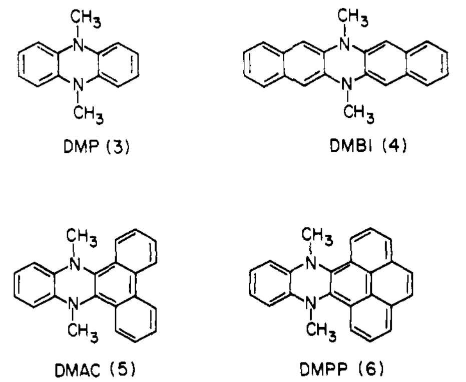


Figure 2. Dihydrophenazines used as catalytic chemiluminescence activators.

Table II. Temperature Dependence of the Excited Acetone Yield from Thermolysis of Dioxetanone **2a**[a]

temp, °C	$\phi_s^* \times 10^4$	temp, °C	$\phi_s^* \times 10^4$
30.0	10	9.8	5.7
25.1	8.4	4.8	4.8
20.5	7.4	0.3	4.5
15.4	6.3	−5.0	3.9

[a] $C_2Cl_3F_3$ solutions. Yields were determined relative to the yield at 30.0 °C. Estimated error is ±10%. For full details, see Experimental Section.

had been purified by different techniques. As indicated in Table I, virtually identical results were obtained in the four solvents. Thus any catalytic component to the decomposition of **2a** would fortuitously have to be equally efficient in all solvents investigated. The possibility of a catalytic impurity in the dioxetanone sample is excluded by the finding that the decomposition rate constant is independent (±1%) of both the initial dioxetanone concentration (0.1-3 mM) and the batch of dioxetanone stock solution. Also, addition of the chelating agent ethylenediaminetetraacetic acid (EDTA) had no effect on the rate constant of decomposition. In fact, the powerful catalytic effect of added cupric ion[16b] was completely suppressed by adding Na_4EDTA. Finally, the entropy of activation for thermolysis of **2a** at 25°C is ±3 eu in the four solvents of Table I, a value inconsistent with a bimolecular catalysis path.[17] In addition to the above experimental observations, the close agreement between observed activation parameters and those calculated earlier by Richardson and O'Neal on the basis of a unimolecular biradical process[18] supports an uncatalyzed unimolecular decomposition of **2a.**

Yield of Excited States from the Unimolecular Thermolysis of Dimethyldioxetanone. The yields of excited singlet and triplet acetone produced from **2a** were determined relative to the yields of excited singlet and triplet acetone from the thermolysis of **1a,** which are fairly well established at 0.2[19,20a] and 30%,[20] respectively. The total time-integrated fluorescence and phosphorescence intensities from **2a** were compared directly with those from **1a** under identical conditions. The efficiencies of singlet and triplet acetone generation from thermolysis of **2a** at 30 °C in $C_2Cl_3F_3$ thus measured are 0.1 and 1.5%, respectively.[21]

The efficiency of excited singlet acetone generation (ϕ_s^*) is significantly dependent upon the reaction temperature, as is indicated in Table II. These data afford a temperature coefficient for ϕ_s^* of (4.2 ± 0.2) kcal mol^{-1}. This is the first reported example of a temperature-dependent, singlet-excited-state yield from the thermal unimolecular reaction of the 1,2-dioxetane ring system.[22]

II. Activator-Catalyzed Chemiluminescence. Kinetics of the Activator-Catalyzed Reaction of Dimethyldioxetanone. The addition of any of several easily oxidized, emitting aromatic hydrocarbons or amines to benzene or dichloromethane solutions of **2a** results in greatly enhanced chemiluminescence. Moreover, addition of these molecules accelerates the rate of reaction of **2a.** The magnitude of this rate acceleration is quite remarkable. The half-life of **2a** in benzene at 24.5 °C is approximately 20 min; in the presence of just 1×10^{-3} M dimethyldihydrophenazine (**3**) (DMP), the half-life of **2a** is 1 s! The reaction is first order in both **2a** and aromatic hydrocarbon (or amine). Acetone is still produced quantitatively. Moreover, the hydrocarbon is not consumed in the reaction,[23] but rather serves as a catalyst for the decomposition of the dioxetanone. These molecules will subsequently be referred to as catalytic chemiluminescence activators (ACT). The kinetic behavior is thus described by the simple rate law of eq 2, where k_1 is the rate constant for unimolecular reaction and k_2 is the bimolecular rate constant for the activator-catalyzed reaction. The kinetics of the catalyzed reaction for a series of activators including four dihydrophenazines (Figure 2) are analyzed according to eq 2 in Figure 3. While the unimolecular rate constant k_1, the intercept of Figure 3, is independent of activator identity, the bimolecular rate constant k_2, the slope of Figure 3, is highly dependent on the nature of the activator as summarized in Table III. In fact, k_2 in benzene at 24.5 °C is over 13 000 times larger for DMP (**3**) than for rubrene.

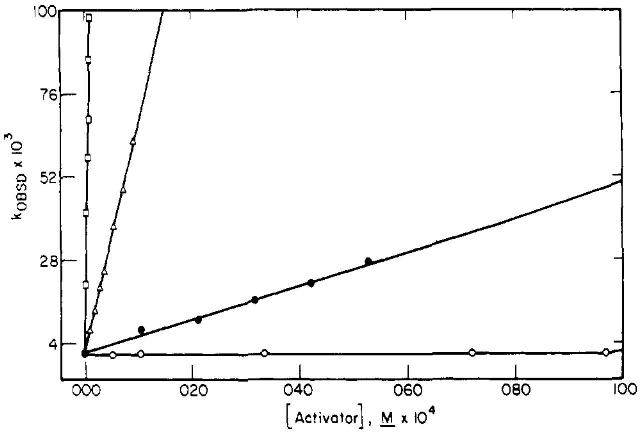


Figure 3. Effect of activator identity and activator concentration on the observed first-order decay of **2a** in argon purged benzene at 24.5 °C: (□) DMP; (△) DMBI; (●) dimethyl-6-aminochrysene; (○) rubrene.

$$k_{obsd} = k_1 + k_2[ACT] \qquad (2)$$

The data of Table III indicate a broad relationship between the one electron oxidation potential of the activator and the magnitude of k_2. In general, the more easily oxidized activator (lowest E_{ox}) has a larger k_2 associated with it, suggesting an endothermic one electron transfer from activator to dioxetanone in the rate-determining step of the catalytic reaction.

However, the one electron oxidation potential of the activator does not always predict the magnitude of the bimolecular rate constant k_2, as best exemplified by the pair rubrene and 1,3-diphenylisobenzofuran (DPBF). While their oxidation potentials vary only slightly, the bimolecular rate constant measured for DPBF is 65 times that measured for rubrene. Importantly, DPBF, unlike rubrene, is consumed in the reaction with **2a,** generating *o*-dibenzoylbenzene (by VPC). Apparently a second bimolecular reaction, the rate constant of which is independent of oxidation potential, contributes to, and in fact in this case dominates, the measured bimolecular rate constant k_2. The electron transfer rate constant, which we term k_{cat}, thus is only a part of the measured bimolecular rate constant k_2.

Table III. Activator Properties and the Catalytic Reaction with Dimethyldioxetanone in Benzene at 24.5 °C

activator	E_{ox}, V[a]	E_s, kcal mol^{-1}[b]	ϕ_{fl}[c]	k_2, M^{-1} s^{-1}	% bimolecular[d]
DMP	0.11[e]	72	0.36	800 ± 20	95
DMAC	0.14	59	0.04	180 ± 20	82
DMPP	0.22	56	0.03	230 ± 10	85
DMBI	0.46	69	0.88	65 ± 5	62
N,*N*-dimethyl-*p*-anisidine	0.49[e]			560 ± 10	93
N,*N*-dimethyl-6-aminochrysene	0.70[f]			4.8 ± 0.2	11
tri-*p*-tolylamine	0.75[e]	74		0.46 ± 0.02	1.1
DPBF[g]	0.79[e]	65	0.96[h]	4.0 ± 0.2	9.3
rubrene	0.82	54	1.00[i]	0.06 ± 0.01	0.16
tetracene	0.95[j]	60	0.16[i]	0.010[k]	0.026
BPET[l]	0.97	51	0.67[m]	0.010[k]	0.026
perylene	1.00	65	0.89[i]	0.0052[k]	0.013
BPEA[n]	1.165[e]	62	0.96[m]	0.0012[k]	0.003

[a] Versus SCE, determined by cyclic voltammetry in CH_3CN solution with tetrabutylammonium perchlorate. This work unless otherwise noted. [b] Singlet energy, assigned from 0-0 band of fluorescence spectrum. [c] Fluorescence efficiency in benzene at 25 °C. This work unless otherwise noted. [d] Percent of reaction that proceeds through the bimolecular path at [ACT] = 2×10^{-5} M, and $k_1 = 7.8 \times 10^{-4}$ s^{-1}. [e] Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Non-Aqueous Systems"; Marcel Dekker: New York, 1970. [f] Cyclic voltammetry anodic peak, cathodic peak not observed. [g] 1,3-Diphenylisobenzofuran. [h] Olmsted III, J.; Akashah, T. *J. Am. Chem. Soc.* **1973,** *95,* 6211. [i] Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: London, 1970. [j] Bard, A. J.; Santhanam, K. S. V.; Malog, J. T.; Phelps, J; Wheeler, L. O. *Discuss. Faraday Soc.* **1968,** *45,* 167. [k] Calculated relative to the experimentally determined k_2 of rubrene by comparison of activated chemiluminescence intensity (Figure 4). [l] 5,12-Bis(phenylethynyl)tetracene. [m] Reference 47. [n] 9,10-Bis(phenylethynyl)anthracene.

Chemiluminescence from the Activator-Catalyzed Reaction of Dimethyldioxetanone. The luminescence observed when the activators of Table III are added to benzene solutions of **2a** corresponds to fluorescence from the excited singlet state of the activator. The spectrum of the chemiluminescence emission in all cases is identical with the photoexcited fluorescence spectrum of the activator. The relative initial instantaneous chemiluminescence intensity is highly dependent upon the nature of the activator employed; after correcting for differences in fluorescence quantum yields, photomultiplier tube and monochromator efficiencies, a 100 000-fold range in intensity is observed. The corrected relative intensity is uniquely predicted by the one electron oxidation potential of the activator. This relationship, shown in Figure 4, holds for all activators investigated including DPBF. It demonstrates that the chemiluminescence results from a bimolecular catalytic reaction (of rate constant k_{cat}) which involves an endothermic one electron transfer from activator to dioxetanone in the rate-determining step.

Further evidence that the activators truly catalyze the formation of excited singlet states comes from measurement of the temperature dependence of the initial instantaneous chemiluminescence intensity. This procedure gives the activation energy for that fraction of the reaction which leads to activator fluorescence (i.e., E_{chl}). The activation energy for formation of perylene singlet from **2a** in dichloromethane is 16.1 ± 0.6 kcal mol^{-1}, while that for 9,10-bis(phenylethynyl)anthracene (BPEA) under identical conditions is 18.0 ± 0.6 kcal mol^{-1}.[24] This compares with the activation energy for formation of acetone singlet from **2a** in dichloromethane of 24.8 ± 0.4 kcal mol^{-1} and a kinetic activation energy for unimolecular decomposition of 21 kcal mol^{-1} (Table I). While many species have been found to catalyze a "dark" reaction path of 1,2-dioxetanes, this is the first reported example of chemiluminescent catalysis, $E_{chl} < E_a$, for this ring system.[3c,25]

Yield of Excited States from the Activator-Catalyzed Reaction of 2a. The yield of excited singlet states from the activator catalyzed reaction of **2a** was determined relative to the yield of acetone excited states from the thermolysis of tetramethyldioxetane (**1a**). The total time-integrated chemiluminescence intensity for dichloromethane solutions of **2a** containing 2×10^{-5} M rubrene was compared with acetonitrile solutions of **1a** containing 9,10-dibromoanthracene as a triplet energy acceptor.[26] After correction for the spectral response of the photomultiplier tube and the monochromator, and using 30% as the efficiency of excited acetone production from **1a**,[20] the measured total intensity ratio shows that, in dichloromethane at 24.5 °C, 10 ± 5% of the dioxetanone molecules that react by the bimolecular path lead to the formation of rubrene singlet excited state.

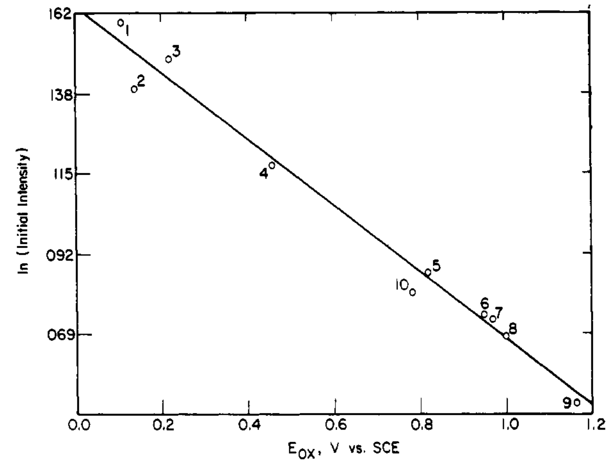


Figure 4. Correlation of the initial chemiluminescence intensity in benzene at 24.5 °C, corrected for fluorescence efficiency and photomultiplier tube and monochromator response, with the oxidation potential of activator: (1) DMP; (2) DMAC; (3) DMPP; (4) DMBI; (5) rubrene; (6) tetracene; (7) BPET; (8) perylene; (9) BPEA; (10) DPBF.

Discussion

I. Unimolecular Chemiluminescence. The effect of temperature on the efficiency of chemiluminescence from dimethyldioxetanone is composed of the temperature effect on all steps leading to and including luminescence. The temperature dependence of the fluorescence efficiency of acetone is negligible in the range investigated.[15b] Therefore, E_{chl} measures the composite activation energy for the formation of excited singlet acetone. The standard kinetic activation energy, E_a, however, measures the barrier to the lowest energy transition state available to the unimolecular reaction of **2a**. Our finding that

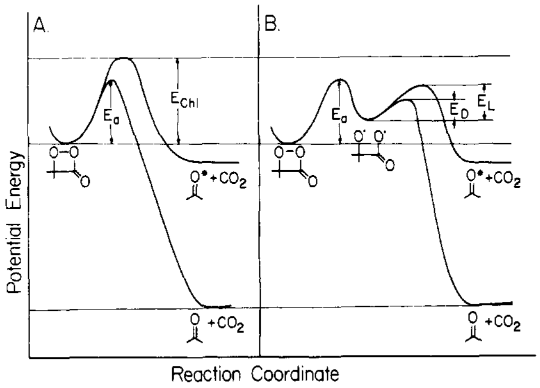


Figure 5. Limiting reaction mechanisms for thermal unimolecular fragmentation of dimethyldioxetanone to acetone and CO_2. Two concerted reactions are represented in A. In B, a path leads to an intermediate biradical which has two exit channels.

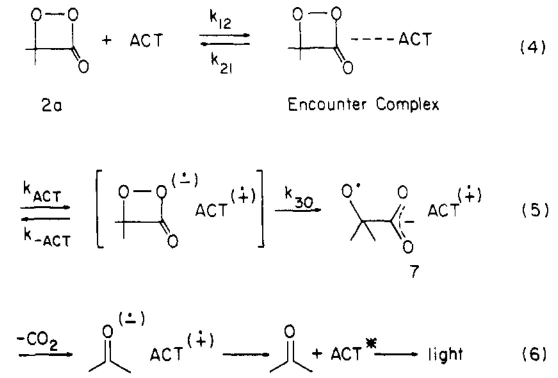
E_{chl} is 3-4 kcal mol^{-1} higher than E_a, as summarized in Table I, requires that there be two or more competitive parallel pathways with discrete transition states for dimethyldioxetanone decomposition. The more highly activated of these paths leads to excited states, while the lower path leads to "dark" decomposition. While this kinetic analysis cannot reveal the exact nature nor the position along the reaction coordinate of these two transition states, two limiting situations exist, as depicted in Figure 5.

Two competitive concerted reactions are depicted in Figure 5a. In this case the measured difference in activation energies between the dark and light-generating paths is simply the difference in energy between the two transition states. In the mechanism depicted in Figure 5b, a common rate-determining step leads to an intermediate 1,4-biradical. This biradical then partitions between the lower energy path to give ground state acetone, and a higher energy path to generate singlet excited acetone. For this case the temperature dependence of the instantaneous rate of light emission is given by eq 3, where A is a constant composed of instrument parameters and preexponential factors, E_a is the activation energy for formation of the intermediate biradical, E_L and E_D are activation parameters for fragmentation of the biradical to excited and ground state acetone, respectively.[27] This analysis indicates that the difference in activation energies between the light-generating and non-light-generating paths is the difference in transition state energies for the two paths leading from the intermediate biradical. Our data do not provide a distinction between the operation of the two mechanisms of Figure 5. In both cases, the experimentally observed ordering of transition states is readily understood in terms of the Hammond postulate; the more exothermic reaction, formation of ground state products, has the lower activation barrier.

$$I = A \exp\{-[E_a + (E_L - E_D)]/RT\} \qquad (3)$$

Dimethyldioxetanone is qualitatively similar to simply alkyl-substituted dioxetanes in that formation of excited triplets is preferred over singlets. The actual ratio of triplet to singlet products from **2a** is 15, which is small compared with that from nearly all alkyl-substituted dioxetanes that have been studied (in general triplet to singlet ratios of greater than 100 are observed).[3] Benson group additivity calculations[28] indicate that the decomposition of dimethyldioxetanone is nearly 20 kcal mol^{-1} more exothermic than the decomposition of tetramethyldioxetane.[29] The chemiluminescence activation energy of **1a**[15b] is 3 kcal mol^{-1} greater than that of **2a.** At the transition state, therefore, approximately 17 kcal mol^{-1} more energy is available from **2a** than **1a** for formation of excited acetone. The ratios of triplets to singlets may be determined simply by the relative energies of the excited states and the transition states leading to them. In terms of the biradical mechanism, the formation of both singlet and triplet acetone from the biradical intermediate derived from **2a** is quite exothermic. A relatively low triplet to singlet ratio results. From tetramethyldioxetane, formation of singlet acetone from the biradical requires significantly more energy than formation of triplet, and the high triplet to singlet ratio of 150 is observed. The nearly statistical triplet to singlet ratio of excited methylglyoxal (whose excited state energies lie approximately 20 kcal mol^{-1} below those of acetone) from the thermolysis of 3-acetyl-4,4-dimethyl-1,2-dioxetane was recently rationalized in these terms.[30] Not this line of reasoning, however, nor any mechanism yet postulated to explain the chemical formation of excited states, can explain why the *total* yield of acetone excited states from the thermolysis of **2a** is nearly 20 times lower than the excited acetone yield from the less exothermic thermolysis of **1a.**

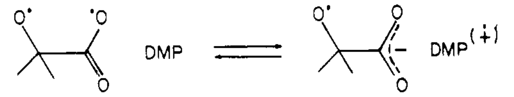
Scheme I



II. Activator-Catalyzed Chemiluminescence. The findings described herein on the activator-catalyzed chemiluminescence of dimethyldioxetanone are fully consistent with the generalized mechanism for chemical light formation which we have recently identified as chemically initiated electron-exchange luminescence (CIEEL).[31] The proposed sequence as applied to dimethyldioxetanone is shown in Scheme I. In short, the light-generating sequence is initiated by electron transfer from the activator (ACT) to the dioxetanone. Subsequent decarboxylation gives acetone radical anion. Annihilation of acetone radical anion and activator radical cation generates the excited state of the activator.

Formation of an encounter complex by diffusion together of reactants (rate constant k_{12}) is the initial event of any bimolecular reaction. The reverse reaction, k_{21}, is diffusion limited as well in the Weller model for electron transfer,[32] which we adopt. Thus the encounter complex of eq 4 is expected to enjoy only a fleeting lifetime. In fact, we have not been able to detect the complex in the electronic absorption spectrum of activator-dioxetanone mixtures.

The key feature of the proposed pathway is composed of the electron transfer (k_{ACT}) and bond cleavage (k_{30}) steps, and we shall analyze them in some detail. The electron transfer within the encounter complex is endergonic and thus does not occur spontaneously. The mechanism of the activation is analyzed in Figure 6. Consider a stretching of the oxygen-oxygen bond of the encounter complex. One possible result of this motion is that the bond cleaves homolytically (just as we suspect in the unimolecular reaction) yielding a new complex of activator and 1,4-biradical. In Figure 6 this path is shown as the correlation of the encounter complex (ACT- - -O-O) with the state ACT- -[O•O•]. There is, however, another electronic configuration available to the bond-cleaved state, one in which an electron has been transferred from ACT to the fragmented peroxide. The relative energies of these two species can be estimated from electrochemical measurements. Comparison of the electrochemical oxidation potential of DMP with that of alkyl carboxylate anions[33] (which we must use as a model for **7a**) predicts that the state $ACT^{+\cdot}$- -[$O^-O\cdot$] lies at least 18 kcal



(7)

7a

mol^{-1} lower in energy than the biradical state. Thus, stretching the oxygen–oxygen bond of the peroxide–activator encounter complex leads to an avoided crossing[34] (dotted region of Figure 6) of the biradical and electron-transferred state and this simple motion, therefore, provides a path for the electron transfer. The vibrationally excited radical ion pair shown in brackets in eq 5 may be an intermediate or, more likely, a transition state. In any case, we suspect that the oxygen–oxygen bond of this state cleaves rapidly ($k_{30} \gg k_{-\mathrm{ACT}}$), giving the radical ion pair **7**.

The correlation of the initial chemiluminescence intensity, which is proportional to the magnitude of the catalytic rate constant k_{cat} (the experimentally observed rate constant for electron transfer), with the oxidation potential of the activator, follows directly from the above considerations.[35] We can express k_{cat} in terms of the oxidation potential of the activator (E_{ox}), the reduction potential of the peroxide (E_{red}), and the Coulombic attraction between the developing oppositely charged radical ions (E_{coul}), as in eq 8, where K is a constant. The factor α is similar to the well-known transfer coefficient which generally takes a value between 0.3 and 0.7 for electrode reactions.[36] Only a fraction (α) of the total free energy change, as measured by the thermodynamic quantities E_{ox} and E_{red}, is realized as an increase in the activation barrier. Since the chemiluminescence intensity is proportional to k_{cat}, the plot of ln (intensity) vs. E_{ox} in Figure 4 yields a straight line of slope $-\alpha/RT$, where $\alpha = 0.3$. We have observed this slope from the CIEEL reaction of other peroxides as well.[31,37]

$$\ln k_{\mathrm{cat}} = \ln (K) + \frac{\alpha(E_{\mathrm{red}} + E_{\mathrm{coul}})}{RT} - \frac{\alpha(E_{\mathrm{ox}})}{RT} \quad (8)$$

One notable feature of the correlation of relative initial chemiluminescence intensity with activator oxidation potential in Figure 4 is the widely varying nature and structure of the activators that follow this relationship. One apparent exception is zinc tetraphenylporphyrin. It behaves as the other activators in the reaction with dimethyldioxetanone in that the reaction follows first-order kinetics, it is not consumed by **2a**, and it follows eq 2. Its initial chemiluminescence intensity, however, appears to be at least an order of magnitude larger than is predicted by its oxidation potential (0.73 V vs. SCE)[38] and Figure 4. The catalytic rate constant k_2, moreover, is consistent with this large intensity. We are continuing to investigate this apparent anomaly.

According to eq 8, the magnitude of k_{cat} will also be dependent on the reduction potential of the peroxide. Comparison of catalytic rate constants for various peroxides bears this out. Diphenoyl peroxide, a diacyl peroxide, reacts with rubrene in dichloromethane 20 times faster than dimethyldioxetanone, a peroxy ester, under similar conditions.[1b,31] Peroxy esters are more difficult to reduce than diacyl peroxides.[39] Simple alkyl peroxides are even more difficult to reduce.[39] Consistent with this, we have not yet detected kinetically an activator-catalyzed component of the reaction of tetramethyldioxetane, even with DMP, the most easily oxidized activator of the present series.

The lack of a measurable acceleration of the rate constant of tetramethyldioxetane decomposition by DMP does not, however, exclude significant light generation by a CIEEL pathway in this system. A small CIEEL component, even one too small to discern kinetically, but which had a high efficiency of excited state generation, could easily account for a significant fraction of the chemiluminescence, since it would be competing with the rather inefficient singlet production of the unimolecular reaction.

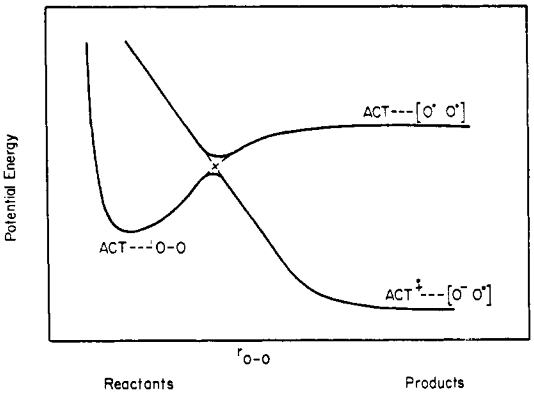


Figure 6. State correlation diagram for the activated electron transfer with simultaneous cleavage of the oxygen–oxygen bond.

This is in fact the situation at hand with **2a**. The continuity of the intensity vs. oxidation potential plot (Figure 4) demands that, even for the more difficultly oxidized hydrocarbons, the majority of the chemiluminescence results from the activator-catalyzed path. Yet, as indicated in Table III, only a very small fraction of the dioxetanone molecules may be reacting via this path. Under the conditions of the intensity experiment ([activator] = 2×10^{-5} M), for example, no rate acceleration is observed for any of the aromatic hydrocarbons. Yet our results show that in this experiment only 15% of the light produced when perylene is the activator arises from energy transfer from acetone singlet; the remaining 85% is derived from the CIEEL path.[40] With rubrene as activator at 2×10^{-5} M, only 1% of the light results from energy transfer. The remaining 99% comes from the CIEEL path, and still there is no experimentally discernible effect of rubrene on the rate of the reaction. This finding is a reflection of the much greater light producing potential of the CIEEL reaction compared with the unimolecular fragmentation of **2a**.

Importantly, these ideas demonstrate the inapplicability of the use of 9,10-diphenylanthracene (DPA) ($E_{\mathrm{ox}} = 1.22$ V) as an energy transfer acceptor in the measurement of carbonyl excited state yields from the unimolecular reaction of dioxetanones, and even question the reliability of its use with dioxetanes. Upon extrapolation to infinite DPA concentration, as is the standard procedure,[41] even a very small k_{cat} yields an infinite rate. At infinite DPA concentration, the CIEEL component of the total light yield may well be substantial.

In Scheme I we suggest that the radical anion species **7** decarboxylates to give acetone radical anion. In fact our results do not distinguish between this and the other possible pathway of carbon–carbon bond cleavage, namely, loss of neutral acetone and formation of carbon dioxide radical anion. In either case, the fragmentation converts a relatively easily reduced species (**7**) to a highly reducing species, be it acetone or carbon dioxide radical anion, in the same solvent cage as activator radical anion. Evidence that the entire light-generating sequence occurs within the initial solvent cage comes from the observation that the yield of light is not affected by oxygen or small amounts of water. Free radical ions would be expected to react rapidly with these species.

The final step of the chemiexcitation sequence is annihilation of the radical ions to form the excited state of the activator. The energy available for excited state generation is simply the sum of the oxidation potential of the activator and the reduction potential of acetone (or carbon dioxide). Unfortunately, a rigorous analysis of the energetics of the annihilation (based on electrochemical data) is not possible. No reversible electrochemical reduction of carbon dioxide[42] or of acetone[43] has been reported. Observed potentials therefore yield only a lower limit to the energetics. Moreover, chemiluminescence experiments were carried out in benzene solvent, in which no electrochemical data can be obtained. We are currently probing the effect of solvent on charge annihilation efficiency in other systems. The continuity of the intensity plot of Figure 4 does suggest that, even for DMP (E_{ox} = 0.11 V; E_{s} = 72 kcal mol^{-1}), the charge annihilation is energy sufficient for formation of DMP singlet. In fact, this continuity indicates that, while the rate of the initial electron transfer depends critically on the activator, the efficiencies of all subsequent steps in the excited state generating sequence are independent of activator, despite their diverse structure.

Conclusion

The dual chemiluminescent pathways for the thermal reaction of dioxetanone **2a** make it a unique member of the dioxetane class. The unimolecular chemiluminescence appears to fall easily within the framework of conventional dioxetanes.[3] For example, triplet acetone is formed some 15 times more efficiently than is singlet excited acetone. The total yield of excited state product from **2a,** however, is more than 20 times less than that of tetramethyldioxetane. The low yield is reflected in the difference in the activation energies between the chemiluminescent and the dark reaction paths. There may be a similar relationship between the yield of excited states and activation energy operating for tetraalkyldioxetanes as well. In these cases, however, the magnitude of the activation energy difference may be too small to detect experimentally. We can offer no explanation for the comparatively low yield (despite the large reaction exothermicity) of electronically excited states from **2a.**

The involvement of the CIEEL process in the thermolysis of **2a** immediately offers new insight into many previously perplexing proposals of dioxetane or dioxetanone intermediacy in various chemi- and bioluminescent reactions. For example, the discovery of activated chemiluminescence for **2a,** and the finding that intramolecular electron transfer can generate a very high yield of electronically excited singlet,[45] has prompted us to speculate that an intramolecular version of the CIEEL mechanism is operating in the bioluminescence of the firefly.[44] Our experience with **2a,** and other peroxides capable of reactions releasing sufficient energy to populate electronically excited states, indicates that the most important light-generating process is the CIEEL reaction. We are continuing to probe the generality of this conclusion and the details of the reaction mechanism.[54]

Experimental Section

General. Proton magnetic resonance spectra were recorded on a Varian Associates EM-390 instrument, with tetramethylsilane as internal standard. UV spectra were recorded on a Cary 14 spectrometer. Mass spectra were obtained with Varian MAT CH-5 and 731 mass spectrometers. Elemental analyses were performed by Mr. J. Nemeth and Associates, Department of Chemistry, University of Illinois, Urbana. Melting points are uncorrected. Liquid chromatography was performed on neutral alumina unless otherwise noted.

Chemiluminescence Measurements. The photon counting technique was used, employing an EMI 9813B or 9816B photomultiplier tube. Spectral resolution was achieved with a Jarrel-Ash 0.25 M monochromator. The band-pass under high resolution conditions (as were used in obtaining the spectra in Figure 1) is calculated by using data provided by the manufacturer to be 5 nm. For low-resolution conditions (as were used in obtaining relative activator intensities, see below), the band-pass is calculated to be 26 nm. Sample temperature was regulated to within ±0.05 °C by means of a Haake constant-temperature circulating bath. A National Bureau of Standards thermometer was used to calibrate sample temperatures.

Chemiluminescence Solvents. Benzene (Burdick and Jackson Laboratories; distilled in glass) and $C_2Cl_3F_3$ (Freon 113, Matheson) were shaken with sulfuric acid, saturated sodium bicarbonate, and water, dried over calcium chloride, passed through basic alumina, stirred over ethylenediaminetetraacetic acid (Na_4EDTA), and distilled. Carbon tetrachloride (Mallinckrodt spectrograde) was irradiated through Pyrex in the presence of benzophenone to remove sources of abstractable hydrogen and was then passed through basic alumina and distilled. Dichloromethane (Mallinckrodt spectrograde) was distilled from P_2O_5. Fluorobenzene (Aldrich) was passed through basic alumina and distilled from Na_4EDTA. Trichlorofluoromethane was distilled prior to use.

Dimethyldioxetanone (2a). Preparation was by the dicyclohexylcarbodiimide (DCC) mediated dehydrative cyclization of α-hydroperoxyisobutyric acid, as detailed by Adam and co-workers.[5] The dioxetanone was prepared in CCl_4, $C_2Cl_3F_3$, or fluorobenzene. After purification by bulb-to-bulb distillation (with codistillation of solvent), the peroxide solutions were stored in Teflon-lined vials on dry ice. The dioxetanone concentration, typically 0.03 M, was determined by ^{1}H NMR at −10 °C, using either *p*-dichlorobenzene or dibenzyl ether as internal standard. The kinetics of the thermolysis of dilute benzene solutions of **2a** were independent of the batch of dioxetanone, as were the chemiluminescence emission spectra.

Tetramethyldioxetane (1a) was prepared and purified as described by Kopecky and co-workers.[46]

Activators. Rubrene, tetracene, and perylene (Aldrich) were chromatographed eluting with benzene, and were then recrystallized from purified benzene. 9,10-Bis(phenylethynyl)anthracene (BPEA) and 5,12-bis(phenylethynyl)tetracene (BPET) were prepared by published procedures[47] and were purified by chromatography. Zinc tetraphenylporphyrin (Sigma), purified according to Barnett et al.,[48] was chlorin free (≤1%) by visible absorption spectroscopy. 5,10-Dimethyl-5,10-dihydrophenazine (DMP) (**3**), prepared according to Gilman,[49] was purified by chromatography eluting with 25% ether in hexane, sublimation (90 °C, 2 × 10^{-5} mm), and recrystallization from benzene-hexane. 9,14-Dimethyl-9,14-dihydrodibenzo[*a,c*]phenazine (DMAC) (**5**) was prepared and purified according to published procedures.[50] *N,N*-Dimethyl-6-aminochrysene was prepared by dimethyl sulfate methylation of 6-aminochrysene.[51] 1,3-Diphenylisobenzofuran (Aldrich) was chromatographed eluting with 2% ether in hexane and recrystallized from hexane. *N,N*-Dimethyl-*p*-anisidine was prepared as detailed by Leonard.[52]

6,13-Dimethyl-6,13-dihydrodibenzo[*b,i*]phenazine (4). 6,13-Dihydrodibenzo[*b,i*]phenazine (0.52 g, 1.8 mmol, Aldrich) was stirred in 15 mL of dry tetrahydrofuran. Lithium diisopropylamine, prepared from 4.2 mmol of diisopropylamine and 4.2 mmol of *n*-butyllithium, was added dropwise, affording a deep red solution which was stirred at room temperature for 1.5 h. Iodomethane (1.2 mL, 19 mmol) was added, discharging the red color and yielding a green precipitate. After dilution with water, the mixture was CH_2Cl_2 extracted. Drying ($MgSO_4$) and concentration gave 528 mg of crude **4**. Chromatography, eluting with 12% THF in hexane, yielded 200 mg (35%) of pure **4**, mp >300 °C after recrystallization from benzene-hexane, as pale yellow plates: ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 6 H, methyl), 6.76 (s, 4 H, aromatic), 7.10-7.25 and 7.45-7.60 (symmetric m, 8 H, aromatic); MS (70 eV) *m/e* (rel abundance) 311 (20), 310 (87), 296 (30), 295 (100), 286 (19), 285 (97), 155 (24), 148 (24), 140 (36); molecular ion (calcd for $C_{22}H_{18}N_2$, *m/e* 310.1466), 310.1469; UV (benzene) $\lambda_{\max}$ (log ε) 296 (4.63), 397 (4.06).

Anal. Calcd for $C_{22}H_{18}N_2$: C, 85.10; H, 5.84; N, 9.06. Found: C, 85.01; H, 5.87; N, 8.93.

9,14-Dimethyl-9,14-dihydrophenanthro[4,5-*abc*]phenazine (6). Freshly cut sodium (520 mg, 22.6 mmol) was stirred in 15 mL of dry tetrahydrofuran. Phenanthro[4,5-*abc*]phenazine[53] (700 mg, 2.3 mmol) was added in portions over 0.5 h, and the resulting mixture was stirred at room temperature for 5 h. Iodomethane (1.5 mL, 24 mmol) was added, discharging the black color. To the resulting red solution was added water and then saturated NH_4Cl. Ether extraction, drying of the organic materials and concentration afforded 700 mg of a red-yellow oil. Chromatography, eluting with 20% ether in hexane, gave 250 mg (33%) of **6** as a yellow orange solid. Samples for chemiluminescence experiments were recrystallized in benzene-hexane: mp 211.5-212 °C; ^{1}H NMR ($CDCl_3$) δ 3.50 (s, 6 H, methyl), 7.05

(m, 4 H, aromatic), 7.76-8.05 (m, 6 H, aromatic), 8.32-8.48 (m, 2 H, aromatic); MS (70 eV) *m/e* (rel abundance) 335 (9), 334 (35), 320 (25), 319 (100), 305 (14), 304 (60), 303 (11), 154 (23); molecular ion (calcd for $C_{24}H_{18}N_2$, *m/e* 334.1466), 334.1468; UV (benzene) λ_{max} (log ϵ) 314 (4.53), 328 (4.52), 398 (3.75).

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.39; H, 5.38; N, 8.21.

Chemiluminescence Intensity Activation Energy, E_{chl}. Samples were prepared at 0 °C by dilution of dimethyldioxetanone stock solution (either $C_2Cl_3F_3$ or CCl_4) in the appropriate solvent (normally 50 μL in 2 mL). Typical dioxetanone concentrations were 9×10^{-4} M. The air-saturated solutions were transferred to a quartz cell equipped with a Teflon stopcock, placed in the thermostated cell holder and allowed to equilibrate over 4 min. That thermal equilibration was achieved was demonstrated by the constancy of chemiluminescence intensity, which was then averaged over the next minute. Thus a total of 5 min was required for the measurement. During this time, even at 15 °C ($k = 1.5 \times 10^{-4}\ s^{-1}$), less than 5% of the dioxetanone has reacted. This is verified by the constancy of the intensity (within 5% experimental error) recorded over the 1-min measurement. Typically the intensities of two to three runs at each temperature were averaged. Intensities were measured at 5 or 6 temperatures in the range of −4 to +14 °C. The derived activation energies are summarized in Table I.

Absolute Yields of Singlet and Triplet Excited Acetone from Thermolysis of 2a at 30.0 °C. The yield of light from **2a** was determined by direct comparison of the total time-integrated acetone fluorescence (air-saturated solution) and phosphorescence (argon-saturated solution) intensities with that from the thermolysis of tetramethyldioxetane (**1a**) in $C_2Cl_3F_3$ at 30.0 °C. The total integrated light intensity I_n for thermolysis of **1a** was determined according to eq 9, where I_0 is the instantaneous intensity at time zero, and k is the rate constant for the decay of the chemiluminescence intensity. The rate constant at 30.0 °C, $k_{30°C}$, was determined according to eq 10, where k_{tn} is the rate constant for thermolysis of **1a** at temperature T_n. Rate constants were measured at five temperatures between 60 and 80 °C by monitoring the decay of chemiluminescence from **1a.** A least-squares analysis of a plot of ln (k_{tn}) vs. $(1/T_t - 1/T_n)$ where T_t = 313.14 K (Table IV) affords $k_{30°C} = (1.7 \pm 0.2) \times 10^{-6}\ s^{-1}$. The total acetone fluorescence intensity from **2a** was 0.6 ± 0.1 times that from **1a.** The total acetone phosphorescence intensity from **2a** was 0.05 ± 0.01 times that from **1a.** Using 0.2[19] and 30%[20] as the singlet and triplet yields from **1a,** this comparison gives 0.1 and 1.5% for the singlet and triplet yields, respectively, from **2a** at 30.0 °C.

$$I_n = I_0[1/k] \qquad (9)$$

$$\ln (k_{tn}) = \ln k_T - E_a/R(1/T_t - 1/T_n) \qquad (10)$$

Temperature Dependence of the Singlet Excited Acetone Yield from Thermolysis of 2a. The relative total time integrated acetone fluorescence intensities in air-saturated $C_2Cl_3F_3$ solutions, 3.4×10^{-4} M in **2a,** were determined at eight temperatures between −5 and 30 °C. Results are summarized in Table II. For temperatures of 9.8 °C and above, the total integrated intensity was measured directly. For lower temperatures, initial instantaneous intensities were measured, and the total intensities calculated by eq 9. The required rate constants, k_{tn}, were obtained according to eq 10 employing the experimentally determined rate constants from the range 9.7 to 34.0 °C as shown in Table V.

Initial Intensities from the Activator-Catalyzed Reaction of 2a. Intensities were determined at 2×10^{-5} M in activator (to minimize self-absorption) in benzene solution at 24.5 °C. The intensities were measured at the wavelength of maximum activator fluorescence, under low resolution conditions, such that the emission spectra were Gaussian. Corrections for photomultiplier tube and monochromator efficiencies were made by using data supplied by the manufacturer and the center of gravity of the emission spectra. A small acetone emission was subtracted.

Solutions of activator in benzene were argon purged at 6 °C for 4 min, and were then equilibrated at 24.5 °C for 5 min. The dioxetanone stock solution was then injected directly into the cell (typically 10 μL to 2 mL). The initial intensity was then obtained by extrapolation of the first-order decay back to zero time. At most, a 10-s extrapolation was required. Control experiments showed that activator fluorescence was not quenched by the addition of the small amount of air saturated fluorobenzene or $C_2Cl_3F_3$ dioxetanone solutions.

Table IV. Rate Constants for Tetramethyldioxetane (**1a**) Thermolysis[a]

temp, °C	10^4k, s^{-1}	
59.30	0.924 ± 0.002	
65.00	1.74 ± 0.01	E_a = (27.1 ± 0.6) kcal mol^{-1}
70.10	3.25 ± 0.01	log A = (13.8 ± 0.5)
75.05	6.04 ± 0.02	
80.70	10.6 ± 0.2	

[a] Air-saturated $C_2Cl_3F_3$ solutions, 10^{-4} M in **1a,** in sealed tubes. Determined by monitoring decay of acetone fluorescence intensity. All errors are standard deviations.

Table V. Rate Constants for Thermolysis of **2a** in $C_2Cl_3F_3$

temp, °C	10^4k, s^{-1}	temp, °C	10^4k, s^{-1}
34.40	(18.3 ± 0.2)[a]	9.70	(0.798 ± 0.001)[a]
30.00	(11.1 ± 0.1)[a]	4.80	(0.40 ± 0.01)[b]
25.10	(5.89 ± 0.01)[a]	0.30	(0.21 ± 0.01)[b]
20.50	(3.35 ± 0.01)[a]	−5.00	(0.094 ± 0.003)[b]
15.35	(1.75 ± 0.01)[a]		

[a] Experimental values, from chemiluminescence decay. Air-saturated solutions, 3.4×10^{-4} M in **2a.** All errors are standard deviations.
[b] Calculated by least-squares analysis of eq 10.

Chemical Yield of Acetone from the DMAC-Catalyzed Decomposition of 2a. The concentration of **2a** in a fluorobenzene stock solution was determined by ^1H NMR at −10 °C, using dibenzyl ether as internal standard. To this was added, at 0 °C, a solution of DMAC in benzene, bringing the concentration of DMAC to 2.3×10^{-3} M. At this concentration of DMAC, essentially 100% of the reaction of **2a** proceeds by the catalyzed path. Determination of the acetone concentration gave a yield of 96-100%.

Acknowledgment. We thank Professor L. Faulkner for a gift of tri-*p*-tolylamine. Mr. Brian Dixon measured the oxidation potentials and the fluorescence quantum yields of the dihydrophenazines. This work was supported in part by the Office of Naval Research, in part by the National Science Foundation, and in part by the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Listings of observed rate constants for the unimolecular and the activator-catalyzed thermolysis of **2a** (Tables VI and VII) (3 pages). Ordering information is given on any current masthead page.

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(23) The exceptions in the present series of activators are *N,N*-dimethyl-6-aminochrysene (DMACh) and 1,3-diphenylisobenzofuran which are consumed in the reaction with **2a.** In these cases the kinetics therefore were carried out with excess activator and first-order behavior was observed. The electrochemical oxidation of DMACh is irreversible.

(24) These values represent a composite activation energy for all steps leading to and including luminescence. For example, the temperature dependence of the rate of separation of the cage ion pairs (see below) is also included: Werner, H.-J.; Schulten, Z.; Schulten, K. *J. Chem. Phys.* **1977,** *67,* 646.

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(26) (a) The fluorescence efficiency of 9,10-dibromoanthracene was taken to be 10% at 25 °C and the triplet-singlet energy transfer efficiency 25%.[20a,26b] (b) Bernefel'd, V. M.; Chumavskii, E. V.; Grinev, M. P.; Kuryatnikov, Y. I.; Artem'ev, E. T.; Dzhagatspanyan, R. V. *Bull. Acad. Sci. USSR, Phys. Ser.* (*Eng. Transl.*) **1970,** *3,* 597.

(27) Application of the steady-state approximation for [acetone*] leads to eq 11. Under the conditions of the experiment, [**2a**] is constant. Therefore when $k_L \ll k_D$, eq 11 reduces to eq 3.

$$\text{intensity} \propto k_A[\mathbf{2a}][k_L/(k_L + k_D)] \qquad (11)$$

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(54) NOTE ADDED IN PROOF. Subsequent to the submission of this manuscript, a report by Adam and Cueto on dimethyldioxetanone chemiluminescence appeared: Adam, W.; Cueto, C. *J. Am. Chem. Soc.* **1979,** *101,* 6511. Several of the observations reported in that paper are contrary to our experience and warrant further discussion. We have not been able to detect kinetically catalysis of the reaction of **2a** by high oxidation-potential activators such as DPA. In contrast, Adam and Cueto claim to have observed catalysis by DPA kinetically. However, their data indicate that the *reaction* of **2a** is actually *faster* in the absence of DPA (entry 37, Table I of Adam and Cueto) than in its presence (entries 31–33, Table I of Adam and Cueto). This incongruity indicates that Adam's reported rate constants in this case are not of sufficient precision to be used as evidence of catalysis. Moreover, Adam and Cueto's claim (footnote 19) that their k_{obsd} is dependent on the concentration of **2a** is internally inconsistent with their report (eq 2 and Table I) of first-order decay of the chemiluminescence intensity. As stated above, it is our experience that, for carefully purified solutions of **2a,** the observed rate constants are independent of concentration. Finally, our explanation for the observed slope of −0.3/*RT* (Figure 3 and footnote 25 of Adam and Cueto) is incorrectly interpreted in Adam's report. The meaning of the magnitude of the slope is discussed fully above.

Absence of Stereoelectronic Control in the Photochemistry of Two Diastereomeric β,γ-Epoxy Ketones

Semiramis Ayral-Kaloustian and William C. Agosta*

Contribution from the Laboratories of The Rockefeller University, New York, New York 10021.

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Abstract: The preparation and photolysis of ketones **5, 8,** and **11** are described. Both diastereomeric spiro epoxy ketones **5** and **8** yield the same products, **12** and **13,** at the same rate (± ~3%); spiro cyclopropyl ketone **11** gives **16–18,** and a labeling experiment with **11D** showed that these products arise through stereospecific cleavage of the axial cyclopropyl bond of **11** (see **20D**). These results indicate that, while opening of the cyclopropane ring of **11** is under stereoelectronic control, as expected, there is no observable stereoelectronic effect in cleavage of the epoxide ring of **5** and **8.** An explanation for this behavior is offered.

There is strong evidence that an important set of photochemical reactions of β,γ-cyclopropyl ketones involves α cleavage, subsequent rearrangement of the initial cyclopropylmethyl radical to a homoallyl radical, and then product formation from the resulting radical pair or biradical.[1] This pathway, first suggested some 12 years ago,[2] is shown in eq 1, X = CH_2. More recently an analogous sequence has been put forward for related photochemical reactions of β,γ-epoxy ketones.[3] These steps are shown in eq 1, X = O, and they satisfactorily account for the behavior of a variety of substrates.[3-5]

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