Chemiluminescent Thermolysis of α-Peroxylactones

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Abstract: A comprehensive study of the chemiluminescent decomposition of three α-peroxylactones (dimethyl α-peroxylactone (1), phenyl n-butyl α-peroxylactone (2), and diphenyl α-peroxylactone (3)) has been undertaken. Each compound decomposes to yield CO₂ and the corresponding ketone in high yield. The chemiluminescent species produced in these reactions have been characterized by a number of different measurements including spectral distribution of direct chemiluminescence, lifetimes, energy transfer, activation parameters, and photochemical reactions. Excited state chemiluminescence efficiencies have also been evaluated. It is shown that a combination of conventional kinetic measurements and “step analysis” of the chemiluminescence intensity provides a means of evaluating the activation energies for the deactivation paths of electronically excited states that precede the emission step responsible for chemiluminescence. The latter activation energies may also be monitored directly in some cases by measurement of excited-state lifetimes as a function of temperature. The agreement between the activation energies generated from chemiluminescence data and direct photoexcitation measurements is within the experimental error. The results for 1 are compared to those for tetramethyldioxetane (4) (both produce electronically excited acetone) and are found to be in excellent agreement.

Introduction

Investigation of the energetics, kinetics, activation parameters, and chemiexcitation parameters of decomposition of 1,2-dioxetanes has provided a wealth of information concerning chemiluminescence mechanisms. The overwhelming proportion of published work deals with 1,2-dioxetanes, and only brief reports of α-peroxylactones have appeared, possibly because of the difficulties of synthetic entries into this family of high energy content molecules. As a result of our recent discovery that α-peroxylactones may be conveniently synthesized by reaction of ketones and phosphite oxonites, we have been able to initiate a comprehensive study of the chemiluminescent decomposition of these important high-energy compounds. Our goals in this investigation were (a) to identify the excited-state species; (b) to quantify the chemiexcitation parameters; (c) to evaluate the activation parameters for the decomposition of dimethyl α-peroxylactone (1), phenyl n-butyl α-peroxylactone (2), and diphenyl peroxylactone (3); (d) to determine the activation energy for decay of the excited-state species involved in the chemiluminescence process; (e) to compare the excitation parameters of 1 and tetramethyldioxetane (4); and (f) to evaluate the activation parameters for the decomposition of 4 in the gas phase.

We report here our progress toward achieving these goals and show how a combination of chemiluminescence measurements and...
conventional kinetic measurements allow evaluation of the activation energies for the dominant "dark" deactivation pathways of electronically excited states.

**Derivation of Temperature Coefficients from Chemiluminescence Measurements**

Under appropriate experimental conditions, there is a strict proportionality between the instantaneous intensity of chemiluminescence ($I$) and the reaction rate ($r$). For the case of direct chemiluminescence measurements from decomposition of α-peroxylactones we consider the simple kinetic scheme 4,

\[ D \rightarrow *K + \text{CO}_2 \quad *\phi_k \]  
\[ D \rightarrow *K + \text{CO}_2 \quad (1 - *\phi)k_s \]  
\[ *K \rightarrow *K + \hbar \nu \quad k_e \]  
\[ *K \rightarrow \text{no light} \quad k_d \]  

where $*\phi$ is the efficiency of formation of an excited ketone, $k_s$ is the rate constant of total disappearance of α-peroxylactone, and $k_e$ and $k_d$ are the rate constants for emission and dark deactivation of $*K$, the electronically excited ketone, respectively.

Under the conventional steady-state approximation we may relate two experimental observables, $I$ and $r$, to the theoretical quantities listed in the kinetic scheme. We have thus

\[ I = *\phi \phi_k [D] \]  
\[ I = \phi_c K[I] [D] \]

where $\phi_c$ and $\phi_k$ are the appropriate efficiencies of form $*K$ and the decomposition of $D$, respectively.

We may write eq 6 as

\[ I = *\phi k_s k_d k_e^{-1} [D] \]

According to eq 6, since the instantaneous rate of light emission is proportional to $*\phi_k k_s [D]$, then at the very onset of luminescence $I/d$ is small compared to the total luminescence integrated over complete reaction. In effect $[D]$ is constant within the experimental error during the measurement of $I$, so that any variation in $I$ as a function of temperature must be due to variations in $\phi_c K[I]$ and $k_e$ as functions of temperature. This procedure for determining the temperature coefficient of chemiluminescence ($E_{CL}$) is termed step analysis. 14 The temperature coefficient of $k_e$ may be determined experimentally by standard kinetic measurements and application of the Arrhenius equation. In this case, the temperature dependence may be associated with the conventional Arrhenius activation $E_a$. If $\phi_c, K[I]$, and $k_e$ are temperature dependent, then the temperature coefficient, $E_{CL}$, of $I$ derived from conditions where $[D]$ does not change (within the experimental error of measuring $I$) and will not equal $E_a$, so that a discrepancy $\Delta E$ will exist, i.e.,

\[ \Delta E = E_a - E_{CL} \]

We interpret $E_a$ as the conventional "activation energy" for unimolecular decomposition of dioxygenates. The derived quantity $E_{CL}$ is interpreted as a composite of activation parameters of all steps preceding and including the luminescence step.

Since $*\phi$ has been shown to be temperature independent in the case of dioxygenates 15 and since radiative rate constants of emission ($k_e$) generally show negligible temperature dependences, it is possible to associate $\Delta E$ with the temperature dependence of $k_d$. More specifically we can associate $\Delta E$ with the activation energy for the dominant deactivation pathway for the electronically excited ketone, $*K$.

| Table I. Excited State and Excitation Parameters for α-Peroxylactone |  |
|---|---|---|
| α-peroxylactone | $\phi$ (S) | $\phi$ (T) | $\tau_{1/2}$ (25 °C) |
| 1 | 0.001 | 0.06 | 973 |
| 2 | 0.11 | 0.05 | 280 |
| 3 | 0.44 | 0.45 | 373 |
| 4 | 0.001 | 0.3 | 7364 (53 °C) |

4 In CFC13. 5 Half-life of dioxygenates (s). 6 In CH3Cl.

Although a number of assumptions must be made in associating $\Delta E$ with the activation energy of a photochemical process, in certain cases both $\Delta E$ and the temperature dependence of $k_d$ may be measured experimentally so that the latter may be measured as a function of temperature and the Arrhenius parameters $E_a$ for the deactivation process may be derived and compared. Moreover, whenever the $E_a$ cannot be easily measured experimentally, the step analysis of chemiluminescence intensity can provide a reasonable quantitative piece of information, i.e., $\Delta E$.

**Results**

**Identification of Excited-State Species Produced in α-Peroxylactone Decomposition.** Both acetone singlet and triplet states are produced in the thermolysis of 1 and are readily identified by their characteristic fluorescence and phosphorescence spectra and behavior toward oxygen quenching. 5 The direct chemiluminescence from nitrogen-purged CFC13 solutions of 1 consists mainly of acetone phosphorescence ($\lambda_{max}$ ~420 nm), whereas in oxygenated solutions the direct chemiluminescence from 1 is nearly pure fluorescence ($\lambda_{max}$ ~400 nm). The yields of $S_1$ and $T_1$ states of acetone from 1 were obtained by comparison of the indirect chemiluminescence of tetramethyl-1,2-dioxetane (4) from 9,10-dibromoanthracene and 9,10-diphenylanthracene as standard, 10 based on the literature report that the excited-state yield for decomposition of 4 is temperature independent. 16 The excited-state yield for decomposition of 1 is the same within the 10% experimental error at temperatures 23, 50, and 75 °C.

That valerophenone triplets are produced during thermolysis of 2 in CFC13 is evidenced by the observation of acetoephone (product of type II reaction of triplet valerophenone) among the reaction products 6 (eq 12). A Stern–Volmer quenching analysis of the indirect chemiluminescence of 2 (9,10-dibromoanthracene as an energy acceptor 7 and monitoring of 9,10-dibromoanthracene fluorescence) yields a lifetime of 9 ± 2 ns for the chemiexcited species produced from 2. This lifetime is consistent with that reported for valerophenone triplets prepared by photoexcitation. 8

The yield of triplet-state benzophenone was determined by means of its characteristic reaction with 2-methyl-2-buten (eq 11). 9 The results are summarized in Table I.

amplifier and discrimination level, are different from a set of measurements to the other. Therefore, there is no direct comparison possible.

The rate constant was derived from the decay of chemiluminescence in nitrogen-saturated Freon-11 solution and in the gas phase. The concentrations of dimethyl α-peroxylactone and tetramethylidioxetane are \(2 \times 10^{-3}\) and \(1 \times 10^{-4}\) \(M\), respectively. The concentrations of diphenyl α-peroxylactone and phenyl n-butyl α-peroxylactone are \(1 \times 10^{-3}\) \(M\), determined by iodometric titration. The concentration of perylene used as a fluorescer is \(1 \times 10^{-4}\) \(M\). The measurement was performed in the gas phase. The pressure of tetramethylidioxetane was estimated as 1 Torr.

The solutions used here are the same as the solutions used in the measurements listed in Table II. The instrumental settings, i.e., gain of amplifier and discrimination level, are different from a set of measurements to the other. Therefore, there is no direct comparison possible among the sets of measurements. The intensity (counts/min) of one measurement presents the average count over at least a 10-min period. The intensity listed here is the average of three or more independent measurements. The background of the instrument is less than 10 counts/min. The measurement was performed in the gas phase.

The rate constants in nitrogen-saturated solution for 1 and 4 are found to be identical with those in oxygen-saturated solution. The chemiluminescence from 2 and 3 was not detectable in oxygen-saturated solution. The chemiluminescence intensities from steady-state measurements of the decompositions of 1–4 are summarized in Table III. The decay constant for total disappearance of dioxytane as a function of temperature. \(E_{\text{CL}}\) is the temperature coefficient for chemiluminescence derived from step analysis. Solutions are oxygen saturated. \(E_{\text{d}}\) is the conventional Arrhenius activation energy derived from measurements of the rate constant for total disappearance of dioxytane as a function of temperature.
rate constants of acetone phosphorescence in nitrogen-saturated Freon-11 solution are summarized in Table IV. The values of \( E_p, E_{CL}, \) and \( E_d \) derived from data in Tables II–IV are summarized in Table V. The rate constants and chemiluminescent intensities of the decomposition of tetramethyldioxetane in air-saturated benzene solution are summarized in Table VI.

### Table VI. Rate Constants of the Decomposition of Tetramethyldioxetane and Intensities of Step-Function Analysis of Tetramethyldioxetane in Air-Saturated Benzene Solution

<table>
<thead>
<tr>
<th>rate constant, s(^{-1})</th>
<th>temp, °C</th>
<th>intensity(^a)</th>
<th>temp, °C</th>
<th>intensity(^b)</th>
<th>temp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3.20 ± 0.02) \times 10^4</td>
<td>82 ± 0.3</td>
<td>(5.61 ± 0.28) \times 10^2</td>
<td>89.0 ± 0.3</td>
<td>(1.33 ± 0.02) \times 10^2</td>
<td>51.0 ± 0.2</td>
</tr>
<tr>
<td>(1.95 ± 0.08) \times 10^4</td>
<td>76.2 ± 0.3</td>
<td>(2.80 ± 0.14) \times 10^2</td>
<td>82.0 ± 0.3</td>
<td>(3.88 ± 0.05) \times 10^1</td>
<td>46.5 ± 0.2</td>
</tr>
<tr>
<td>(9.47 ± 0.05) \times 10^4</td>
<td>70.4 ± 0.3</td>
<td>(1.56 ± 0.07) \times 10^2</td>
<td>76.2 ± 0.3</td>
<td>(3.04 ± 0.10) \times 10^1</td>
<td>41.1 ± 0.2</td>
</tr>
<tr>
<td>(6.89 ± 0.04) \times 10^4</td>
<td>70.4 ± 0.2</td>
<td>(1.95 ± 0.02) \times 10^2</td>
<td>70.4 ± 0.2</td>
<td>(1.95 ± 0.02) \times 10^2</td>
<td>35.4 ± 0.2</td>
</tr>
<tr>
<td>(3.39 ± 0.17) \times 10^4</td>
<td>63.3 ± 0.2</td>
<td>(9.68 ± 0.20) \times 10^1</td>
<td>63.3 ± 0.2</td>
<td>(9.68 ± 0.20) \times 10^1</td>
<td>30.5 ± 0.2</td>
</tr>
</tbody>
</table>

\(^a\) The concentration of tetramethyldioxetane is 1.2 \times 10^{-3} M. \(^b\) The intensity is the counting rate/10 s. The background of the instrument is less than 10 counts/min. \(^c\) The maximum intensity was used.

The direct experimental value of \( \Delta E \) is not available. However, from the temperature dependence of the quenching of type II reaction of valerophenone triplets, a value of \( E_q \sim 6 \) kcal/mol was derived.\(^{12}\) This value is close to the experimental value of \( \Delta E = 7.4 \pm 1.0 \) kcal/mol measured for decomposition of 2. At this point we can imagine the small discrepancy to be due to extra contributions to \( \Delta E \) in our system, or to an inaccurate derivation of \( E_q \) for valerophenone triplets.

The direct experimental value of \( E_q \) for benzophenone triplets was determined and found to be 0.0 ± 1 kcal/mol. The experimental value of \( \Delta E \) was determined to be 0.2 ± 1 kcal/mol, so that \( \Delta E \) and \( E_q \) values are identical within the experimental error.

#### Interpretation of \( \Delta E \) and \( E_q \)

The fact that \( \Delta E \) and \( E_q \) are experimentally indistinguishable for 1, 3, and 4 and nearly so for 2 supports the postulate that these quantities refer to the same activated step for each system; i.e., \( \Delta E \) and \( E_q \) refer to the same activation energies for the dominant deactivation processes of \( K_k \).

The question now arises as to the nature of that step.

As for acetone singlets \( k_2 \) is readily associated with \( k_{Sp} \), the rate constant for intersystem crossing. In organic molecules, \( T_1 \) conversions are generally rate determined by the extent of spin–orbit coupling between \( S_1 \) and \( T_1 \); we assume that \( T_2 \) is not thermally accessible to \( S_1 \). As a result, \( k_{Sp} \) is expected to be temperature independent, as is indeed found to be the case experimentally.

For acetone triplets, \( k_4 \) may be associated with some intramolecular radiationless process. An attractive candidate is photochemical \( \alpha \)-cleavage. The activation energy for photochemical \( \alpha \)-cleavage of acetone in the vapor phase is reported to be 6.4 kcal/mol,\(^{13} \) a value within the experimental error of \( \Delta E \). If this interpretation is correct, then chemiluminescence methods can be employed to measure activation energies for photochemical processes.

For valerophenone triplets, \( k_4 \) may be associated with type II reaction. Such a process is believed to possess a substantial activation energy, although we feel that \( \Delta E \) may reflect an additional energy; i.e., the magnitude of \( \Delta E \) seems a bit too high in the light of literature values.\(^{12}\)

For benzophenone triplets, \( k_4 \) is probably associated with impurity quenching of some sort. Such processes are commonly diffusion controlled and as such require small or negligible activation energies.\(^{21}\)

#### Discussion

The data summarized in Tables I and V all refer to CFCl\(_3\) as solvent. Since solvent effects on the kinetic parameters, excitation efficiencies, activation parameters, and excited-state lifetimes are well-known, comparison to literature data in other solvents must be made with the possibility of solvent effects in mind.

For example, a value of \( E_q \sim 28 \) kcal/mol for decomposition of 4 in acetonitrile is reported.\(^{5} \) However, in solvent the values of \( \Delta E \) and \( E_q \) for acetone singlets and triplets were found to agree within the experimental error. The absolute values of \( \Delta E \) and \( E_q \) were \( \sim 3 \) kcal/mol in acetonitrile for acetone triplets.\(^{14}\)

The decomposition of methyl 1-adamantyl \( \alpha \)-peroxylactone is reported to have \( \Delta H^\circ \sim 14 \) kcal/mol. However, the accuracy of this value is suspect as a measure of a unimolecular decomposition pathway, since larger activation energies are well-known. If this is a catalytic pathway probably dominates the decomposition, as was the case for the tetracyclofundecane-1,2-dioxetane system in alcoholic solvents.\(^{21} \)

Our data suggest that values of \( E_q \) in the range 18–22 kcal/mol are typical for simple peroxylactones. The decomposition of tert-butyl \( \alpha \)-peroxylactone yields a value of \( E_q = 18.0 \) kcal/mol,\(^{26} \) a value more consistent with our results. A value of \( E_q = 23 \) kcal/mol has been reported for 1.\(^{15}\)

The experimental efficiency of excited-state formation of 1,2-dioxetanes is generally in the range 0.1–0.8 and the primary yields of triplets are generally 10–200 times greater than the primary yields of singlets.\(^{1} \) Our results suggest that \( \alpha \)-peroxylactones are qualitatively similar to 1,2-dioxetanes with respect to the overall excited-state efficiency (\( \phi_S \sim 0.06, 0.11, \) and 0.35 for 1, 2, and 3, respectively). The \( \phi_S/\phi_L \) ratio of 60 for 1 is also quite in line with the reported values for 1,2-dioxetanes.\(^{15}\)


\(^{(12)} \) J. Grotewold, D. Soria, and C. M. Previtali, *J. Photochem.*, 1, 471 (1972/73).


of the chemiexcitation parameters is consistent with qualitatively similar mechanisms for the formation of electronically excited fragments from 1,2-dioxetanes and α-peroxylactones. Although α-peroxylactones have been commonly invoked as important intermediates in bioluminescent processes, the fact that simple examples of such compounds mainly yield triplets contrasts with the fact that fluorescence (e.g., via chemiexcitation of singlets) is observed in the biosystems. A clever mechanistic escape from this dilemma is available in which a catalyzed decomposition of α-peroxylactones dominates the inherent unimolecular decomposition. A constraint on such a catalytic mechanism is the observation that formation of excited singlet states is dominant over formation of triplets. Irrespective of the mechanistic details for such a catalysis, such a situation has been demonstrated experimentally. In the case of the chemiluminescent decomposition of oxalate esters, the reaction rate and chemiluminescence efficiency are acceptor concentration dependent. Furthermore, the luminescence observed is acceptor fluorescence. A charge-transfer mechanism involving an acceptor-α-peroxylactone complex has been proposed for this system. An electron-transfer mechanism has also been suggested to explain the observed catalysis and enhancement of excitation efficiency by fluorescent acceptor in the chemiluminescent decomposition of diphenyl peroxide. The recent observation that chemiluminescence of 1,2-dioxetanes may be enhanced by silica gel may be still a further manifestation of catalytic chemiexcitation pathways.

Although the thermochemistry of the decomposition of α-peroxylactones has not yet been determined experimentally, a semiquantitative treatment based on group additivity relationships is possible. In Figure 1 we compare the energetics of the decomposition of dimethyl α-peroxylactone to that of tetramethyl-1,2-dioxetane. The exothermicity of the α-peroxylactone is expected to be greater than that for 1,2-dioxetanes. The ΔHº for thermolysis of α-peroxylactones is smaller than that of comparably substituted 1,2-dioxetanes. Recently, it has been reported that the route for excited singlet acetone formation from 1 has a higher activation energy than that for ground-state acetone formation. This conclusion was based on the difference between Eₕ and Eₐ, which were evaluated to be 22.3 ± 0.3 kcal/mol and 25.6 ± 0.1 kcal/mol in Freon-113, respectively. The latter value for ECL differs substantially from the value derived from our experiments. On the other hand, the quantum yield (0.08%) and Eₕ for the excited singlet acetone formation are the same as the data reported here (0.1% and 22.3 kcal/mol, respectively). The discrepancy between the literature data and our data on ECL (25.6 ± 0.1 vs. 21.6 ± 0.8 kcal/mol) is, of course, crucially relevant to the question whether the formation of excited singlet acetone from 1 requires a higher energy than is required for formation of ground-state acetone.

Several possible sources exist for the discrepancy between the reported and our value of ECL. A step-function measurement of chemiluminescence intensity as a function of temperature is used to derive ECL. This derivation is based on a crucial assumption, namely, that the consumption of starting material, 1, is negligible during the time period of the measurement. A simple check of this assumption is to demonstrate that the decay of chemiluminescence does not occur (within the experimental error) during a measurement and to demonstrate that a "used" sample gives the same intensity as a "fresh" sample. In order for the assumption to hold properly, measurements should be taken at temperatures as low as possible. In our work, the measurement was done between −5 and −27 °C, while in the literature work the measurement was performed in the temperature range 14 to −1 °C. From our work, a significant decay of chemiluminescence would have been observed in the latter temperature range.

In order to demonstrate that a proper temperature range is crucial for extracting accurate values of ECL from step-function measurements, a compound for which the equality of ECL and Eₕ has been well established, tetramethyldioxetane (4), was used as a model system. From the decay of 4 in air-saturated benzene, the activation energy, Eₕ, was derived as 25.4 ± 0.2 kcal/mol, in good agreement with published measurements. The step-function measurement, two temperature ranges, 30–51 and 63–89 °C, were employed. In the low temperature range, a constant chemiluminescence intensity was recorded. Furthermore, used samples showed the same intensity as a fresh sample (Figure 2). These observations demonstrate that the temperature range is crucial for evaluation of ECL from step-function measurements. Analyzing the intensity of chemiluminescence of 4 as a function of temperature results in values of ECL of 25.1 ± 0.3 and 26.9 ± 0.7 kcal/mol for "low" and "high" temperature ranges, respectively. A consistency of Eₕ and ECL derived from the low-temperature range is expected and found (25.4 ± 0.2 vs. 25.1 ± 0.3 kcal/mol). On the other hand, the discrepancy of Eₕ and ECL derived from the high-temperature range is such that ECL > Eₕ by about 2 kcal/mol. We conclude that the use of a higher temperature range could be responsible for the discrepancy in the values of Eₕ reported here and reported earlier.

**Experimental Section**

Freon-11 (Matheson) was chromatographed with a basic alumina (Fisher, activity I) column and then distilled. Gas- (nitrogen or oxygen) saturated solutions were prepared by bubbling the gas into the samples through a small glass capillary at −78 °C for over 10 min, followed by immediate closing of the cell. The cell was an ordinary quartz tube equipped with a Teflon stopcock. In addition to temperature control, the
cell reflector reflects chemiluminescent photons on a convex lens, which directs the photons onto the cathode of a photomultiplier tube.

The decays of direct or indirect (with fluoroscen) chemiluminescence from tetramethyldioxetane and α-peroxylactones were measured with a photomultiplier tube (Centronic-P4283TIR). The signal was amplified with an Ortec 113 preamplifier and Ortec 471 amplifier and was discriminated with an Ortec 550, SCA-701, multi-channel analyzer with an external MCS to preset the period of each channel in the range from 0.1 to 9 x 10^6 s. The samples were kept at a constant temperature with variation 0.2 °C over the whole measurement period. The rate constant (k) was obtained by least-squares calculation according to the equation

\[ \ln \left( \frac{I(t)}{I(0)} \right) = -k \cdot \tau \]

where I is the chemiluminescence intensity and τ is the time. The activation parameters A and E were calculated from four or more rate constants, according to the equation

\[ k = A \cdot e^{-E/kT} \]

where k is a constant. The intensity, I, is the average of at least three independent measurements, and typically the measurements were obtained from one fresh and two used samples.

The preparations of dimethyl α-peroxylactone and tetramethyldioxetane followed the procedures reported in previous papers.4,8 The fluoroscen 9,10-diphenylanthracene, 9,10-dibromoanthracene, and perylene were obtained from Aldrich. The fluoroscenes were chromatographed with basic alumina (Fisher, activity 1) in CH_2Cl_2 solution and then crystallized from hexane.

**Tetramethyldioxetane (4).** In the gas-phase study, the sample cell is a Pyrex tube equipped with an O-ring high-vacuum stopcock. Five sample cells were connected with a cooling trap via glass joints (10/30). The sample cells were kept at 0 °C until they were ready to be used. The temperature ranges for decay and step function measurements were 70–41 and 53–35 °C, respectively.

**Preparation of Diphenyl α-Peroxylactone (3) (IR 1870 cm^-1, CFC_1).** Diphenylketene was prepared from benzil.22 Triphenyl phosphite (Alidarich) was vacuum distilled. Triphenyl phosphite (4.9 mmol) in 5 mL of CH_2Cl_2 (or CFC_1) was ozonized at -78 °C. After the excess of ozone had been removed by N_2, 2.4 mmol of diphenylketene in 1 mL CH_2Cl_2 (or CFC_1) was added over a 10-min period, the temperature of the ozonide solution being maintained at -23 °C. The solution was kept at -23 °C for an additional 1.5 h in order to ensure that all the ozone had decomposed.19 Then the solution was kept at -78 °C until it was ready to be used. An attempt to separate 3 in pure form from the reaction solution by low-temperature column chromatography was unsuccessful. The concentration of 3 was estimated by iodometric titration.

**Kinetic and Quantum Yield Measurements of Diphenyl α-Peroxylactone (3).** A 5 x 10^-3 M solution of 3 in CFC_1 was used in the kinetic studies. A 5 x 10^-3 M solution of perylene26 was used as a fluoroscope. In the solutions studied, the concentration of triphenyl phosphite was estimated to be 1 x 10^-2 M. There is no effect (5%) on the decay rate of chemiluminescence due to triphenyl phosphite for concentrations of the latter up to 5 x 10^-2 M.

The cycloaddition reactions of triplet benzophenone and 2-methyl-2-butene was used to estimate the quantum yield of triplet benzophenone formation from 3. In the presence of 0.95 M triphenyl phosphite, the quantum yield of this addition in degassed methylene chloride was measured as 0.17 based on the yield of oxetanes in degassed benzene solution, which was reported as 0.22 under the conditions that the initial concentration of butene was 0.9 M and the consumption of butene was less than 10%.

Into 2.56 mmol of 3 in 6 mL of CH_2Cl_2 (containing 0.95 M triphenyl phosphite), 5.7 mmol of 2-methyl-2-butene was added at -78 °C. The solution was degassed (four freeze–pump–thaw cycles at 10^-4 mm). During the degassing, temperature was maintained at either 2 K or 27 °C. After the sample tube was sealed, the solution left at room temperature overnight in the dark. The products were analyzed by quantitative VPC with a 6.5 ft length, 1/4 in. diameter, 3% SE-30 on Chromosorb Q column. The yield ratio of oxetanes (0.06 mmol) to benzophenone (0.96 mmol) was measured to be 0.06. After correction for the quantum yield of cycloaddition, the quantum yield of triplet benzophenone formation from 3 was 35%. The major product of the reaction of 3 and triphenyl phosphite oxide is a polyester, ca. 1.5 mmol.

**Preparation of Phenyl α-Butylketene (8).** Diethyl phenylmalonate (5, Aldrich, 0.6 mol) was added slowly to 300 mL of ethanol containing 0.6 g-atoms of sodium at 50 °C. n-Butyl bromide (Aldrich, 0.61 mol) was added to the solution over 1 h. The solution was then refluxed for about 30 h until the solution became neutral. Ethanol was removed by distillation. Sodium bromide was washed away with 200 mL of water (twice). Diethyl phenyl-n-butylnaloylate (6) was distilled out of the reaction mixture (135 °C at 0.05 Torr, yield 60%).

**Preparation of Phenyl α-Butylketene (8) (30 min) was added to 2 mol of NaOH in 800 mL of water. The reaction mixture was refluxed gently for about 40 h until the aqueous layer remained. Phenyl-n-butylnaloylamic acid (7) was extracted with ether from the preacidified solution and solidified at 5 °C after the ether was removed. The solid, 7, was washed twice with 100 mL of boiling benzene, yield 50%. The entire procedure was performed under N2. Perfluoroacetic anhydride (Aldrich, 14.2 mL) was added to 70 mL of diethyl ether containing 11.3 g of 7 and a yellow, homogeneous solution resulted. After all volatile compound had been removed, a colorless residue was distilled at up to 140 °C (1 Torr). The phenyl-n-butylnaloyl (8) was collected at 0 °C as distillate.

**Preparation of Phenyl α-Peroxylactone (2) (IR 1860 cm^-1, CFC_1).** Analogous to the preparation of 3, 1.72 mmol of phenyl-n-butylnaloylketene in 1 mL of CFC_1 was added over a 1 min period to 3.2 mmol of triphenyl phosphite oxide–CFC_1 solution (20 mL, N_2 bubbling) at -23 °C. The solution was kept at -23 °C for an additional 1.5 h and then stored at -78 °C.

An attempt to separate 2 in pure form from reaction solution by column chromatography was unsuccessful. The concentration of 2 was estimated with iodometric titration.

**Kinetic and Quantum Yield Measurements of Phenyl α-Butylketene (2).** Freon-11 solutions of 2 of a concentration less than 2 x 10^-3 M were used in the kinetic studies. 9,10-Dibromomethantracene (9 x 10^-3 M) and perylene (2 x 10^-3 M) were used as energy acceptor and fluoroscope in the measurement of valerophenone lifetime and the study of kinetics, respectively. The temperature ranges of decay and step function measurements are 35 to 20 and -9 to -23 °C, respectively. In the solution studies, the concentration of triphenyl phosphite was estimated...
Table VII. Intensity of DBA Fluorescence Sensitized by Triplet Valerophenone in the Solution Containing Phenyl-n-Butyl α-Peroxy lactonea,b

<table>
<thead>
<tr>
<th>intensity (arbitrary units)</th>
<th>[DBA], M</th>
<th>intensity (arbitrary units)</th>
<th>[DBA], M</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00 × 10^{-3}</td>
<td>6.27 × 10^{-4}</td>
<td>1.36 × 10^{-3}</td>
<td>2.82 × 10^{-4}</td>
</tr>
<tr>
<td>2.40 × 10^{-3}</td>
<td>5.01 × 10^{-4}</td>
<td>1.04 × 10^{-3}</td>
<td>2.04 × 10^{-4}</td>
</tr>
<tr>
<td>1.88 × 10^{-3}</td>
<td>3.76 × 10^{-4}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a The concentration of phenyl-n-butyl α-peroxy-lactone was estimated by iodometric titration to be 2.5 × 10^{-3} M. b Measurement was performed in nitrogen-saturated Freon-11 solution at room temperature.

The intensity of acetone fluorescence was measured as a function of temperature with a Perkin-Elmer MPF-2A spectrophotometer. In the range of -20 to 50 °C, the intensity of acetone fluorescence does not change if an appropriate correction for concentration variation resulting from the solvent expansion and constriction is made. An air-saturated Freon-11 solution containing 0.05 M acetone was used for these measurements.

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Methylketene. Ion Chemistry and Proton Affinity

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Abstract: The gas-phase ion chemistry of methylketene has been investigated using a quadrupole ion store (quistor) as an ion/molecule reaction chamber. The reaction sequences have been elucidated by the new technique quistor resonance ejection (QRE), which closely resembles ion cyclotron double resonance (ICDR). The ion chemistry of methylketene is analogous to that of ketene, and the nonreactive species m/z 57 (C₂H₂O⁺) is the major product at long storage times. The equilibrium for proton transfer between methyl acetate and methylketene ([CH₃COOH]H⁺ + CH₃CHCO⁻ + CH₃CH₂CO₂CH₃) has been studied and the proton affinity (PA) of methylketene was found to be 845 ± 3 kJ mol⁻¹, based on a value for PA(CH₂CO₂CH₃) of 839 kJ mol⁻¹ relative to the PA(i-C₄H₈) at 828 kJ mol⁻¹.

Introduction

Ketenes and their dimers have been of great interest to researchers because of their frequent appearance as intermediate products in chemical reactions and their great potential as reactants in a number of organic syntheses. ¹ A corresponding interest in the behavior of such compounds in the gas phase has evolved. A recent communication from this laboratory² reported on the ion chemistry of ketene itself, and was in excellent agreement with concurrent work done by Vogt et al.³ We reported also a value for the proton affinity of ketene which was consistent with recently reported values by other workers.⁴ ⁵ ⁶ The heat of formation of the tert-butyl ion, which is taken as a primary standard for that part of the proton-affinity scale relevant to ketene, has been redetermined recently⁶ and this necessitates a realignment of the proton-affinity scale. The most recent value for PA(i-C₄H₈) is now 828 kJ mol⁻¹.