cell placed in the ESR cavity. A minimal current was passed through and scanning begun.

The radical signal was observed by using the line-sharpening technique of Glarum.[14] Coupling constants have been reported in Table II. Measured *g* values: **3**, 2.003 79; **4**, 2.003 98; **5**, 2.003 55.

Generation of Neutral Monoradicals. Sample (**6**–**9**) (6 mg) and 2 mg of PbO_2 were weighed together and manually mixed with a spatula. Approximately one-third of this mixture was placed in an ESR cell, with about 1 mL of dry xylene. The cell was purged thoroughly with nitrogen and placed in the ESR cavity. A weak signal was generally observed, which could not be enhanced by variations in the temperature conditions. The *g* values of the monoradicals derived from oxidation of **8** and **9** were determined to be 2.003 84 and 2.003 76 ± 0.0001, respectively.

Cyclic Voltammetry. A three-electrode cell was used, having platinum wire working and auxiliary electrodes and a saturated calomel reference electrode. Sample solutions were 1 mM in anthraquinoid compounds with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte in dichloromethane which had been dried and distilled over P_2O_5. For compounds **1**, **3**, and **5**, each wave satisfied the reversibility criteria for the electrode process:[15] the ratio of cathodic and anodic peak currents, i_{pc}/i_{pa}, becomes close to unity as the scan rate is decreased, and a plot of peak current vs. the square root of the scan rate is linear passing through the origin for both cathodic and anodic peaks. Compound **2** satisfied the reversibility criteria for the first reduction wave, but accurate values for the peak currents for the second reduction wave could not be obtained. Compound **4** also satisfied the reversibility criteria for the first reduction wave, but failed to meet the criteria for the second wave.[16] For all of the compounds, the separation between cathodic and anodic peaks decreased with slower scan rates for both waves reaching minimal values of 0.08–0.1 V. Thus electron transfer must be somewhat slower than the fast transfer which occurs in completely reversible cases.[17]

Acknowledgments. This work was supported by Grant CHE76-80374 from the National Science Foundation.

Supplementary Material Available: Cyclic voltammetric data (2 pages). Ordering information is given on any current masthead page.

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[14] Glarum, S. H. *Rev. Sci. Instrum.* **1965**, *36*, 771.

[15] Adams, R. "Electrochemistry at Solid Electrodes"; Marcel Dekker: New York, 1969. Nicholson, R.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

[16] Full data from the cyclic voltammograms are available on microfilm upon request.

[17] For a typically reversible case, the peak separation is expected to be 0.058 V independent of scan rate.

Chemiluminescent Thermolysis of α-Peroxylactones

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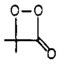
New York, New York 10027. *Received November 2, 1979*

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 CO_2 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 chemiexcitation 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.[1] The overwhelming proportion of published work deals with 1,2-dioxetanes, and only brief reports of α-peroxylactones have appeared,[2] 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 ketenes and phosphite ozonides,[3] 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.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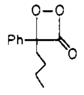
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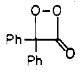
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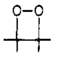
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We report here our progress toward achieving these goals and show how a combination of chemiluminescence measurements and

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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[4a]

$$D \rightarrow {}^*K + CO_2 \qquad {}^*\phi k_a \tag{1}$$

$$D \rightarrow K + CO_2 \qquad (1 - {}^*\phi)k_a \tag{2}$$

$$ {}^*K \rightarrow K + h\nu \qquad k_e \tag{3}$$

$$ {}^*K \rightarrow \text{no light} \qquad k_d \tag{4}$$

where $^*\phi$ is the efficiency of formation of an excited ketone, k_a 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

$$I = {}^*\phi\phi_e k_a[D] \tag{5}$$

$$I = \phi_{CL} k_a[D] \tag{6}$$

where ϕ_e and ϕ_{CL} are the appropriate efficiencies of form *K and the decomposition of D, respectively.

We may write eq 6 as

$$I = {}^*\phi k_a[D]k_e(k_e + k_d)^{-1} \tag{7}$$

In the case of the ketones studied, k_d is generally much larger than k_e under the experimental conditions (room temperature in fluid solution) so that to a good approximation

$$I = {}^*\phi k_a k_e k_d^{-1}[D] \tag{8}$$

According to eq 6, since the instantaneous rate of light emission is proportional to $\phi_{CL}k_a[D]$, then at the very onset of luminescence $\int I\,dt$ 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 ϕ_{CL} and k_a as functions of temperature. This procedure for determining the temperature coefficient of chemiluminescence (E_{CL}) is termed step analysis.[4c,14] The temperature coefficient of k_a 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 $\phi_{CL}k_a$ is 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 ΔE will exist, i.e.,

$$\Delta E = E_a - E_{CL} \tag{9}$$

We interpret E_a as the conventional "activation energy" for unimolecular decomposition of dioxetanes. 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 dioxetanes[4b] and since radiative rate constants of emission (k_e) generally show negligible temperature dependences, it is possible to associate ΔE with the temperature dependence of k_d. More specifically we can associate ΔE with the activation energy for the dominant deactivation pathway for the electronically excited ketone, *K.

Table I. Excited State and Excitation Parameters for α-Peroxylactones[a]

α-peroxylactone	$^*\phi$ (S_1)	$^*\phi$ (T_1)	$\tau_{1/2}$ (25 °C)[b]
1	0.001	0.06	973
2		0.11	280
3		0.4[c]	373
4	0.001	0.3	7364 (53 °C)

[a] In $CFCl_3$. [b] Half-life of dioxetanes (s). [c] In CH_2Cl_2.

Although a number of assumptions must be made in associating ΔE with the activation energy of a photochemical process, in certain cases *both* ΔE 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_d for the deactivation process may be derived and compared. Moreover, whenever the E_d cannot be easily measured experimentally, the step analysis of chemiluminescence intensity can provide a reasonable quantitative piece of information, i.e., ΔE.

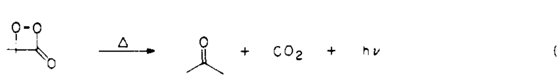
Results

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 $CFCl_3$ solutions of **1** consists mainly of acetone phosphorescence (λ_{max} ~420 nm), whereas in oxygenated solutions the direct chemiluminescence from **1** is nearly pure fluorescence (λ_{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.[4b] 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 $CFCl_3$ is evidenced by the observation of acetophenone (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-butene (eq 11).[9] The results are summarized in Table I.



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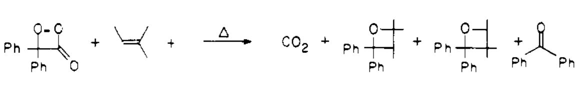

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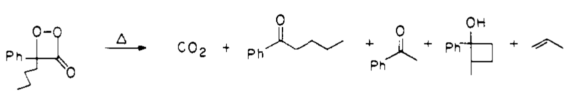

(12)

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Table II. Rate Constants[a] of Decomposition of α-Peroxylactones and Tetramethyldioxetane

compd	rate constant, s^{-1}	temp, °C (±0.2 °C)	compd	rate constant, s^{-1}	temp, °C (±0.2 °C)
1[b]	$(4.68 \pm 0.08)10^{-4}$	22.0	2[c]	$(9.84 \pm 0.06)10^{-3}$	34.5
	$(2.51 \pm 0.06)10^{-4}$	17.0		$(7.08 \pm 0.04)10^{-3}$	31.1
	$(1.52 \pm 0.06)10^{-4}$	13.0		$(4.67 \pm 0.04)10^{-3}$	26.5
	$(0.81 \pm 0.01)10^{-4}$	5.0		$(2.17 \pm 0.03)10^{-3}$	21.0
3[c]	$(3.84 \pm 0.02)10^{-3}$	31.1	4[b]	$(1.38 \pm 0.01)10^{-3}$	74.0
	$(2.27 \pm 0.04)10^{-3}$	26.0		$(8.61 \pm 0.08)10^{-4}$	69.9
	$(1.02 \pm 0.01)10^{-3}$	17.9		$(5.00 \pm 0.05)10^{-4}$	65.2
	$(6.1 \pm 0.1)10^{-4}$	13.5		$(2.23 \pm 0.03)10^{-4}$	59.6
	$(4.52 \pm 0.08)10^{-4}$	10.9		$(1.18 \pm 0.03)10^{-4}$	55.0
	$(2.3 \pm 0.2)10^{-4}$	5.0		$(9.41 \pm 0.08)10^{-5}$	53.0
4[d]	$(5.91 \pm 0.12)10^{-3}$	69.3			
	$(2.48 \pm 0.05)10^{-3}$	59.5			
	$(1.19 \pm 0.02)10^{-3}$	54.0			
	$(4.51 \pm 0.09)10^{-4}$	46.1			
	$(2.38 \pm 0.05)10^{-4}$	41.0			

[a] The rate constant was derived from the decay of chemiluminescence in nitrogen-saturated Freon-11 solution and in the gas phase. [b] The concentrations of dimethyl α-peroxylactone and tetramethyldioxetane are 2×10^{-3} and 1×10^{-5} M, respectively. [c] The concentrations of diphenyl α-peroxylactone and phenyl *n*-butyl α-peroxylactone are 1×10^{-3} M, determined by iodometric titration. The concentration of perylene used as a fluorescer is 1×10^{-4} M. [d] The measurement was performed in the gas phase. The pressure of tetramethyldioxetane was estimated as 1 Torr.

Table III. Intensities of Steady-State Measurements of Decomposition of α-Peroxylactones and Tetramethyldioxetane at Different Temperatures (Step-Function Analysis)[a]

compd	rel intensities[b] (arbitrary units)	temp °C (±0.2 °C)	solution satd with	compd	rel intensities[b] (arbitrary units)	temp, °C (±0.2 °C)	solution satd with
1	$(2.14 \pm 0.04)10^{4}$	−2.3	N_2	1	$(5.66 \pm 0.08)10^{3}$	−5.1	O_2
	$(1.19 \pm 0.05)10^{4}$	−6.3	N_2		$(2.16 \pm 0.02)10^{3}$	−10.2	O_2
	$(5.9 \pm 0.3)10^{3}$	−12.0	N_2		$(1.08 \pm 0.06)10^{3}$	−16.0	O_2
	$(3.29 \pm 0.01)10^{3}$	−17.4	N_2		$(4.4 \pm 0.2)10^{2}$	−22	O_2
	$(1.56 \pm 0.02)10^{3}$	−24.2	N_2				
4	$(6.96 \pm 0.02)10^{3}$	40.4	N_2	4	$(1.10 \pm 0.01)10^{4}$	38.2	O_2
	$(4.15 \pm 0.03)10^{3}$	36.5	N_2		$(3.58 \pm 0.04)10^{3}$	31.9	O_2
	$(2.07 \pm 0.02)10^{3}$	30.8	N_2		$(1.81 \pm 0.03)10^{3}$	27.2	O_2
	$(1.09 \pm 0.04)10^{3}$	26.0	N_2		$(8.25 \pm 0.06)10^{2}$	22.8	O_2
	$(6.0 \pm 0.2)10^{2}$	21.6	N_2		$(4.70 \pm 0.07)10^{2}$	19.5	O_2
2	$(2.20 \pm 0.04)10^{3}$	−9.0	N_2	3	$(1.49 \pm 0.01)10^{4}$	−8.0	N_2
	$(1.00 \pm 0.06)10^{3}$	−12.9	N_2		$(8.23 \pm 0.39)10^{3}$	−12.7	N_2
	$(1.14 \pm 0.11)10^{3}$	−17.2	N_2		$(4.43 \pm 0.02)10^{3}$	−17.0	N_2
	$(5.8 \pm 0.5)10^{2}$	−22.4	N_2		$(2.16 \pm 0.01)10^{3}$	−21.0	N_2
	$(4.0 \pm 0.4)10^{2}$	−27.1	N_2		$(1.37 \pm 0.10)10^{3}$	−26.8	N_2
4[c]	$(5.52 \pm 0.02)10^{4}$	53.2					
	$(3.52 \pm 0.04)10^{4}$	48.2					
	$(2.27 \pm 0.01)10^{4}$	43.7					
	$(1.25 \pm 0.06)10^{4}$	38.0					

[a] 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. [b] 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. [c] The measurement was performed in the gas phase.

Table IV. Decay Rate Constant of Acetone Phosphorescence in Nitrogen-Saturated Freon-11 Solution[a]

rate constant, s^{-1}	temp, °C	rate constant, s^{-1}	temp, °C
$(6.53 \pm 0.25)10^{5}$	23.0 ± 0.2	$(3.88 \pm 0.14)10^{5}$	11.7 ± 0.2
$(5.55 \pm 0.30)10^{5}$	16.9 ± 0.2	$(3.09 \pm 0.08)10^{5}$	2.9 ± 0.2

[a] The concentration of acetone is 0.5 M.

Table V. Comparison of E_a, E_{CL}, ΔE, and E_d[a]

dioxetane	E_a[b]	E_{CL}[c]	ΔE	E_d
1	22.3 ± 0.6	T_1 16.0 ± 0.2[d]	6.3 ± 0.8	6.0 ± 0.4[f]
		S_1 21.6 ± 0.8[e]	0.7 ± 0.8	0.0 ± 0.2[g]
2	19.5 ± 0.7	12.1 ± 0.3[d]	7.4 ± 1.0	(~6)[12]
3	18.3 ± 0.5	18.1 ± 0.8[d]	0.2 ± 1.3	0.0 ± 1.0[f]
4	30.3 ± 0.5	T_1 23.8 ± 0.4[d]	6.5 ± 0.9	6.0 ± 0.4[f]
		S_1 30.6 ± 0.7[e]	0.3 ± 1.2	0.0 ± 0.2[g]
	25.7 ± 0.3	19.5 ± 0.4	6.2 ± 0.7	6.4[11]

[a] All measurements were taken in $CFCl_3$ solvent, except the final row, which was measured in gas phase. [b] E_a is the conventional Arrhenius activation energy derived from measurements of the rate constant for total disappearance of dioxetane as a function of temperature. [c] E_{CL} is the temperature coefficient for chemiluminescence derived from step analysis. [d] Solutions are nitrogen saturated. [e] Solutions are oxygen saturated. [f] Measured by the temperature dependence of lifetime of triplet ketone. [g] Measured by the temperature dependence of fluorescence intensity of acetone.

Activation Parameters from Conventional and Chemiluminescent Measurements. The rate constants of decompositions of **1**–**4** are summarized in Table II. The rate constants in nitrogen-saturated solution for **1** and **4** are found to be identical with those in oxygen-saturated solution. The chemiluminscence 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

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

rate constant, s^{-1}	temp, °C	intensity[b]	temp, °C	intensity[b]	temp, °C
$(3.20 \pm 0.02)10^{-3}$	82 ± 0.3	$(5.61 \pm 0.28)10^{3}$	89.0 ± 0.3	$(1.33 \pm 0.02)10^{2}$	51.0 ± 0.2
$(1.95 \pm 0.08)10^{-3}$	76.2 ± 0.3	$(2.80 \pm 0.14)10^{3}$	82.0 ± 0.3	$(8.38 \pm 0.05)10^{1}$	46.5 ± 0.2
$(9.47 \pm 0.05)10^{-4}$	70.4 ± 0.3	$(1.56 \pm 0.06)10^{3}$	76.2 ± 0.3	$(4.47 \pm 0.04)10^{1}$	41.1 ± 0.2
		$(6.89 \pm 0.04)10^{2}$	70.4 ± 0.2	$(1.95 \pm 0.02)10^{1}$	35.4 ± 0.2
		$(3.39 \pm 0.17)10^{2}$	63.3 ± 0.2	$(9.68 \pm 0.20)10^{0}$	30.5 ± 0.2

[a] The concentration of tetramethyldioxetane is 1.2×10^{-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.

rate constants of acetone phosphorescence in nitrogen-saturated Freon-11 solution are summarized in Table IV. The values of E_a, 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.

Comparison of the Experimental Values of E_a, E_{CL}, and E_d. In the case of **1**, it is possible to determine the three activation parameters E_a, E_{CL}, and E_d for both S_1 and T_1, since chemiluminescence in the form of both fluorescence and phosphorescence can be observed from $CFCl_3$ solutions of **1**. Moreover, the results with **1** may be compared directly with those for **4**, since each compound produces both acetone singlets and triplets, albeit with different efficiencies. Of course, the E_a values should be independent of one another, since two different compounds are involved. However, since the acetone singlets and/or triplets produced should behave similarly with respect to their deactivation pathways (if the dominant deactivation paths are the same in both experimental conditions), the derived values of E_d for S_1 and T_1 should be identical and equal to ΔE. In fact, this expectation is nicely met (Table V). The deactivation of S_1 of acetone is temperature independent in the range investigated ($E_d = 0.0 \pm 0.2$ kcal/mol). For acetone singlets from **1** and **4** the values of ΔE are 0.6 ± 0.8 and 0.3 ± 1.2 kcal/mol, respectively. The deactivation of T_1 of acetone is strongly temperature dependent in the range investigated ($E_d = 6.0 \pm 0.4$ kcal/mol). For acetone triplets from **1** and **4** the values of $\Delta E = 6.3 \pm 0.8$ and 6.5 ± 0.9 kcal/mol, respectively. The agreement between ΔE and E_d is quite pleasing and impressive, since the measured values of E_a for **1** and **4** differ by $\sim$8 kcal/mol. Moreover, acetone phosphorescence can be observed easily from the decomposition of **4** in the gas phase. The value of ΔE derived from this measurement is 6.2 ± 0.7 kcal/mol, which is quite consistent with the value of E_d reported by Cundall, 6.4 kcal/mol, as the activation energy of α-cleavage of acetone triplet in the gas phase.[11]

In the case of valerophenone, a direct experimental value of E_d is not available. However, from the temperature dependence of the quenching of type II reaction of valerophenone triplets, a value of $E_d \sim 6$ 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 ΔE in our system, or to an inaccurate derivation of E_d for valerophenone triplets.

The direct experimental value of E_d for benzophenone triplets was determined and found to be 0.0 ± 1 kcal/mol. The experimental value of ΔE was determined to be 0.2 ± 1.3 kcal/mol, so that ΔE and E_d values are identical within the experimental error.

Interpretation of ΔE and E_d. The fact that ΔE and E_d 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., ΔE and E_d refer to the same activation energies for the dominant deactivation processes of *K. The question now arises as to the nature of that step.

For acetone singlets k_d is readily associated with k_{ST}, the rate constant for intersystem crossing. In organic molecules, $S_1 \rightarrow T_1$ 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).[13] As a result, k_{ST} is expected to be temperature independent, as is indeed found to be the case experimentally.

For acetone triplets, k_d may be associated with some intramolecular radiationless process. An attractive candidate is photochemical α-cleavage. The activation energy for photochemical α-cleavage of acetone in the vapor phase is reported to be 6.4 kcal/mol,[11] a value within the experimental error of ΔE. If this interpretation is correct, then chemiluminescence methods can be employed to measure activation energies for photochemical processes.

For valerophenone triplets, k_d may be associated with type II reaction. Such a process is believed to possess a substantial activation energy, although we feel that ΔE may reflect an additional energy; i.e., the magnitude of ΔE seems a bit too high in the light of literature values.[12]

For benzophenone triplets, k_d is probably associated with impurity quenching of some sort. Such processes are commonly diffusion controlled and as such require small or negligible activation energies.[23]

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 $E_a \sim 28$ kcal/mol for decomposition of **4** in acetonitrile is reported.[5] However, in this solvent the values of ΔE and E_d for acetone singlets and triplets were found to agree within the experimental error. The absolute values of ΔE and E_d were $\sim$3 kcal/mol in acetonitrile for acetone triplets.[14]

The decomposition of methyl 1-adamantyl α-peroxylactone is reported to have $\Delta H^{\ddagger} \sim 14$ kcal/mol. However, the accuracy of this value is suspect as a measure of a unimolecular decomposition pathway, since $\Delta S^{\ddagger}$ for the reaction is reported as -24 eu.[2a] We suggest that some catalytic pathway probably dominates the decomposition, as was the case for the tetramethyl-1,2-dioxetane system in alcoholic solvents.[21a] Our data suggest that values of E_a in the range 18–22 kcal/mol are typical for simple peroxylactones. The decomposition of *tert*-butyl α-peroxylactone yielded a value of $E_a = 18.0$ kcal/mol,[2a] a value more consistent with our results. A value of $E_a = 23$ 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 α-peroxylactones are qualitatively similar to 1,2-dioxetanes with respect to the overall excited-state efficiency ($^*\phi \sim 0.06$, 0.11, and 0.35 for **1**, **2**, and **3**, respectively). The $^*\phi_T/^*\phi_S$ ratio of 60 for **1** is also quite in line with the reported values for 1,2-dioxetanes.[15] The similarity

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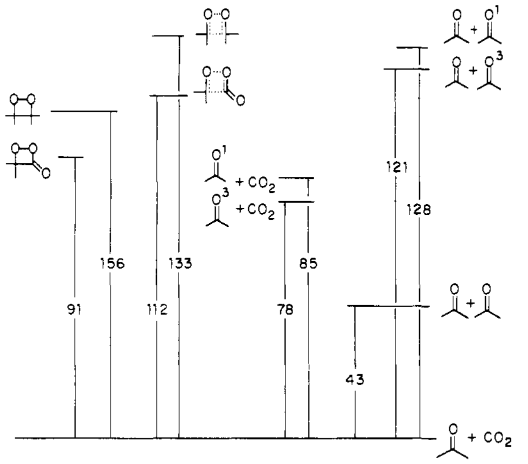

Figure 1. Summary of the estimated thermochemistry of dioxetane and peroxylactone decomposition (units in kcal/mol).

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.[16a,16b] 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.[16c] 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 diphenoyl peroxide.[16d] 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.[17]

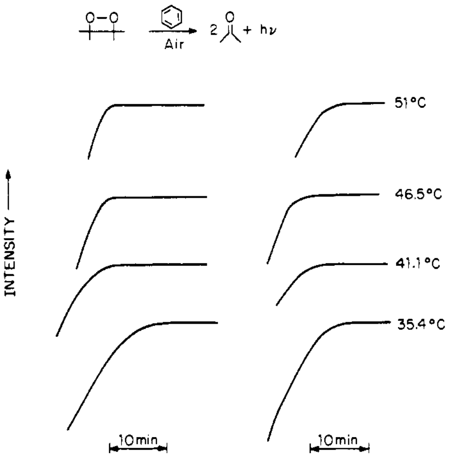

Figure 2. A record of direct chemiluminescent intensities (logarithmic scale in arbitrary units) from used and fresh tetramethyldioxetanes in air-saturated benzene solution.

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.[24] 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 ΔH^{*} 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.[2c] This conclusion was based on the difference between E_a and E_{CL}, which were evaluated to be 22.3 ± 0.3 and 25.6 ± 0.1 kcal/mol in Freon-113, respectively. The latter value for E_{CL} differs substantially from the value derived from our experiments. On the other hand, the quantum yield (0.08%) and E_a 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 E_{CL} (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[2c] and our value of E_{CL}. A step-function measurement of chemiluminescence intensity as a function of temperature is used to derive E_{CL}. 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 E_{CL} from step-function measurements, a compound for which the equality of E_{CL} and E_a has been well established, tetramethyldioxetane (**4**), was used as a model system. From the decay of **4** in air-saturated benzene, the activation energy, E_a, was derived as 25.4 ± 0.2 kcal/mol, in good agreement with published measurements.[21] In the step-function measurement, two temperature ranges, 30–51 and 63–89 °C, were employed. In the low temperature range, a constant chemiluminescent 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 E_{CL} from step-function measurements. Analyzing the intensity of chemiluminescence of **4** as a function of temperature results in values of E_{CL} of 25.1 ± 0.3 and 26.9 ± 0.7 kcal/mol for "low" and "high" temperature ranges, respectively. A consistency of E_a and E_{CL} 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 E_a and E_{CL} derived from the high-temperature range is such that $E_{CL} > E_a$ 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 E_a reported here and reported earlier.[2c,g]

Experimental Section

Freon-11 (Matheson) was chromatographed with a basic alumina (Fisher, activity 1) 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

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cell holder 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 fluorescer) 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. The data were stored in a multichannel analyzer with an external MCS to preset the period of each channel in the range from 0.1 to 9 × 10^8 s. The samples were kept at a constant temperature with variation 0.2 °C over the whole measurement period. The rate constant (k_a) was obtained by least-squares calculation according to the equation

$$\ln (I_{t_2}/I_{t_1}) = \ln ([\mathrm{D}]_{t_2}/[\mathrm{D}]_{t_1}) = -k_a(t_2 - t_1) \qquad (13)$$

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

$$k_a = A \exp(-E_a/RT) \qquad (14)$$

where T is in K.

In the step-function steady-state measurement, a constant intensity (with experimental error <2%) was recorded over 10 min at a constant temperature (±0.2 °C) with the same instrument setup used in the decay of intensity measurements. Because of the constant intensity (Figure 2) over the measurement period, the concentration of D can be assumed to be constant, and the temperature coefficient E_{CL} was calculated according to the equation

$$I = k \exp(-E_{\mathrm{CL}}/RT) \qquad (15)$$

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.[3,18]

The fluorescers 9,10-diphenylanthracene, 9,10-dibromoanthracene, and perylene were obtained from Aldrich. The fluorescers 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). An excess amount of **4** was added to the cooling trap and degassed at 77 K. After a vacuum (5 × 10^{-5} Torr) had been reached, the cooling trap was isolated from the vacuum pump and warmed up to room temperature. At room temperature, **4** was sublimed into the sample cells. After the vapor pressure of **4** had reached a maximum value (~1 Torr), the sample cells were closed with a stopcock and disconnected from the cooling trap. 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. The chemiluminescence spectrum (maximum at 440 nm) was measured at 60 °C on a Perkin-Elmer MPF-3L equipped with a Hamamatsu R-777-4 phototube.

In the solution-phase studies (benzene and Freon-11), 1.2 × 10^{-3} M solutions of **4** were employed. The temperature ranges for decay and step function measurements were 80–55 and 50–20 °C, respectively.

Dimethyl α-Peroxylactone (1) (IR 1870 cm^{-1}; NMR δ 1.81 s, $CFCl_3$). The chemiluminescent spectrum of **1** was measured with a photomultiplier tube (Centronic Q4292T) equipped with an Aminco quarter meter monochromator. A 5 × 10^{-3} M nitrogen-saturated solution at 20 °C was used in this measurement (solvent 1:1 $CFCl_3/CH_2Cl_2$). A 5 × 10^{-3} M solution of **1** in $CFCl_3$ was used in the kinetic studies. The temperature ranges for decay and step function measurements were 23 to 10 and −5 to −27 °C, respectively.

The quantum yield of excited acetone from **1** (1.9 × 10^{-3} M, C_6H_6 at 23 °C) was estimated by comparing indirect chemiluminescent intensities with **4** (1.2 × 10^{-3} M, C_6H_6, 30% triplet acetone and 0.1% singlet acetone).[1,5,10] The fluorescers used in this measurement were 9,10-diphenylanthracene and 9,10-dibromoanthracene.[10]

Preparation of Diphenyl α-Peroxylactone (3) (IR 1870 cm^{-1}, $CFCl_3$). Diphenylketene was prepared from benzil.[22] Triphenyl phosphite (Aldrich) was vacuum distilled. Triphenyl phosphite (4.9 mmol) in 5 mL of CH_2Cl_2 (or $CFCl_3$) 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 $CFCl_3$) 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 ozonide 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 × 10^{-3} M solution of **3** in $CFCl_3$ was used in the kinetic studies. A 5 × 10^{-5} M solution of perylene[20] was used as a fluorescer. In the solutions studied, the concentration of triphenyl phosphate was estimated to be 1 × 10^{-2} M. There is no effect (≤5%) on the decay rate of chemiluminescence due to triphenyl phosphate for concentrations of the latter up to 5 × 10^{-2} M.

The cycloaddition reaction 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 phosphate, 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[9] 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 phosphate), 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 77 K or −78 °C. After the sample tube was sealed, the solution was left at room temperature overnight in the dark. The products were analyzed by quantitative VPC with a 6.5 ft length, $^1/_8$ 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, 0.17, the quantum yield of triplet benzophenone formation from **3** was 35%. The major product of the reaction of **3** and triphenyl phosphite ozonide is a polyester, ca. 1.5 mmol.

Preparation of Phenyl-*n*-Butylketene (8). Diethyl phenylmalonate (**5**, Aldrich, 0.6 mol) was added slowly to 300 mL of ethanol containing 0.6 g-atom 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*-butylmalonate (**6**) was distilled out of the reaction mixture (135 °C at 0.05 Torr, yield 60%).

6 (0.5 mol) was hydrolyzed by 2 mol of NaOH in 800 mL of water. The reaction mixture was refluxed gently for about 40 h until only the aqueous layer remained. Phenyl-*n*-butylmalonic 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 N_2. 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*-butylketene (**8**) was collected at 0 °C as distillate.

Preparation of Phenyl *n*-Butyl α-Peroxylactone (2) (IR 1860 cm^{-1}, $CFCl_3$). Analogous to the preparation of **3**, 1.72 mmol of phenyl-*n*-butylketene in 1 mL of $CFCl_3$ was added over a 10-min period to 3.2 mmol of triphenyl phosphite ozonide–$CFCl_3$ 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 *n*-Butyl α-Peroxylactone (2). Freon-11 solutions of **2** of a concentration less than 2 × 10^{-3} M were used in the kinetic study. 9,10-Dibromoanthracene[7] (9 × 10^{-5} M) and perylene (3 × 10^{-5} M) were used as energy acceptor and fluorescers in the measurement of valerophenone lifetime and the study of kinetics, respectively. The temperature ranges of decay and step-function measurement are 35 to 20 and −9 to −23 °C, respectively. In the solution studies, the concentration of triphenyl phosphate was esti-

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Table VII. Intensity of DBA Fluorescence Sensitized by Triplet Valerophenone in the Solution Containing Phenyl *n*-Butyl α-Peroxylactone[a,b]

intensity (arbitrary units)	[DBA], M	intensity (arbitrary units)	[DBA], M
3.00×10^5	6.27×10^{-4}	1.36×10^5	2.82×10^{-4}
2.40×10^5	5.01×10^{-4}	1.04×10^5	2.04×10^{-4}
1.88×10^5	3.76×10^{-4}		

[a] The concentration of phenyl *n*-butyl α-peroxylactone 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.

mated to be 2.8×10^{-2} M, and resulted in no effect on the decay rate of chemiluminescence.

The quantum yield of triplet valerophenone formation was estimated by the type II reaction of valerophenone. In the presence of 0.15 M triphenyl phosphate, the quantum yield of type II reaction in air-saturated Freon-11 was measured as 0.44 by comparing with the yield of acetophenone in degassed benzene solution, in which the quantum yield was reported as 0.4.[8] A solution of 1.72 mmol of **3** in 21 mL of $CFCl_3$ containing 0.15 M triphenyl phosphate was left at room temperature overnight. The products were analyzed by quantitative VPC with 4% QF-1 mixed with 1% Carbowax 20M on Chromosorb Q column. (The triphenyl phosphate was removed by passing the solution through a silica gel column before injecting into the VPC.) The ratio of acetophenone (0.047 mmol) to valerophenone (1.16 mmol) was 0.048; therefore, the lower limit for the quantum yield of excited valerophenone was 11%. (The other isolated product of the reaction of **2** and triphenyl phosphite ozonide is a polyester, ca. 0.2 mmol.)

Direct Measurement of E_d for Excited Acetone and Benzophenone. The intensity of acetone fluorescence was measured as a function of temperature with a Perkin-Elmer MPF-2A spectrophotometer. In the temperature range from −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.

The lifetime of acetone phosphorescence was measured as a function of temperature by the single-photon-counting method. In the temperature range from 2.9 to 23 °C, the measurement provided a value of E_d equal to 6.0 ± 0.4 kcal/mol for a nitrogen-saturated Freon-11 solution containing 0.5 M acetone.

The lifetime of benzophenone phosphorescence was measured as a function of temperature by the single-photon-counting method. In the temperature range from −20 to 22 °C the lifetime is about 35 ± 3 μs and is essentially temperature independent. For these experiments the concentration of benzophenone was 1×10^{-3} M in nitrogen-saturated Freon-11 solution.

Measurement of the Lifetime of Valerophenone Generated from 2. It has been reported that 9,10-dibromoanthracene (DBA) can quench triplet acetophenone with rate constant 3.8×10^8 M^{-1} s^{-1} at 40 °C in benzene solution.[7] Assuming that DBA is capable of quenching valerophenone as well as acetophenone, the rate constant in Freon-11 at 25 °C is estimated to be 4.4×10^8 M^{-1} s^{-1} after the correction for the viscosity difference between Freon-11 at 25 °C and benzene at 40 °C. Phenyl *n*-butyl α-peroxylactone was synthesized by reaction of 0.57 mmol of phenyl-*n*-butylketene and 1.6 mmol of triphenyl phosphite in 20 mL of Freon-11 solution. The intensities of DBA fluorescence as a function of DBA concentration are summarized in Table VII.

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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 ($C_3H_5O^+$) is the major product at long storage times. The equilibrium for proton transfer between methyl acetate and methylketene ($(CH_3COOCH_3)H^+ + CH_3CHCO \rightleftharpoons CH_3CH_2CO^+ + CH_3COOCH_3$) 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($CH_3CO_2CH_3$) of 839 kJ mol^{-1} relative to the PA(i-C_4H_8) 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.[1-3] A corresponding interest in the behavior of such compounds in the gas phase has evolved. A recent communication from this laboratory[4] reported on the ion chemistry of ketene itself, and was in excellent agreement with concurrent work done by Vogt et al.[5] We reported also a value for the proton affinity of ketene which was consistent with recently reported values by other workers.[5-7] 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 recently[8] and this necessitates a realignment of the proton-affinity scale. The most recent value for PA(i-C_4H_8) is now[9] 828 kJ mol^{-1}.

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