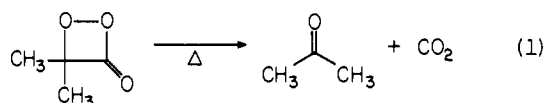# Communications to the Editor

Kinetics of Unimolecular Dioxetanone Chemiluminescence. Competitive Parallel Reaction Paths

Sir:

The thermal unimolecular reaction of the 1,2-dioxetane ring system to generate electronically excited-state carbonyl containing compounds is by far the most carefully and extensively studied of all chemiluminescent reactions.[1] The mechanism for this intriguing transformation has been hotly debated by proponents of stepwise and concerted decomposition paths. The ammunition in this controversy ranges from purely theoretical calculations[2] to experimental substituent, solvent, and isotope effects.[3] Of pivotal importance to the dissection of the reaction path have been studies of kinetics and of excited-state yields for variously substituted dioxetanes. In a previous report we showed that the major chemiluminescent pathway for dimethyldioxetanone in the presence of an easily oxidized fluorescer is chemically initiated electron-exchange luminescence.[4] In this communication we describe our findings on the uncatalyzed unimolecular thermal fragmentation of dimethyldioxetanone (**1**) to acetone and CO_2[5] (eq 1).

$$CH_3 \overset{O-O}{\underset{CH_3}{\diagup\diagdown}} \overset{O}{\underset{O}{}} \xrightarrow{\Delta} \overset{O}{\underset{CH_3\diagup\diagdown CH_3}{}} + CO_2 \qquad (1)$$

Thermolysis of **1** in argon-purged $C_2Cl_3F_3$ leads to readily detected chemiluminescence. The emission spectrum under these conditions is a composite of acetone fluorescence and phosphorescence, Figure 1a. For comparison, the chemiluminescence spectrum from tetramethyldioxetane is shown in Figure 1b. These emission spectra are superimposable, as are the spectra of air-saturated samples. These observations serve to confirm generation of excited acetone and rule out any involvement of an emissive acetone excimer from tetramethyldioxetane.[6]

The activation energy for the thermal decomposition of **1** was determined by two different techniques in a series of four solvents. First, the total rate of reaction of **1** was measured at several temperatures by monitoring the chemiluminescence decay.[7] Standard Arrhenius analysis of the decay rate constants gives the activation energies, E_a, shown in Table I. Second, the activation energy for that fraction of the total reaction that leads to electronically excited singlet states, E_{Chl}, was determined by probing the effect of temperature on the instantaneous chemiluminescence intensity.[8] Critically, and in contrast to the activation parameters of simply substituted dioxetanes studied thus far, E_{Chl} for **1** is 3–4 kcal/mol greater than E_a, and this difference is independent of the solvent.

The yield of excited-state acetone from thermolysis of **1** also demonstrates the unusual effect of temperature. Thermolysis of **1** in $C_2Cl_3F_3$ at 30.0 °C generates electronically excited singlet and triplet acetone with efficiencies of 0.1 and 1.5%, respectively.[9] The singlet excited acetone yield, ϕ_S*, depends significantly upon the reaction temperature, as is shown in Table II. These data afford a temperature coefficient for ϕ_S* of $+4.2 \pm 0.2$ kcal/mol, which represents the difference in activation energies between a higher energy path leading to light generation and the dark decomposition of **1**. This is the first reported example of a temperature-dependent singlet
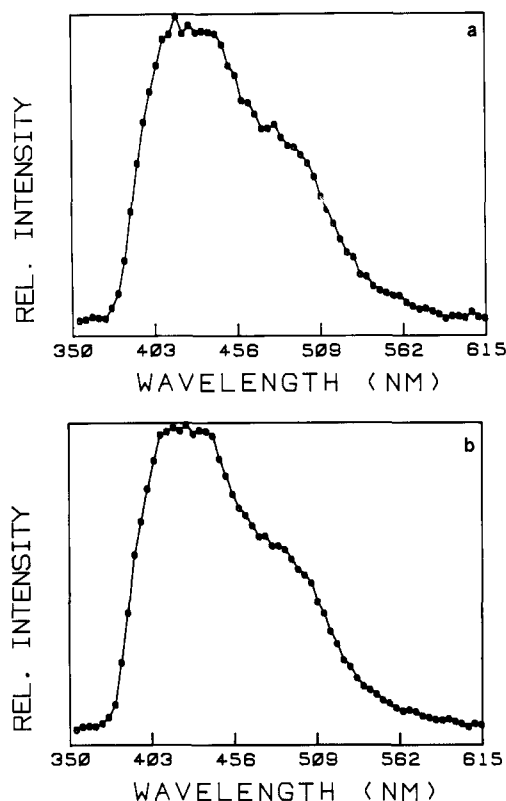

Figure 1. Chemiluminescence emission spectrum from thermolysis of dioxetanone **1** (a) and tetramethyldioxetane (b) in argon purged $C_2Cl_3F_3$.

Table I. Activation Parameters for the Thermolysis of Dioxetanone **1**[a]

solvent	E_a, kcal/mol[b]	E_{Chl}, kcal/mol[c]
$C_2Cl_3F_3$	22.3 ± 0.3[d]	25.6 ± 0.1
CCl_4	21.3 ± 0.3[e]	24.5 ± 0.5
PhH	21.8 ± 0.1[e]	24.9 ± 0.4
CH_2Cl_2	20.8 ± 0.1[e]	24.8 ± 0.4

[a] Air-saturated solutions, $\sim 5 \times 10^{-4}$ M in **1**. [b] Typical range of temperature over which rate constants were determined was 15 to 40 °C. [c] Typical range of temperature over which chemiluminescence intensity was determined was -1 to 14 °C. [d] Eyring activation enthalpy: $\Delta H^\ddagger = 21.7$ kcal/mol; activation entropy, $\Delta S^\ddagger = 0 \pm 1$ eu. [e] Solutions contained 5% Na_4EDTA.

Table II. Temperature Dependence of the Singlet Excited Acetone Yield from thermolysis of **1**[a]

temp, °C	ϕ_S* $\times 10^4$	temp, °C	ϕ_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. See ref 9a.

excited-state yield from the thermal unimolecular reaction of the 1,2-dioxetane ring system.[10]

While trace amounts of catalytic impurities[11] might be expected to induce a parallel dark path of dioxetanone decom-
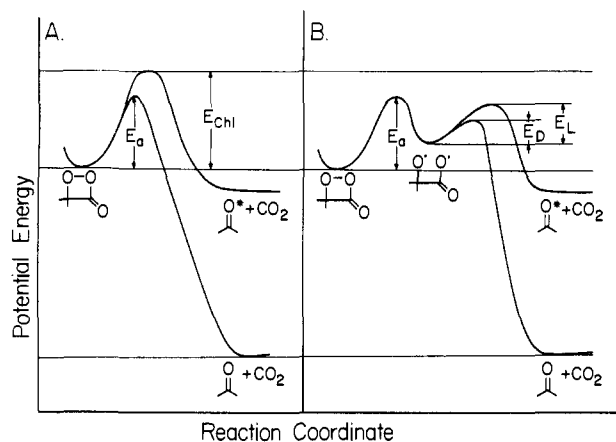
Figure 2. Limiting reaction mechanisms for thermal unimolecular fragmentation of dimethyldioxetanone to acetone and CO_2. Part A represents the concerted process with two transition states. Part B shows a path proceeding through an intermediate biradical with at least two exit channels.

position, and hence result in a lowering of the apparent activation energy, E_a, several experimental observations make such an explanation of our results exceedingly unlikely. Significantly, identical results were obtained for the four solvents, purified by different techniques,[12] of Table I. Thus solvent impurity catalysis would fortuitously have to be equally efficient in all four solvents. Also, the decomposition rate was independent ($\pm 1\%$) of the initial concentration of **1**, thereby excluding a possible catalytic impurity in the dioxetanone sample. Furthermore, addition of the chelating agent Na_4EDTA to the reaction mixture had no effect on the observed rate constant. In fact, the powerful catalytic effect of added cupric ion,[13] the metal ion most effective in catalyzing dioxetane decomposition,[11] was completely suppressed by added Na_4EDTA. Finally, the entropy of activation for the thermolysis of **1** is -1 ± 3 eu for the four solvents in Table I. This value is inconsistent with a bimolecular catalysis path, for which a large negative activation entropy would be expected.

The effect of temperature on the efficiency of chemiluminescence from dioxetanone **1** is composed of the temperature dependence of the efficiencies of all steps leading to photon generation. The temperature dependence of the fluorescence efficiency of acetone is negligible under these conditions.[8b] Thus, E_{Chl} measures the composite activation energy for the formation of excited singlet acetone. The standard Arrhenius activation energy, E_a, on the other hand, provides a measure of the barrier to the lowest energy transition state available to the system (see below). Our finding that E_{Chl} is 3–4 kcal/mol higher than E_a requires that there be two or more competitive pathways with discrete transition states for dioxetanone decomposition. The position of these transition states along the reaction coordinate cannot be revealed by this kinetic analysis. Two limiting situations exist, as depicted in Figure 2. In Figure 2a two competitive concerted reactions are represented. In this case the measured difference in activation energy between the light generating and dark paths is equated to the difference in energies between the two transition states. In the mechanism shown in Figure 2b, a common rate-determining step leads to generation of an intermediate biradical. This biradical proceeds along a lower energy path to generate ground-state acetone and by a more highly activated route to produce singlet excited acetone. The temperature dependence of the instantaneous chemiluminescence intensity for this case is given by

$$I = A \exp\{-[E_a + (E_L - E_D)]/RT\} \qquad (2)$$

where A is a constant composed of the preexponential factors

and instrument parameters, E_a is the previously defined activation energy for formation of the intermediate biradical, and E_L and E_D are the activation energies for fragmentation of the intermediate to excited- and ground-state acetone, respectively.[14] Thus, this analysis indicates that the difference in the 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.

While our data do not provide a distinction between operation of the two limiting mechanisms depicted in Figure 2, several points merit discussion. Simple qualitative arguments based upon current theories of pericyclic reactions put forth by Turro and Devaquet[15] predict that the lower activation energy route should be the one that leads to excited-state generation. This prediction is inconsistent with our experimental findings. On the other hand, the experimentally observed ordering of transition states for both limiting mechanisms depicted in Figure 2 is easily understood in terms of the Hammond postulate in which the most exothermic reaction (formation of ground state products) has the lowest activation barrier. However, neither this line of reasoning, nor any mechanism yet postulated to explain chemical formation of excited states, is capable of explaining why the total yield of acetone excited states from the thermolysis of **1** is nearly 20 times *lower* than the excited acetone yield from the *less exothermic* thermolysis of tetramethyldioxetane.[16] This observation remains a mystery in need of further investigation.

In summary, our investigation of the kinetics of the thermal unimolecular reaction of dioxetane **1** has revealed that dual paths are operative. Further experimental resolution of the reaction coordinate is difficult. This reaction may be ideally suited for investigation by ab initio theoretical methods. Such an analysis is planned.

References and Notes

(1) For leading references, see T. Wilson, *Int. Rev. Sci.: Phys. Chem., Ser. Two,* **9,** 265 (1976).
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(4) S. P. Schmidt and G. B. Schuster, *J. Am. Chem. Soc.,* **100,** 1966 (1978).
(5) Dimethyldioxetanone (1) was prepared and purified according to the procedure of Adam: W. Adam, A. Alzerreca, J.-C. Liu, and F. Yany, *J. Am. Chem. Soc.,* **99,** 5768 (1977).
(6) Y. Haas and G. Yahad, *Chem. Phys. Lett.,* **48,** 63 (1977). Tetramethyldioxetane was prepared by the procedure of Kopecky: K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J.-Y. Ding, *Can. J. Chem.,* **53,** 1103 (1975).
(7) Light was detected by the photon counting technique. The disappearance of 1 was strictly first order for at least five half-lives over the entire temperature range studied.
(8) (a) T. Wilson and A. P. Schaap, *J. Am. Chem. Soc.,* **93,** 4126 (1971); (b) H.-C. Steinmetzer, A. Yekta, and N. J. Turro, *ibid.,* **96,** 292 (1974).
(9) (a) The yield of light was determined by direct comparison with the total integrated acetone fluorescence and phosphorescence intensities from the thermolysis of tetramethyldioxetane (TMD) in $C_2Cl_3F_3$. The yields of singlet and triplet excited acetone from TMD were taken to be 0.2[9b,c] and 30%,[9b] respectively. Adam[9d] has previously reported a singlet excited acetone yield of 0.05% from the thermolysis of 1 at 23 °C. His triplet yield, however, is unreliable owing to the unexpected involvement, in the presence of rubrene, of an additional efficient chemiluminescence mechanism.[4] A triplet to singlet excitation efficiency ratio of 20 has also been reported previously for 1.[9e] (b) T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *J. Am. Chem. Soc.,* **98,** 1086 (1976). (c) N. J. Turro and P. Lechtken, *ibid.,* **94,** 2886 (1972). (d) W. Adam, G. A. Simpson, and F. Yany, *J. Phys. Chem.,* **78,** 2559 (1974). (e) N. J. Turro, P. Lechtken, G. Schuster, J. Orell, and H.-C. Steinmetzer, *J. Am. Chem. Soc.,* **96,** 1627 (1974).
(10) P. Lechtken, *Chem. Ber.,* **109,** 2862 (1976).
(11) P. D. Bartlett, A. L. Baumstark, and M. Landis, *J. Am. Chem. Soc.,* **96,** 5557 (1974).

(12) Benzene (Burdick and Jackson) and $C_2Cl_3F_3$ (Freon 113, Matheson) were shaken with H_2SO_4, passed through basic alumina, and distilled. Dichloromethane (Mallinckrodt Spectrograde) was distilled from P_2O_5. Carbon tetrachloride (Mallinckrodt Spectrograde) was irradiated (Pyrex) in the presence of benzophenone, passed through basic alumina, and distilled.

(13) Addition of $\sim 10^{-7}$ M $CuCl_2$ (with 1% MeOH for solubility) increased the rate of decomposition of 1 in CH_2Cl_2 by a factor of ~ 10.

(14) Invoking the steady-state approximation for [acetone*] leads to eq 3, where, under the experimental conditions, [1] is constant.[8] For the case where $k_L \ll k_D$, eq 3 reduces to eq 2.

$$I \propto k_A [1][k_L/(k_L + k_D)] \qquad (3)$$

(15) N. J. Turro and A. Devaquet, *J. Am. Chem. Soc.*, **97**, 3859 (1975).

(16) (a) Calculated values of $\Delta H_f°$ follow: dioxetanone 1, ca. -88 kcal/mol;[16b] tetramethyldioxetane, -68.8 kcal/mol.[16c] (b) W. H. Richardson and H. E. O'Neal, *J. Am. Chem. Soc.*, **94**, 8665 (1972); (c) W. H. Richardson and H. E. O'Neal, *ibid.*, **92**, 6553 (1970).

(17) Fellow of the Alfred P. Sloan Foundation, 1977-1979.

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Synthesis of Homopropargylic and α-Allenic Alcohols from Lithium Chloropropargylide, Trialkylboranes, and Aldehydes[1]

Sir:

During the past few years there has been a surge of interest in development of novel routes for α-allenic alcohols. This has arisen as a consequence of the α-hydroxyallene structural feature being contained in many natural substances[2] and synthetic physiologically active compounds.[3] A number of the latter have proven to be powerful hypertensive and antiinflammatory agents.

Recently we reported that protonation with acetic acid of organoboranes derived from trialkylboranes and lithium chloropropargylide (**1**) afforded alkylallenes **2** (eq 1).[4,5] In

$$ClCH_2C{\equiv}CLi \xrightarrow[\text{2. } CH_3CO_2H, 25\,°C]{\text{1. } R_3B, -90\,°C} H_2C{=}C{=}CHR \qquad (1)$$
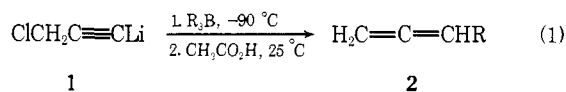
exploring the chemistry of organoboranes leading to **2**, we have now uncovered operationally simple, high-yield syntheses of homopropargylic (**4**) and α-allenic alcohols (**5**) via sequential treatment of **1** with trialkylboranes and aldehydes. The overall reactions represent efficient 1,3- and 1,1-dialkylations, respectively, of the readily available propargyl chloride, and thus pave the way to α-allenic and homopropargylic alcohols not readily accessible via previously available methodologies.[6]

The most remarkable feature of these synthetic transformations is the discovery that the alcohol which is specifically formed depends on the temperature at which the organoborane precursor is maintained prior to its reaction with the aldehyde.
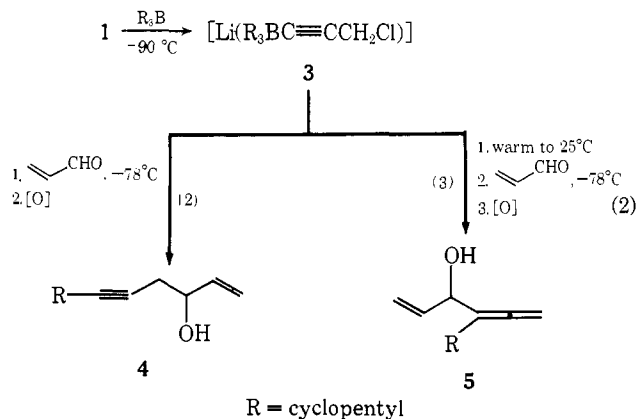
$$1 \xrightarrow[-90\,°C]{R_3B} [Li(R_3BC{\equiv}CCH_2Cl)]$$
$$\mathbf{3}$$

$$(2)$$

$$R = \text{cyclopentyl}$$

Table I. Yield of Homopropargylic and α-Allenic Alcohols

		isolated yields, %[a,b]	
		$RC{\equiv}CCH_2C$-	$R^1(HO)CHC$-
R_3B, R	R^1CHO, R^1	$(OH)HR^1$	$(R){=}C{=}CH_2$
(cyclopropyl)	C_2H_5	89 (99)	80 (99)
	$c\text{-}C_6H_{11}$	88 (99)	86 (99)
	$t\text{-}C_4H_9$	86 (100)	79 (96)
	C_6H_5	86 (100)	85 (99)
	$H_2C{=}CH$	75 (97)	84 (100)
	$(E)\text{-}CH_3\text{-}CH{=}CH$	84 (100)	84 (100)
(2-methylcyclopropyl) CH_3	$i\text{-}C_3H_7$		78 (96)[c]
(cyclopentyl)	C_2H_5		77 (98)
$n\text{-}C_6H_{13}$	C_2H_5	85 (99)[d]	73 (98)[d]

[a] The numbers in parentheses are isomeric purities. [b] The spectral data of the alcohols obtained were consistent with the assigned structures. [c] The stereochemistry of the 2-methylcyclopentyl moiety has not been determined. [d] The alcohol contained 7% of the isomeric alcohol resulting from the reaction of 1 with the organoborane derived from addition of BH_3 to the 2 position of 1-hexene.

Thus, addition of the carbonyl compound to the organoboron intermediate at -78 °C produces, after oxidative workup, nearly exclusively the homopropargylic alcohol (eq 2). On the other hand, if the organoborane is first brought to room temperature and then treated with the aldehyde at -78 °C, the α-allenic alcohol is obtained essentially free of contamination by the corresponding homopropargylic alcohol (eq 3).

A typical procedure for the preparation of the homopropargylic alcohol **4** is as follows. Propargyl chloride (20 mmol) in THF (10 mL) was cooled to -90 °C (liquid nitrogen-methanol bath) and then reacted with a solution of butyllithium (20 mmol, 1.6 M) in hexane while the temperature was maintained below -80 °C during the addition. The reaction mixture was stirred for an additional 10 min and, then, to the resultant lithium chloropropargylide (**1**, 20 mmol) was added a solution of tricyclopentylborane (20 mmol, 1.66 M) in THF by a double-ended needle[7] over a 15-min period, with the temperature being kept below -80 °C during the addition. The mixture was stirred for 30 min at -78 °C (dry ice–acetone bath) and then treated with a solution of 2-propenal (20 mmol) in THF (4 mL) while the temperature was maintained below -67 °C during the addition. After the mixture was stirred for 1 h at -70 °C, it was brought to room temperature (30 min), treated with methanol (10 mL), and oxidized at 30–50 °C with 3 N NaOH (7.2 mL) and 30% H_2O_2 (4.8 mL). Ether extraction, drying (MgSO$_4$), and distillation afforded 2.44 g (75%) of **4**.

The corresponding α-allenic alcohol **5** was obtained by a slight modification of the experimental procedure described for the preparation of **4**. Thus, the organoborane derived from **1** and tricyclopentylborane was allowed to warm to room temperature prior to addition of the 2-propenal at -78 °C. A summary of the experimental results obtained for the syntheses of various homopropargylic and α-allenic alcohols is given in Table I.

It is gratifying to note that the preparations of both types of alcohols accommodate a variety of structural features in both the alkylborane and aldehyde moieties.[8] Moreover, α,β-unsaturated aldehydes, such as acrolein and crotonaldehyde, react exclusively in a 1,2 fashion as exemplified by the preparation of the alcohols **4** and **5**. However, it should be pointed out that the procedures utilize only one of the three available alkyl groups of the trialkylborane. Attempts to circumvent this by using *B*-alkyl-9-borabicyclo[3.3.1]nonanes[9]