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Gas-Phase Chemiluminescence Study of Chemically Activated Tetramethyl-1,2-dioxetane Formed from the Reaction of $O_2({}^1\Delta_g)$ with 2,3-Dimethyl-2-butene

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Chemically activated tetramethyl-1,2-dioxetane has been prepared by the reaction of $O_2(^{1}\Delta_g)$ with 2,3-dimethyl-2-butene at temperatures of 450 to 775 K and a pressure of 0.25 Torr. The observed product of the reaction was excited $^{1}n\pi^{*}$ (S₁) acetone, which was identified by chemiluminescence spectra of the acetone (S₁ \rightarrow S₀) transition. Neither acetone (T_i) nor any other excited states were observed under the above conditions. The temperature dependence of the chemiluminescence gave an activation energy for the cycloaddition reaction of 8610 ± 200 (1 σ) cal/mol. The quantum yield for acetone (S₁) was 4 × 10⁻³ per reactive collision; its (1 σ) error is estimated as ± a factor of 3. Chemiluminescence spectra taken at $O_2(^{3}\Sigma_{g})$ partial pressures greater than 2 Torr showed formaldehyde (S₁ \rightarrow S₀) bands. This is attributed to the well-known hydrocarbon "cool flame" mechanism, due to the presence of methyl radical formed by the thermal decomposition, in two steps, of 2,3-dimethyl-3-hydroperoxy-1-butene, another product path for the title reaction. This is the first report on the chemically activated decomposition of tetramethyl-1,2-dioxetane.

Introduction

The decompositions of 1,2-dioxetanes have been widely studied because these interesting processes yield electronically excited singlet- and triplet-state carbonyl compounds as products.^{1-13,19,21a,22} Tetramethyl-1,2-dioxetane (TMD) is the prototype, and by far the most studied, molecule in this class. The vast majority of the many previous investigations of TMD have been devoted to the *thermal decomposition* in solution. In contrast, we report the *first* study of *chemically activated* TMD prepared by the gas-phase cycloaddition of $O_2({}^{1}\Delta_g)$ with tetramethylethene (TME), reaction 1,

$$O = O(^{1}\Delta_{0}) + (CH_{3})_{2}C = C(CH_{3})_{2} \xrightarrow{a}$$

$$\begin{array}{c} O \longrightarrow O \# \\ & & \\ & & \\ CH_3 \longrightarrow C \longrightarrow C \longrightarrow CH_3 \xrightarrow{b} (CH_3)_2 C \Longrightarrow O^* (S_1) + (CH_3)_2 C \Longrightarrow O \quad (1) \\ & & \\ & \\ &$$

where # denotes vibrational excitation and * denotes electronic excitation. The lack of prior data stems from the fact that most olefins having allylic hydrogen react preferentially with $O_2({}^{1}\Delta_g)$ to form allylic hydroperoxide.¹³⁻¹⁵ The reactants $O_2({}^{1}\Delta_g)$ and tetramethylethene (TME) are believed to be capable of forming tetramethyl-1,2-dioxetane,¹³ but prior to the present work no evidence for this had been reported. These reactants are known to form the allylic hydroperoxide 2,3-dimethyl-3-hydroperoxy-1-butene,²⁶ with a low activation energy.^{14,15} Through careful control of the reaction conditions we have observed the dioxetane pathway, reaction 1, and measured the CL activation energy and the quantum yield of acetone S₁ product. The chemical activation transition state contains significantly more internal energy than the *thermal decomposition* transition state. This important difference is apparent upon inspection of the reaction coordinate diagram. Figure 1 was constructed by using bomb calorimetry data on the enthalpy of formation of TMD¹⁶ and other thermochemical and photochemical data.⁴¹ The activation energy, E_{1a} , was taken from the present work. The local maximum of energy labeled TS_{1a} is the *chemical activation* transition state, located 26 kcal/mole above TS_{1b}, the *thermal decomposition* transition state. Both transition states are connected to the electronic ground state of TMD, shown in the center of Figure 1.

Excited carbonyls have been observed by chemiluminescence in studies of the gas-phase reactions of $O_2({}^1\Delta_s)$ with various olefins and were attributed to the formation and subsequent decomposition of chemically activated dioxetanes by clean bimolecular cycloaddition reactions.^{8,9,22} The initially formed dioxetanes were claimed to be vibrationally excited by an amount that in Figure 1 corresponds to the quantity $(E_{1a} - \Delta H_{1a}) = 52$ kcal/mol. It is particularly significant that the CL activation energies that we have found in previous experiments done in bulk gas⁸ are close to the threshold translational energies required to observe CL in crossed molecular beams under single-collision conditions.⁹ Conducting olefin plus $O_2({}^1\Delta_g)$ reactions in solution leads to dioxetane molecules with thermal Boltzmann energy distributions because collisions with solvent molecules deactivate the initial adducts. Several such solution-phase studies of singlet oxygenation reactions have reported spectroscopic evidence for the presence of dioxetane products.11,12

Dioxetane rings with many different substituents on carbon atoms 3 and 4 have been prepared and subjected to *thermal*



Figure 1. Reaction coordinate diagram. Abscissa is reaction coordinate with chemical species drawn above appropriate regions. Ordinate is standard enthalpy of formation from the elements at 1 Atm and 298 K, ΔH^0_{298} . Data sources are given in ref 41.



Figure 2. Schematic of experimental apparatus in lengthwise cross section. Discharge gas enters through inlet 1, inlet 2 is for added gas and pressure measurement, inlet 3 is for olefin reactant, and outlet 4 goes to the pump. Other symbols are M = microwave cavity, LT = Wood's horn light trap, C = copper heat pipe, H = heaters, I = insulation, T = thermocouple position, W = quartz window, and S = monochromator entrance slit. The drawing is not to scale.

decomposition.^{1,2} Mechanistic inferences have been drawn from comparisons of activation energies and quantum yields for excited carbonyl products as a function of the substituents. Another approach is to compare experiments done upon the same dioxetane as a function of internal energy, using different excitation methods. To date there has been no reported comparison of thermal decomposition results with chemical activation results for any dioxetane. We believe this to be a critical shortcoming that must be redressed. Because its thermal decomposition has received so much attention, the most desirable dioxetane for making such a comparison is TMD.

Experimental Section

Discharge flow reactor techniques were used for the present work. The experimental procedures and the apparatus, shown schematically in Figure 2, differed somewhat from those used in a recent report.²² The Pyrex glass reactor had an inside diameter of 2.2 cm. The olefin inlet was located 19 cm upstream of the observation window and on the line of sight of the monochromator. This design gave the best compromise between maximum optical depth of the glowing gas and minimum contact time of the reactants.

The temperature-controlled portion of the reactor was surrounded by a custom built oven. Proceeding outward in concentric layers, the oven consisted of a heat sink of copper pipe, two half-cylindrical nichrome wire-ceramic heaters, two half-cylindrical insulating vestibules of machinable ceramic fiber, and several wrappings of clear plastic tape. Temperature was controlled within ± 0.5 deg by a microprocessor that monitored the reading of a chromel-alumel thermocouple placed on the outside of the Pyrex reactor wall. The entire assembly was mounted in a kinematically designed cradle bolted to an optical bench. The olefin inlet was located at the beginning of the heated region at its upstream end. The oven ended 4 cm from the observation window on the downstream end.

The gas entering the heated region was at room temperature. Numerical solutions of the heat equation for a gaseous cylinder show that the temperature of the gas 3 cm into the heated region will be within 2 deg of the wall temperature under all experimental conditions used in this work.²³ Therefore it was assumed that the gas temperature was equal to the wall temperature that was measured by the thermocouple.

After leaving the reactor the gas passed through a stainless steel bellows, throttle valve, Roots-type booster pump, and then a large mechanical pump. When operated with the mechanical pump on and booster pump off the bulk flow velocities were 10 to 20 m/s and when both pumps were running flow velocities were 40–80 m/s.

Spectra were obtained with a 1/2-m f/6.9 grating monochromator with reciprocal dispersion of 3.4 nm/mm and single photon counting detection, described previously.²² The monochromator entrance slit was 8 cm from the observation window. The absolute photon sensitivity as a function of wavelength was determined by using the actinometric data of Fontijn, Meyer, and Schiff for the O + NO reaction.²⁴ With monochromator slits of 4 mm \times 20 mm (the maximum opening) and the above geometry, the sensitivity in the region 300-500 nm was approximately 1 count per 6000 photons emitted into 4π steradians within the observed reactor volume. The quantum yield of formaldehyde S1 from the reaction of ethyl vinyl ether plus $O_2({}^1\Delta_g)$, reported previously, is $5.6 \times 10^{-4.8b}$ This is an average of many measurements taken in an earlier apparatus and considered to be very reliable. Therefore this reaction was used as a secondary standard. This was particularly convenient since a calibration could be performed at any time with no alteration of the apparatus other than switching the reagent introduced at inlet 3 of Figure 2.

The system's order-of-magnitude detection limits are as follows: H₂CO (S₁), 10⁷ molecules cm⁻³; acetone (S₁), 10⁹ molecules cm⁻³. The detection limits are for repetitive scanning and cumulative summing of spectra over a period of 5 h at a spectral slit width of 3.4 nm. The resultant spectra from such runs showed a signal-to-noise ratio of about 10. For an excited molecule with a fluorescence quantum yield of unity, such as D₂CO S₁, the detection limit would be approximately 3×10^5 molecules cm⁻³.

Once confidence was established in the identity of the observed excited state, the slits could be opened to allow concentrations more than a factor of 10 lower than the above to be observed. The light intensity from a continuum spectrum passed through a two-slit scanning monochromator is proportional to the square of the width of the slits. This relationship held true for our apparatus and the formaldehyde $(S_1 \rightarrow S_0)$ and acetone $(S_1 \rightarrow S_0)$ spectra. (The vibronic bands of formaldehyde $(S_1 \rightarrow S_0)$ consist of an unresolvably dense manifold of rotational states.) Spectra for identification were taken at a spectral slit width of 3.4 nm and those for Arrhenius plots and quantum yield determinations were taken with a spectral slit width of 13.6 nm.

The olefins used in this work were ethyl vinyl ether, 2,5-dimethylfuran, and tetramethylethene (Aldrich, Gold Label, 99+%). TME is prone to oxidation in ambient air. It was transferred quickly from the manufacturer's sealed vial to the vacuum distillation system. Its exposure to the atmosphere was limited to 60 s or less while at a temperature of -10 °C. All olefins were degassed by three freeze-pump-thaw cycles and purified by bulb-to-bulb distillation at reduced pressure. The experiments used for Arrhenius parameters and quantum yields utilized mixtures of the olefin vapor in helium made at various concentrations from 3 to 35% and stored in 60-L stainless steel tanks. The olefin partial pressures were less than the vapor pressure at the temperature of the laboratory so as to prevent condensation of liquid olefins in the inlet. The flows were taken from the tanks



Figure 3. Plot showing titration of $O_2({}^{l}\Delta_g)$ with 2,5-dimethylfuran. The end point is at 24.2 mTorr of added 2,5-dimethylfuran; see Experimental Section.

to the reactor by using needle valves and polyethylene tubing. This procedure gave very stable flows. Concentrations were determined from the ideal gas law based upon measurements of temperature, pressure, and all flows entering the reactor.

The $O_2({}^{1}\Delta_g)$ was made by passing oxygen or mixtures of oxygen with helium or argon through a Broida-type microwave cavity operated at 2450 MHz and 40 W. A ring of HgO, freshly deposited daily on the discharge tube immediately downstream of the cavity, catalyzed the recombination of $O({}^{3}P)$ to $O_2({}^{1}\Delta_g)$. As previously reported, $O({}^{3}P)$ could not be detected when the HgO deposit had been refreshed within a few hours of the measurement.^{8b}

The concentration of $O_2(^{1}\Delta_g)$ is proportional to the square root of the intensity of the energy pooling "dimol" transition occurring at 634 nm $(I_{634})^{25}$

$$2O_2(^1\Delta_e) \rightarrow 2O_2(^3\Sigma_e) + h\nu \ (634 \text{ nm})$$

This measure of relative concentration was used to determine the end point of a chemical titration with 2,5-dimethylfuran according to reaction 2,²⁶ which is known to have 1:1 reactant stoichiometry.²⁷

$$\int_{O} + O_2 ({}^{1}\Delta_g) \longrightarrow \int_{O-O} (2)$$

At each titration point, values of I_{634} and $(I_{634})_0$ were measured with the flow of dimethylfuran on and off, respectively. The "dimol" band was repeatedly scanned, summed, and integrated to obtain the values of I_{634} and $(I_{634})_0$. The quantity $\{I_{634}/(I_{634})_0\}^{1/2}$ is the fraction of the initial concentration of $O_2({}^{1}\Delta_g)$ remaining at each point. The plot of ln $[\{I_{634}/(I_{634})_0\}^{1/2}]$ vs partial pressure of dimethylfuran, shown in Figure 3, would be a straight line if the reactant concentrations were in the range required to satisfy strictly the pseudo-first-order approximation. The data points of Figure 3 were fitted to a least-squares straight line. The value of the abscissa at which the fitted line crossed the line, ordinate = -2.3, which corresponds to 10% remaining, was taken as the best estimate of the $O_2({}^{1}\Delta_g)$ initial concentration. The intercept of the fitted line with the ordinate was used to calculate the "dimol" intensity corresponding to the initial concentration.

This procedure was dictated by pragmatism. It contains two recognizable errors; the pseudo-first-order approximation is not valid for all values of dimethylfuran pressure, and the end point cannot be taken at 10% remaining. We believe that these two errors will be offsetting to a considerable extent. The procedure was used because the extrapolation required to obtain the end point was reasonably short. The end-point values are believed to be accurate within $\pm 30\%$. The titration results were used only to establish that the activation energy and quantum yield measurements were taken under pseudo-first-order conditions with $O_2({}^{1}\Delta_g)$ in excess. The 30% error is acceptible for this purpose.

The value of I_{634} has been shown to be proportional to $T^{1/2}$, since the rate of the dimol process is proportional to the collision frequency.²⁵ This leads to eq 3.^{8b} Temperature-dependent

$$[O_2({}^{1}\Delta_g)]/[O_2({}^{1}\Delta_g)]_0 = (T_0/T)^{1/4}[(I_{634})_T/(I_{634})_{T_0}]^{1/2}$$
(3)

heterogeneous deactivation of $O_2({}^1\Delta_g)$ on the reactor walls was



Figure 4. Chemiluminescence spectrum obtained from reaction of TME with $O_2({}^{1}\Delta_g)$ at 673 K with $P(O_2) = 3.71$ Torr. The total pressure was 3.77 Torr.



Figure 5. Chemiluminescence spectrum obtained from reaction of TME with $O_2({}^{1}\Delta_g)$ at 775 K with $P(O_2) = 0.21$ Torr. The total pressure was 2.23 Torr.

observed. The value of $[O_2({}^{1}\Delta_g)]$ decreased by 21% when the reactor temperature was raised from 450 to 625 K. It was found empirically that a plot of $[O_2({}^{1}\Delta_g)]$ vs 1/T, in the absence of olefin reactants, was linear with a correlation coefficient of +0.999.

For CL Arrhenius plots, acetone $S_1 \rightarrow S_0$ CL spectra were obtained at eight temperatures from 450 to 625 K, with 25-deg spacing. Integrated spectral areas from 333 to 500 nm were measured. Values of I_{634} and $[O_2({}^{1}\Delta_g)]$ were measured at the temperature extremes of the plot and calculated values of $[O_2({}^{1}\Delta_g)]$ were assigned to the other points by using eq 3 and the empirical wall deactivation relationship. The individual readings of acetone $(S_1 \rightarrow S_0)$ spectral area were normalized by the calculated values of $[O_2({}^{1}\Delta_g)]$. The normalized areas were plotted vs 1/T. The order of the points with respect to temperature was randomly selected.

Results and Discussion

Assigning Chemiluminescence. Several published works report studies of TMD energized with greater than thermal energy by methods other than chemical activation.^{3-7,10} These investigations as well as the many studies of thermal decomposition of TMD all report the formation of acetone S₁ as a primary product.¹⁻⁷ In general, those studies that were conducted in the absence of O₂, and under conditions where electron transfer does not occur, also report the presence of acetone T₁.¹⁻⁷

Figure 4 shows the CL spectrum obtained at 673 K when 3.71 Torr of pure oxygen was used as the discharge gas. The observed vibronic bands are those of the formaldehyde $(S_1 \rightarrow S_0)$ transition.²⁸ Formaldehyde S_1 cannot be obtained from the reactants O_2 ($^{1}\Delta_g$) plus TME by a clean bimolecular process. The Figure 5 spectrum, taken at 775 K, appears to be that of the acetone ($S_1 \rightarrow S_0$) transition, free of discernible formaldehyde bands. The discharge gas consisted of 0.212 Torr of O_2 plus 2.003 Torr of Ar.

Figure 5 was compared to the acetone $(S_1 \rightarrow S_0)$ CL spectra obtained from the reaction of $O_2({}^1\Delta_g)$ with 2-methyl-1-(N,Ndimethylamino)propene.^{8b,22} The spectra were identical within experimental error in that peak intensity occurred at 398 ± 3 nm, the ratio of 350-nm intensity to 398-nm intensity was the same, and the 12 distinctive vibronic bands of formaldehyde were absent. It is not clear whether other aliphatic ketones and aldehydes having two or more carbons can be ruled out by using the above criteria. However, such products cannot be formed from $O_2({}^1\Delta_g)$ plus TME by an elementary bimolecular process. Under the conditions of Figure 5, the CL intensity was found to be first order in $O_2({}^1\Delta_g)$ and first order in TME, consistent with product formation by an elementary bimolecular reaction. Acetone S_1 is a known product of reaction 1b. On the basis of the total body of evidence, Figure 5 was assigned as acetone $(S_1 \rightarrow S_0)$ emission.

Spectra obtained at several oxygen pressures intermediate between those of Figure 4 and Figure 5 appeared to be linear combinations of formaldehyde and acetone CL spectra. No attempt was made to determine the coefficients of such combinations as a function of pressure. However, the change in spectral appearance with pressure can be attributed to competing reactions.

Spectra and Reaction Mechanisms

Reactions 1a and 4 are competitive paths for the consumption of TME by $O_2({}^1\Delta_g)$.

At the beginning of this study it was suspected, but not known, that the activation energy for reaction 1a was significantly higher than the known value of 3230 cal/mol for reaction 4.1^4 Hydroperoxides are well-known to decompose unimolecularly by rupture of the O–O bond.²⁹ For *tert*-butyl hydroperoxide the reported Arrhenius form rate constant is $k = (4 \times 10^{15}) \exp[-43000/$

1.987T(K)].²⁹ At 775 K, 2,3-dimethyl-3-hydroperoxy-1-butene

is expected to behave similarly, according to reaction 5.

Alkoxy radicals as a class undergo unimolecular fragmentation at low activation energy to yield alkyl radical plus carbonyl or H atom plus carbonyl. Many such reactions have been studied and an Evans-Polanyi correlation has been reported.³⁰ The reaction of *tert*-butoxy radical is a relevant example.

The allyloxy radical product from reaction 5 has the reaction paths

 $\Delta H_{\rm R} = 14 \text{ kcal/mol}^{43}$

$\Delta H_{\rm B} = 5 \, \rm kcal/mol^{43}$

On the basis of the experimental and estimated thermochemistry,^{31,43} reaction 8 is expected to account for virtually all of the product at 775 K. Furthermore virtually every molecule of 2,3dimethyl-3-hydroperoxy-1-butene formed under the present experimental conditions should proceed to form methyl radical by reactions 5 and 8.

Formaldehyde $(S_1 \rightarrow S_0)$ CL has been observed when mixtures of O₂ and di-*tert*-butyl peroxide^{32,40} (DTBP) or *tert*-butyl hydroperoxide^{32d} (TBHP) were thermally decomposed. The CL required the presence of O₂. The mechanism, while not known with certainty, is believed to be the same as that of formaldehyde CL in cool flames.³² The decompositions of DTBP and TBHP give two and one *tert*-butoxy radicals, respectively. These radicals immediately undergo reaction 6. The chemistry of DTBP and/or TBHP plus O₂ mixtures under mild conditions is esentially the chemistry of methyl radical plus OH radical plus O₂. Similarly, the chemistry expected to occur following the formation of the initial reaction product, 2,3-dimethyl-3-hydroperoxy-1-butene, under the present conditions, is the chemistry of methyl radical plus OH radical plus O_2 .

The presence of added OH when TBHP is substituted for DTBP has no effect on the formaldehyde CL spectrum and little effect on the intensity.^{32d} This is consistent with evidence that hydroperoxides are the autocatalytic initiator and OH is the major chain carrier in hydrocarbon cool flames.⁴⁴ The routes for conversion of R to ROOH and OH in the presence of O₂ are well-known.⁴⁴

Various reactions of methylperoxy radical and methoxy radical have been proposed as the source of the formaldehyde S_1 state in the oxidative decompositions of DTBP and TBHP. In any case, the pressure-dependent reaction

$$CH_3 + O_2 + M \rightarrow CH_3OO + M$$
 (9)

must take place in order for CL to be observed. Reaction 9 has been the subject of many investigations.³³ It is clear from a recent study of the pressure dependence of k_9 that, under all conditions used in the present work, reaction 9 will be third order.³⁴

The partial pressure of O_2 for Figure 5 was lower than that for Figure 4 by a factor of 18. The reduction in total pressure for Figure 5 compared to Figure 4 was a factor of 1.7. To the extent that reaction 9 controls the formaldehyde S_1 concentration, these changes are expected to reduce the fractional contribution of formaldehyde CL in Figure 5 by a factor of approximately 30. It is considered unlikely that there is significant suppression or quenching of the dioxetane pathway due to the increases in total pressure and O_2 partial pressure in Figure 4 as compared to Figure 5. The formaldehyde spectrum of Figure 4 is believed to represent the end result of a series of secondary reactions leading to formaldehyde cool flame CL, with the rate-controlling step being reaction 9.

We claim that Figure 5 represents the spectrum of the decomposition of chemically activated TMD. It shows no detectable evidence of the presence of formaldehyde S_1 . Thus we assumed that CL activation energies and quantum yields, obtained under similar or lower pressure conditions, were due exclusively to reaction 1, with no contribution from cool flame CL.

It is most important to note that formaldehyde S_1 is the only excited carbonyl observed in cool flames regardless of the fuel used.⁴⁵ For purposes of the present discussion, CL arising from thermal decomposition of any peroxides other than dioxetanes can be classified as a "cool flame". It does not matter whether such peroxides come from side reactions or impurities in the starting material. Acetone S_1 cannot be formed directly by a cool flame mechanism.⁴⁵ Furthermore acetone S₁ cannot be formed from formaldehyde S_1 by energy transfer under the experimental conditions of Figure 5. The zero-pressure lifetime of the vibrationless $H_2CO S_1$ state is 10^{-7} s and is dominated by predissociation.³⁶ The concentration of $H_2CO S_1$ was $\leq 10^9$ molecules cm⁻³. Even if all TME consumed ($\approx 5 \times 10^{13}$ molecules cm⁻³ in this experiment) were converted to acetone S₀, the mean time between hard-sphere collisions of acetone S_0 with $H_2CO S_1$ would be $\geq 10^{-5}$ s. These considerations lead to a very high confidence that the acetone $(S_1 \rightarrow S_0)$ spectrum of Figure 5 is due to a primary product of reaction 1.

CL Activation Energy. The temperature dependence of the acetone $(S_1 \rightarrow S_0)$ intensity at low total and O_2 pressures was obtained as described above. The data are shown in Table I. The mean and standard deviation of the mean of the slopes of five separate Arrhenius plots taken on five different days yielded a CL activation energy of 8610 ± 200 (1 σ) cal/mol. This is attributed to reaction 1a.

In previous CL studies of chemically activated dioxetanes formed from cycloaddition of $O_2({}^{1}\Delta_g)$ with olefins we found that the dioxetane adducts had lifetimes of less than 10^{-8} s.⁸ This was an upper limit estimate based upon the absence of collisional stabilization when the total pressure was raised to 25 Torr. In the present experiments the pressure had to be kept below 0.25 Torr; at higher pressures CL could have arisen from side reactions as well as the process of interest. Nevertheless, the previous studies on molecules of size similar to TMD, as well as the potential energy diagram shown in Figure 1, strongly suggest that TMD molecules

TABLE I: Chemiluminescence Intensity Variation with Temperature⁴

data set	<i>T</i> , K	photon count	$E_{\rm a} \pm 1\sigma$," cal/mol
1	624	122 043	
1	600	93 672	
1	573	66 65 1	
1	550	48 867	
1	525	31 768	
1	499	20189	
1	474	14385	
1	450	8717	$8520 \pm 140 (1\sigma)$
2	625	151 578	
2	599	113 992	
2	575	95 000	
2	549	63 280	
2	524	41 051	
2	499	27 332	
2	474	20 27 2	$8180 \pm 280 (1\sigma)$
3	625	140 581	
3	599	112021	
3	574	80 828	
3	552	56742	
3	524	37 260	
3	499	22 767	
3	475	19 344	
3	450	11 007	$8240 \pm 290 (1\sigma)$
4	628	133658	
4	603	106 459	
4	578	76 456	
4	552	50 632	
4	528	31 081	
4	502	22 421	
4	478	14002	
4	453	9 4 5 8	$8870 \pm 240 (1\sigma)$
5	628	133 055	
5	603	107 396	
5	578	75831	
5	553	53 556	
5	528	32 7 2 9	
5	503	18 895	
5	478	14 807	
5	453	7 959	$9260 \pm 290 (1\sigma)$

^a Overall mean and standard deviation = $8610 \pm 200 (1\sigma)$ cal/mol.

formed in these experiments undergo chemiluminescent decomposition without stabilizing collisions. If so, then $k_{1a} \equiv k_1$ and the measured CL activation energy $\equiv E_{1a} \equiv E_1$, ensuring the validity of eq 10.

 $d[acetone S_1]/dt = rate_{1a} =$

 $k_{1a}[\text{TME}][O_2(^1\Delta_g)]\Phi_{\text{TME}} \propto \text{intensity}(\text{acetone } S_1 \rightarrow S_0) (10)$

where $\Phi_{\text{TME}} =$ quantum yield for acetone S₁ formation by reaction 1a. Reaction 4, and all reactions subsequent to it, were assumed to be dark, so that application of eq 10 to the data will in fact yield $\Phi_{1a}(S_1) \equiv \Phi_{\text{TME}}$.

The goal was to measure a valid CL activation energy for one of two competitive paths consuming the reactants. The path of interest, reaction 1a, had the higher E_a . The goal was accomplished by holding the fractional consumptions of both reactants to very small values.

Ashford and Ogryzlo reported $k_4 = (2.2 \times 10^{-13}) \exp\{-3230/1.98 T(K)\}$ cm³ molecule⁻¹ s^{-1.14} Typically $[O_2({}^{1}\Delta_g)] = 9 \times 10^{13}$ molecules cm⁻³ at 625 K in the Arrhenius plot experiments, corresponding to a pseudo-first-order rate constant of $k'_{625} = 1.4$ s⁻¹. The initial value of TME was 3×10^{13} molecule cm⁻³. The contact distance of the reactants was 15 cm, and the bulk flow velocity was 48 m s⁻¹, giving a contact time of 3.1×10^{-3} s in the plug flow approximation. The fraction of the initial TME remaining after this contact time was $\exp\{-k't\} = \exp\{-0.0044\} = 0.996$. The error in $[O_2({}^{1}\Delta_g)]$ was $\pm 30\%$ and there may as much as $\pm 50\%$ error involved in the use of the plug flow approximation. Even with allowance for errors of this magnitude, it is claimed that fractional consumption of TME by both reactions (1a) and (4) at the highest temperature (625 K) used for Arrhenius plots was less than 1%. Therefore the activation energy obtained from these plots can be unambiguously assigned to reaction 1a.

Cycloaddition of Singlet 02 to Olefins



Figure 6. Correlation of activation energy with ionization potential for reactions; olefin $+ O_2({}^{1}\Delta_g) \rightarrow \text{dioxetane}$. The correlation shown is for TME and 13 other olefins that we have previously studied. Data sources are given in ref 42.

The $O_2({}^{1}\Delta_g)$ molecule is considered to be an electrophilic reagent in its reactions with olefins. Theory suggests that the ionization potential of the π orbital, HOMO, of the olefin should be correlated with the activation energy for dioxetane formation.¹³ Figure 6 shows this correlation for TME and 13 other olefins that we have previously studied.^{8,22} The most reactive olefin studied, 2-methyl-1-(*N*,*N*-dimethylamino)propene, lies well below the least-squares line. It is interesting that Kearns predicted that olefins of very low ionization potential might show anomalous behavior due to a reversal of order of the π_{CC} and π_{OO}^* orbitals.¹³

The TME molecule obeys the correlation shown in Figure 6 very well. This fact is taken as additional support for the claim that eq 10 is valid and that acetone $(S_1 \rightarrow S_0)$ CL intensity is a measure of the rate of reaction 1a.

Acetone S_1 Quantum Yield. The quantum yield is defined as the fraction of reactive collisions forming excited S_1 state product.

$$\Phi_{1a}(\mathbf{S}_1) = \frac{d[\operatorname{acetone} (\mathbf{S}_1)]/dt}{d[\operatorname{acetone} (\mathbf{S}_0) + (\mathbf{S}_1)]/dt} = \frac{d[\operatorname{acetone} (\mathbf{S}_1)]/dt}{k_{1a}[\operatorname{TME}][O_2({}^{1}\Delta_g)]}$$
(11)

The activation energy of reaction 1a determined in this study was $8610 \pm 200 (1\sigma)$ cal/mol. The numerator of eq 11 was determined directly from

$$d[acetone (S_1)]/dt = \{SI(S_1 \rightarrow S_0)\}/\Phi_F$$
(12)

where $S = {}^{1}/{}_{6000}$ is the absolute photon sensitivity, $I(S_1 \rightarrow S_0)$ is the measured acetone CL intensity in photons s⁻¹ cm⁻³ emanating from the observed volume, and $\Phi_F = 2.4 \times 10^{-4}$ = fluorescence quantum yield of acetone S₁. We calculated $\Phi_{1a}(S_1) = 4 \times 10^{-3}$. The details of the calculation are given below.

The Arrhenius A factor for reaction 1a was assumed to be the same as the A factor for reaction 4. This assumption has been used previously^{8a,b} and is based upon the theoretical prediction that the same 'CCOO' 1,4-diradical is the initial adduct for both dioxetane (eq 1a) and hydroperoxide (eq 4) product paths.³⁵ In principle both A_{1a} and E_{1a} can be measured experimentally by standard least-squares fitting procedures. We did not take this approach because we believe that the error in the measurement would be considerably larger than the error in the assumption $A_{1a} = A_4$.

The ethyl vinyl ether (EVE) reaction was used as a standard for measurement of the quantum yield of the TME reaction. The ratio of the quantum yields for the reactions of TME and EVE with $O_2({}^{1}\Delta_s)$ is given by

$$\frac{\Phi(\text{TME})}{\Phi(\text{EVE})} = \frac{I(\text{TME}) \exp\{-E_a(\text{EVE})\}[\text{EVE}]\Phi_F(\text{H}_2\text{CO S}_1)}{I(\text{EVE}) \exp\{-E_a(\text{TME})\}[\text{TME}]\Phi_F(\text{acctone S}_1)}$$
(13)

where Φ is absolute quantum yield, Φ_F is fluorescence quantum yield, *I* is spectral intensity integrated over 333-500 nm at 625 K, and E_a is activation energy. Values of the known or measured quantities in eq 13 are $E_a(TME) = 8610 \pm 200 (1\sigma)$ and $E_a(EVE)$

Study of Activated Tetramethyl-1,2-dioxetane

= $12500 \pm 190 (1\sigma) (cal/mol)$,^{8b} $\Phi_{\rm F}(\rm H_2CO~S_1) = 3.0 \times 10^{-2}$,³⁶ and $\Phi_{\rm F}(\text{acetone S}_1) = 2.4 \times 10^{-4.37}$ By use of the previously measured $\Phi(EVE) = 5.6 \times 10^{-4,8b} \Phi(TME) = 4.4 \times 10^{-3}$ was obtained. Three measurements taken on different days showed a precision of $\pm 5\%$. A more realistic estimate of \pm a factor of 2.8 error was obtained by propagation of the errors in $\Phi(EVE)$ and the two activation energies into the final result.

We report a best estimate of $\Phi(TME) = 4 \times 10^{-3} \pm a$ factor of 3 (1 σ), which applies to the decomposition of chemically activated TMD in the gas phase at a total pressure of 0.25 Torr.

Search for Acetone (T_1) . Attempts were made to reduce the partial pressure of O_2 in the reactor so as to reduce quenching and allow observation of any acetone (T_1) present, as was done in a recently reported investigation.²² Acetone (T_1) product was not detected in the present experiments. In all cases the acetone CL spectra observed showed maximum intensity at 398 ± 3 nm and the ratio of 500-nm intensity to 400-nm intensity was constant for all partial pressures of O₂ that were used. Attempts to lower $P(O_2)$ much below 0.2 Torr caused the signal to fall below the detection limit for unambiguous spectroscopic product identification.

In the recent study of 3,3-dimethyl-4-(N,N-dimethylamino)-1,2-dioxetane,²² spectra taken at $P(O_2) = 0.22$ Torr showed a distinct red shift and a T_1/S_1 integrated intensity ratio of 0.28. To convert this ratio into the actual $[T_1]/[S_1]$ concentration ratio would require a reliable measurement of either the phosphorescence quantum yield of the T_1 state or the Einstein A coefficient for the $(S_0 \rightarrow T_1)$ transition,³⁸ data that are not available at the present time. A zero-pressure lifetime of 225×10^{-6} s for the T₁ state in the gas phase has been reported,³⁹ but the contribution of radiationless transitions to this lifetime is not known. If radiationless transitions dominate the decay rate of the T_1 state, then the $[T_1]/[S_1]$ ratio in our earlier work²² may have been very large.

At present we can compare relative, but not absolute, $[T_1]/[S_1]$ ratios from gas-phase chemical activation studies. Clearly, chemically activated TMD yields a much smaller $[T_1]/[S_1]$ ratio than does chemically activated 3,3-dimethy-4-(N,N-dimethylamino)-1,2-dioxetane.²² This result does not conflict with solution-phase measurements of $[T_1]/[S_1]$ from the thermal decomposition of TMD, which appear to be very well established.^{1a}

Concluding Remarks

The quantum yield value reported herein of $\Phi = 4 \times 10^{-3} \pm$ a factor of 3 for the chemically activated decomposition of TMD in the gas phase at 625 K is the same, within experimental error, as the consensus value of $\Phi = (2.5 \pm 1.4) \times 10^{-3}$ reported for the thermal decomposition of TMD in inert solvents at near room temperature.1a

The unsubstituted parent 1.2-dioxetane has been synthesized and its quantum yield for $H_2CO S_1$ product formation upon thermal decomposition has been measured by Adam and Baader.^{2d} They reported $\Phi = 3.1 \times 10^{-6}$, whereas we reported $\Phi = 8 \times 10^{-3}$ in our *chemical activation* study of the ethene plus $O_2({}^1\Delta_z)$ reaction.^{8b} This large discrepancy is easily explained. The potential energy surface for the case of unsubstituted 1,2-dioxetane shows an important difference from Figure 1, namely, inversion of the energy levels of TS_{1b} and S_1 product. For this case, TS_{1b} lies at the energy, $(E_{1b} - \Delta H_{1b}) = (22 + 55) = 77 \text{ kcal/mol},^{2d}$ and formaldehyde S_1 lies at 80.6 kcal/mol. The extraordinarily low thermal $\Phi(S_1)$ is due to the fact that S_1 formation from TS_{1b} is endoergic by 3.6 kcal/mol.^{2d} This is in marked contrast to our chemical activation experiment where TS_{1a} lies at energy (E_{1a} $-\Delta H_1$ = 21 + 90 = 111 kcal/mol.^{8b} As a result, S₁ formation is excergic by 30 kcal/mol, permitting a normally large $\Phi(S_1)$.

The results of the present study support the authority of our earlier publications on dioxetanes.^{8,22} We have long sought to provide a meaningful comparison of chemical activation and thermal decomposition results on the same dioxetane molecule. Otherwise, our work would stand in isolation from the vast body of work done in solution by physical organic chemists.^{1,2} The present report provides the desired comparison. The close

agreement between chemical activation results reported herein and thermal decomposition studies of TMD lends indirect support to our previous studies.8,22

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Registry No. O₂, 7782-44-7; CH₃C(CH₃)=C(CH₃)CH₃, 563-79-1; CH₃COCH₃, 67-64-1; CH₂O, 50-00-0; tetramethyl-1,2-dioxetane, 35856-82-7.

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(41) Data and sources for Figure 1. Values of ΔH^{0}_{298} in kcal/mol are as follows: 2,3-dimethyl-2-butene, -14.2 (ref 18); acetone, -52.0 (ref 18); tetramethyl-1,2-dioxetane, -35 (refs 8a, 16, 19). Excitation energies in kcal/mol are as follows: $O_2(^{1}\Delta_p)$, 22.6 (ref 20); acetone (T_1), 78; acetone (S_1), 85 (ref 21b). Activation energies in kcal/mol are as follows reaction 1a, 8.6 (this mark), acetone (S_1), 26 (ref 1d). work); reaction 1b, 26 (ref 1d).

(42) Data and sources for Figure 6. All ionization potentials were taken

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(43) Data and sources for thermochemistry, eqs 4, 7, and 8. Acetone, $O_2({}^1\Delta_g)$, and TME were taken from ref 41. Methyl and hydroxyl radicals were taken from Baulch et al. (Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J.; Watson, R. T. J. Phys. Chem. Ref. Data 1984, 13, Supplement 2, 1259) as was ethylene $D_{298}^0(C-H) = 108$ kcal/mol used to estimate $\Delta H_0^0(2$ -propenyl) = 60 kcal/mol. The following standard enthalpies of formation in kcal/mol were estimated by using group additivity rules according to ref 31: 2,3-dimethyl-3-buten-2-ol, -57; 2,3-dimethyl-3-bydro-peroxy-1-butene, -40; 3-methyl-3-buten-2-one, -36. The estimate for 2,3-dimethyl-3-buten-2-ol together with D^0_{298} (alcohol O-H) = 104 was used to behavior D^0_{298} (alcohol O-H) = 104 was used to obtain $\Delta dH^0_{1}(2,3-dimethyl-3-buten-2-oxy radical) = -5$. One of the group values used was not available from ref 31 and was estimated. This was $\operatorname{group}[C(O)(C_d)(C)_2] = -5.1 = 1.5 + \operatorname{group}[C(O)(C)_3]$. This basis of the estimate is that Benson³¹ has given two examples of group values where the effect of a similar substitution of C_d for C can be obtained. In one case group $[C(O)(C_d)(H)_2] = 1.6 + group [C(O)(C)(H)_2]$, and in the other case,

Photooxidation of Zinc Tetraphenylporphyrin by Benzoquinone: A Fourier Transform **Electron Paramagnetic Resonance Investigation**

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Fourier transform electron paramagnetic resonance (FT-EPR) has been used to study the photooxidation of zinc tetraphenylporphyrin (ZnTPP) by benzoquinone (BQ). A method was developed for the analysis of the time dependence of the FT-EPR spectra, following pulsed laser excitation of ZnTPP, that gives rate constants for the electron-transfer process as well as for the spin-polarization evolution in paramagnetic species involved in the reaction. It is found that the rate constant of electron transfer from photoexcited triplet ZnTPP to BQ in ethanol is concentration dependent. The data yield a value for the electron-transfer-reaction radius of triplet ZnTPP, the limiting rate constant that would obtain for $[BQ] \rightarrow 0$, and the radical pair lifetime. In addition, values are found for the spin-lattice relaxation times of the BQ⁻ anion radical and triplet porphyrin precursor and for electron transfer from BQ⁻ to BQ.

Introduction

Fourier transform electron paramagnetic resonance¹ (FT-EPR) has proven to be ideally suited for time-resolved studies of photochemical reactions generating (transient) free radicals.²⁻⁸ The method can be used to identify free radicals and to determine the kinetics of their formation and decay. Furthermore, the time evolution of the spectra is determined, in part, by chemically induced electron polarization (CIDEP) mechanisms." These CIDEP effects give an insight into reaction mechanisms and can be used to derive information on spin-state dynamics of paramagnetic species involved in photoinitiated reactions.

A number of FT-EPR studies have been concerned with photoinduced electron transfer from zinc tetraphenylporphyrin (ZnTPP) to duroquinone (DQ) in ethanol.²⁻⁶ The measurements have yielded values for the rate constant (k_{et}) of the electrontransfer reaction, the spin-lattice relaxation time (T_1^R) of the quinone anion radical, the spin-lattice relaxation time (T_1^T) of (precursor) photoexcited triplet ZnTPP (³ZnTPP*), and the lifetime of the transient radical pair [ZnTPP+...DQ-]

The work described here concerns a detailed FT-EPR study of the photoinduced electron-transfer reaction from ZnTPP to benzoquinone (BQ) in ethanol. The objective of the study was to develop and apply a comprehensive method of data analysis that would give the values of all parameters that control the time evolution of the FT-EPR spectra. Of interest as well was the resolution of questions regarding rate constants derived in earlier work. For instance, for ZnTPP/DQ in ethanol a k_{et} value of 6 $\times 10^9$ M⁻¹ s⁻¹ has been reported.⁵ This value is significantly higher than the rate constants for electron transfer involving $ZnTPP/BQ^{10}$ $(1.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ and ZnTPP/DQ¹¹ $(2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ obtained with time-resolved optical spectroscopy. A detailed study of ZnTPP/BQ in ethanol with time-resolved direct detection CW EPR gives 1.25×10^9 M⁻¹ s⁻¹ at 230 K.¹² Moreover, values given for T_1^{T} of ³ZnTPP^{*} at ~250 K range from 50⁵ to 460 ns.³ The lack of agreement between the published values may stem from differences in experimental conditions. Another cause for the

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