5 undergoes a great change in geometry upon removal of one electron.[31]

It is also of interest to compare the $E^{\circ\prime}$ value of **1** with those of polycondensed aromatic hydrocarbons.[5] Such a comparison reveals that the radical cation $\mathbf{1}^{+\cdot}$ is considerably stabilized by solvation in acetonitrile, since the pertinent value is about 0.36 V or 8.3 kcal/mol (=34.7 kJ/mol) lower for **1** than for an aromatic hydrocarbon of the same ionization potential in the gas phase. The stabilization of the monoolefinic radical cation centers in $\mathbf{1}^{+\cdot}$ by the solvent can be rationalized by the presence of the alkyl groups bearing high positive charges, as indicated by the large coupling constants found in the ESR spectrum for the γ- and δ-protons. In energy terms, the ionization potential of **1** in the gas phase is comparable to that of the 14-π-electron system, phenanthrene, while (owing to the extra stabilization by the solvent) the value $E^{\circ\prime}$ for **1** in solution is equal to that of the 18-π-electron system, 1,2-benzanthracene.[5] Another illustrative example for the surprising ease of electron loss from such monoolefins, which are protected by Bredt's rule, is the value $E^{\circ\prime}$ for the bis(homoadamantane) (**9**); it is the same as that of tetraphenylethylene. In this context, it is noteworthy that the radical cation of the latter compound exhibits no reduction wave in the cyclic voltammogram at a scan rate of 200 mV/s. This behavior contrasts with that of $\mathbf{9}^{+\cdot}$ which, like $\mathbf{1}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$, is stable for tens of seconds under analogous conditions. The much higher persistence of these species is due to the steric protection of the radical and cationic centers by the bulky saturated groups. Such substituents preclude the addition reactions which, in the case of tetraphenylethylene, lead to a rapid decay of the radical cation.

Conclusions

As indicated by the large long-range interaction with the γ- and δ-protons, the unusually great electron demand imposed by the high charge density in the monoolefin radical cation causes a substantial hyperconjugative delocalization of spin and charge into the saturated alkyl substituents. The considerable stabilization of the radical cation by this delocalization is greatly reduced when the γ- or δ-hydrogens are replaced by halogen atoms.

Acknowledgment. This work was supported by the National Science Foundations of the U.S.A. (major instrument program) and Switzerland (Project 2.625.080). R.A. thanks the Romnes Foundation for a scholarship. We are indebted to Professor H. Wynberg for a gift of a sample of **9**.

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Kinetics of Gas Phase Tetramethyldioxetane Decomposition and Chemiluminescence

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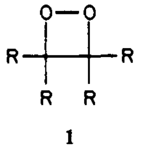
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received May 4, 1981*

Abstract: Pulsed-laser excitation of overtone vibrations or a weak electronic transition in gas-phase tetramethyldioxetane in combination with temporally and spectrally resolved detection of decomposition product luminescence reveals the presence, along with electronically excited acetone, of an additional emitting species which is not observed in solution studies. The emission is at shorter wavelengths than the acetone phosphorescence, and the emitting species has a zero-pressure decay rate of 0.019 ± 0.014 μs^{-1}. The rapid collisional quenching which occurs on roughly every other encounter ($k_q = 5.6\ \mu s^{-1}\ \text{torr}^{-1}$) explains the inability of solution measurements to detect this feature of the tetramethyldioxetane decomposition kinetics. This newly observed component is likely to extend the interpretation of gas-phase decomposition experiments using infrared multiphoton absorption or collisions with fast Xe atoms to excite tetramethyldioxetane.

Dioxetanes (**1**) are four-membered cyclic peroxides which have the intriguing property of efficiently producing electronically excited products upon decomposition and, thus, converting chemical energy to light.[1-4] They are also intermediates in the reaction of singlet oxygen with olefins[2] and are suggested models of bioluminescent processes.[4] The surprising result that dioxetanes produce many more triplet ketone products than excited singlet products continues to stimulate experimental and theoretical efforts to unravel the mechanism of the decomposition. The concerted mechanisms which was first proposed[5] has now given way to one involving a biradical intermediate produced by opening of the O–O bond in the ring,[6,7] but questions of the stability of the biradical remain.[8,9] A GVB–CI calculation by Harding and Goddard[10] predicts a significant local potential energy minimum for the biradical and, in fact, finds the maximum energy along the reaction



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coordinate to be for cleavage of the C–C bond subsequent to breaking the O–O bond, contrary to experiments on substituted dioxetanes.[6,7,9] In a qualitative description of the mechanism, Turro and Devaquet[11] suggest that the biradical rapidly forms products because no barrier to decomposition remains after the O–O bond is broken. In both cases, energetics and subtle features of the crossings of several surfaces which correlate with excited products by the ground-state surface control the partitioning of the products among the various states.[9]

Essentially all the experimental kinetic information available comes from solution measurements although there are three studies of the gas-phase decomposition of tetramethyldioxetane (TMD) using different techniques for energy deposition. In nonreactive solvents,[1-4] the thermal decomposition of tetramethyldioxetane has an activation energy of $E_a \sim 27.6$ kcal mol^{-1} and produces roughly 0.5% excited singlet acetone (^{1}A) and 30% triplet acetone (^{3}A). In the gas-phase experiments, excitation energy comes from energy transfer from laser-excited CH_3F,[12] infrared multiphoton excitation,[13] or collisional excitation by a beam of fast Xe atoms,[14] and in these cases, product luminescence serves as the reaction monitor. We study the gas-phase decomposition of TMD using a new technique[15,16] in which intense laser pulses provide the requisite energy by exciting overtone vibrations of the CH stretching motion, and time-resolved detection of the product luminescence directly reveals rate information. This one-photon excitation adds a precisely known energy increment to the molecule and allows us to determine overtone vibration spectra as well as unimolecular decay rates for the state-selected molecules.[16] Because the temporal evolution and spectrum of the luminescence also reflect the properties of the emitting products and any intermediates leading to them, our experiments offer an opportunity to explore the chemiluminescence kinetics. In this paper, we describe experiments using both overtone vibration and electronic excitation of TMD along with temporally and spectrally resolved product detection to probe the possible intermediate and emitting species in TMD decomposition. Along with the expected electronically excited acetone, these measurements reveal the presence of another emitting species which is not observed in solution studies.

Experimental Approach

The experimental approach which provides the excitation of weak transitions and sensitive, time-resolved detection of resulting product emission in these experiments is the same as that described in our state-selected studies of unimolecular decay of TMD and, consequently, is described only briefly here.[15-17] Excitation photons come from a Nd:YAG excited dye laser, which produces 6-ns pulses at a 10-Hz repetition rate, and are either used directly or shifted to the required wavelength by stimulated Raman scattering in about 20 atm of hydrogen gas. Typically, the excitation beam diameter is 2 mm, and the bandwidth is less than 1 cm^{-1}. The excitation occurs in a room temperature aluminum cell through which TMD, synthesized by a slight variation of the method of Kopecky and Mumford,[17,18] flows from a thermostated sample. A capacitance manometer monitors the total pressure in the cell. An efficient photomultiplier (EMI 9635 B), which has its 45-mm diameter photocathode located 40 mm from the fluorescence region, detects product luminescence, and a 100-MHz bandwidth transient recorder–multichannel analyzer combination captures and averages the resulting signal by summing between 1000 and 20 000 laser pulses. The time constant of the detection system is about 20 ns. Figure 1 shows typical data taken at 11-mtorr pressure in time increments of 500 ns per channel. The total emission intensity passed by a colored glass filter (Corning 4-96) whose transmission is centered at 460 nm with a 180-nm band-pass contributes to the signals shown in Figure 1, but adding a 10-nm band-pass interference filter limits the signal to a small spectral region. Integrating the signal from each of a series of narrow band-pass filters and correcting for the measured filter transmission produces a luminescence spectrum. Because the data are time resolved, integrating only a portion of the signal (see Figure 1) gives luminescence spectra at different times following the excitation. As discussed elsewhere,[16] the signal arises from excitation of TMD and not from acetone which might be produced by thermal decomposition in the cell.

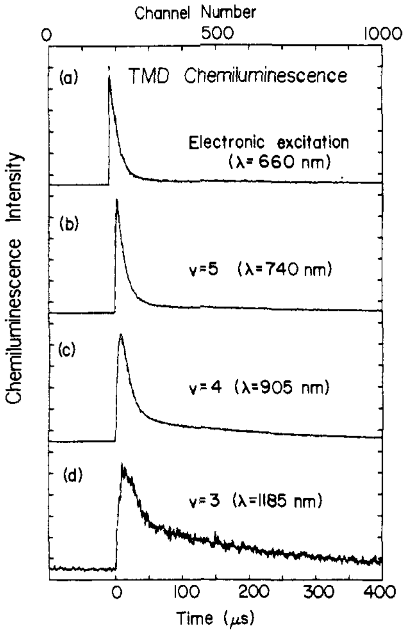

Figure 1. Time-resolved chemiluminescence from TMD decomposition products for different excitations: (a) electronic excitation; (b) $v = 5$ CH stretching excitation; (c) $v = 4$ CH stretching excitation; (d) $v = 3$ CH stretching excitation. The broken curves are nonlinear least-squares fits of the sum of three exponentials to the data.

Results

Product chemiluminescence data from direct excitation of TMD to $v = 3$, 4, or 5 of the CH stretching vibration or from electronic excitation all show two characteristic decay rates (Figure 1). The fast decay occurs in a few microseconds while the slow decay lasts a few hundred microseconds. A slight variation in the rising portion of the signal is just discernible in the data; this variation, which we have examined with much greater time resolution,[16] reflects the different reaction rates resulting from the excitation of various vibrational levels or the rapid (detection electronics limited) rise from electronic excitation. These early portions of the signal contain important information on unimolecular reaction dynamics and represent a unique direct measure of state-selected reaction rates but are not important to the discussion of TMD chemiluminescence kinetics. Careful analysis of the rising portions of the signals yields unimolecular decay rates which agree well with Rice–Ramsperger–Kassel–Marcus (RRKM) theory predictions.[16] Because the unimolecular reaction is quite rapid compared to both the subsequent fast and slow decay of the signal, it does not influence the present analysis of the signal. For example, reaction rate constants for $v = 4$ and $v = 5$ ($k_4 = 0.12$ μs^{-1} and $k_5 = 3.5$ μs^{-1}) substantially exceed the zero-pressure rate constant for the fast decay (0.019 μs^{-1}) discussed below.

The crucial observations are that two distinct decays occur and that their characteristic times are independent of excitation mode (vibrational or electronic) and excitation energy (24 kcal mol^{-1} (λ = 1185 nm) to 43 kcal mol^{-1} (λ = 660 nm)). (Although the energy increment for the lowest energy excitation ($v = 3$) is less than the activation energy, for most TMD molecules the initial thermal energy content combined with the photon energy does exceed the threshold.) Several features of the data clearly identify the excitation at λ = 660 nm as predominantly electronic. The excitation spectrum around 660 nm is smooth with none of the

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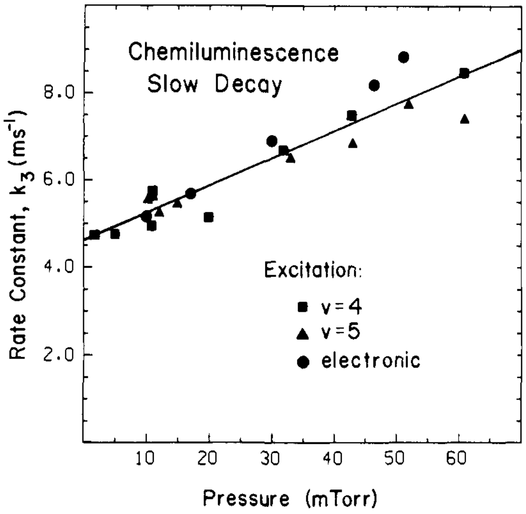

Figure 2. Rate constant for the slow decay of TMD decomposition product luminescence as a function of total pressure for three different excitations.

overtone vibration structure which is present in the other regions, and the rapid rise of the luminescence signal at 660 nm is limited by the detection electronics response time. A small electronic component is present as a smooth background on both sides of the $v = 5$ overtone vibration;[16] excitation of the background produces a luminescence rise limited by the detection electronics while excitation of the overtone vibration yields a much slower signal rise.

Figure 1 also shows that the decomposition pathways are not completely independent of excitation energy in that the relative intensity of the slow portion of the luminescence decreases with increasing energy. The broken curves in Figure 1 are nonlinear least-squares fits to the data by the sum of three exponentials. One term accounts for the rise of the signal while two others, having rate constants k_2 and k_3, describe the fast and slow decay, respectively. Clearly, these two falling exponentials describe the decay well and are uninfluenced by the rate constant for the rise.

Slow Decay. The slow decay arises from the acetone phosphorescence which is expected from the results of solutions studies of TMD. Figure 2 shows the slow decay constant k_3 over the pressure range of 10 to 60 mtorr for excitation of $v = 4$ and 5 of the CH stretch and for excitation of the electronic transition. (The weak signal from $v = 3$ excitation is not included.) The least-squares line yields a zero-pressure rate of $(4.6 \pm 0.4) \times 10^{-3}$ s^{-1} (all uncertainties are two standard deviations of the fit) which agrees with that of triplet acetone (^{3}A),[19] particularly when the pressure dependence of the lifetime is included in analyzing the previous measurements. The collisional quenching rate determined from the slope, $(6.3 \pm 1.0) \times 10^{-2}$ μs^{-1} torr^{-1}, corresponds to relaxation of ^{3}A in fewer than 160 collisions with TMD. (The possibility that the vapor in the cell contains a significant amount of acetone makes this number of collisions an upper limit). Emission spectra taken at long times where only the slow decay remains confirm the identity of the emitter. Figure 3 shows the integrated signal obtained with a series of 10-nm band-pass interference filters for electronic, $v = 4$, and $v = 5$ excitation. The reference spectrum of acetone phosphorescence produced in our apparatus by ultraviolet excitation of acetone at 330 nm and the long-time chemiluminescence spectra are identical within the precision of the measurement.

Fast Decay. The fast decay is a more surprising feature in that solution studies of TMD show no corresponding emission. (An additional emitter seems to be present in the thermal decomposition of trimethyldioxetane in CCl_4, however.)[20] Again, all three excitations produce the same rate constant k_2 and pressure dependences, as shown in Figure 4. The least-squares line has a small intercept, 0.019 ± 0.014 μs^{-1}, corresponding to a zero-pressure lifetime between 30 and 200 μs and a slope of 5.6 ± 0.3 μs^{-1} torr^{-1} which represents quenching in two gas kinetics collisions. This rapid collisional loss explains the failure of solution studies to detect this species since the predicted lifetime based on a simple extrapolation of the gas-phase quenching rate to liquid densities is only 10^{-13} s. Clearly, the collisional loss dominates the decay in our experiment except at the lowest pressures where flight to the cell walls is important. (Loss to the walls also produces the deviation of the measured points from the least-squares line at low pressures.)

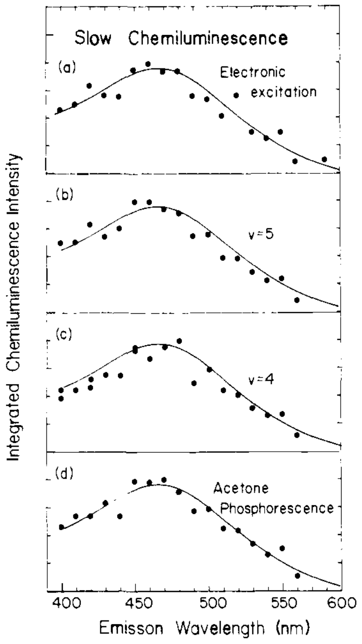

Figure 3. Emission spectra of TMD decomposition products at long times for three different excitations ((a)-(c)). Part d is an acetone phosphorescence spectrum produced by ultraviolet excitation of acetone at 330 nm. The ordinate is the integrated emission signal at long times where only the slow decay contributes.

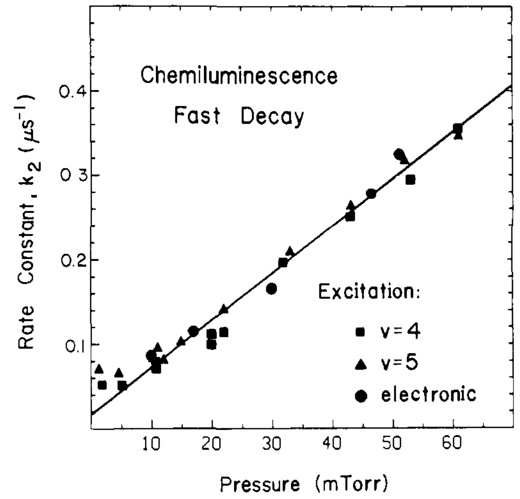

Figure 4. Rate constant for the fast decay of TMD decomposition product luminescence as a function of total pressure for three different excitations.

The emision spectra of the fast portion of the decay (Figure 5) clearly differ from the acetone phosphorescence spectrum but are identical with each other for all three excitations of TMD. Although the blue shift relative to ^{3}A emission agrees qualitatively

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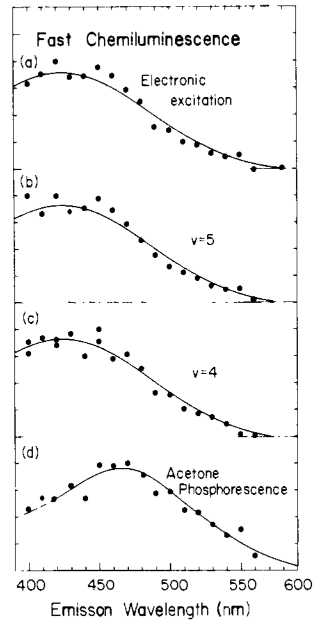

Figure 5. Emission spectra of TMD decomposition products at long times for three different excitations ((a)-(c)). Part d is the same acetone phosphorescence spectrum shown in Figure 3. The ordinate is the integrated emission signal at short times where the fast decay is the dominant contribution.

with the singlet acetone (^{1}A) spectrum, ^{1}A cannot be responsible for the lifetime of the fast decay since even the lower limit to the collisionless lifetime (30 μs) vastly exceeds that for ^{1}A (2.5 ns).[21]

Discussion

The observation of a species besides excited singlet and triplet acetone in the decomposition of TMD adds a new feature to the chemiluminescence kinetics. One possible interpretation of the fast decay is that it arises from a nonradiating intermediate, such as the proposed dioxetane biradical, which is part of the sequential processes producing the excited acetone products. (A nonradiating intermediate which produces only ground-state products is unobservable in our experiment.) Although our data do not uniquely identify the intermediate, they are sufficiently detailed to test the possibility that it is a nonradiating species. Figure 6 is a generalized kinetic scheme for decomposition of TMD through such a dark intermediate following electronic excitation. (The total scheme for overtone vibration excitation is only slightly more complex because the intermediate is produced at a rate determined by the rapid unimolecular decay. The essential features are the same, however, with the decaying portions of the signal being identical (see Figure 1). Thus we consider the case of direct electronic excitation).

The dark intermediate (DI) decays with the rate constant k_{DI} to ^{1}A with a quantum yield $^1\phi_{RXN}$, to ^{3}A with a quantum yield $^3\phi_{RXN}$, and to nonemitting products, represented by ground-state acetone, A, with a quantum yield $^G\phi_{RXN}$. There are two decay paths available to ^{1}A:[22] intersystem crossing (ISC) to ^{3}A which has a measured quantum yield of 1.0 and a rate constant k_{ISC} of 4.0×10^8 s^{-1} [21] as well as fluorescence to A with a quantum yield, ϕ_F, of 0.0012.[21] For ^{3}A, which has a decay constant $^3k = 5 \times 10^3$ s^{-1},[19] the quantum yield for phosphorescence, ϕ_{PH}, is 0.02,[23] and the two nonradiative decay channels are dissociation to $CH_3CO\cdot$ and $CH_3\cdot$ and internal conversion (IC) to high vibrational levels of A.[22] At times long compared to the risetime of the signal, the chemiluminescence emission intensity is

$$I(t) = \phi_F DI_0 {}^1\phi_{RXN} k_{DI}[\exp(-k_{DI}t)] + \frac{\phi_{PH}{}^3k{}^3\phi_{RXN}{}^T k_{DI} DI_0}{k_{DI} - {}^3k}[\exp(-{}^3kt) - \exp(-k_{DI}t)] \quad (1)$$

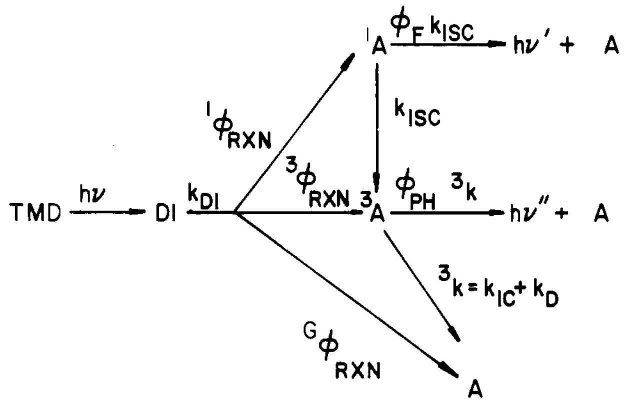

Figure 6. Generalized kinetic scheme for decomposition of TMD through a dark intermediate following electronic excitation.

where DI_0 is the concentration of DI at $t = 0$, and because the quantum yield for intersystem crossing is $\phi_{ISC} = 1$, the total yield of ^{3}A is $^3\phi_{RXN}{}^T = {}^3\phi_{RXN} + {}^1\phi_{RXN}$. The first term in eq 1 is the contribution from acetone fluorescence while the second term describes the acetone phosphorescence component. (Because we wish to describe the total emission, terms for both $h\nu'$ and $h\nu''$ are included (see Figure 6).) The two terms have rather different temporal behavior, with the first being a single exponential decay while the second rises (as k_{DI}) and subsequently decays (as ^3k), and their relative amplitudes determine whether the sum shows a net rise with rate constant k_{DI} or a net decay with k_{DI}. In either case, the slowest decay is always controlled by ^3k, and eq 1 is simply the sum of two exponentials, $I(t) = A_{DI} \exp(-k_{DI}t) + A_3 \exp(-{}^3kt)$. We can assess the possibility of a dark intermediate being present by making a qualitative prediction as to whether the k_{DI} term appears as a rise or a fall on the basis of our measured value of k_{DI} (and ^3k) and known acetone photophysics. As shown below, this predicts that the dark intermediate produces a rising exponential, contrary to our observations.

Collecting the coefficients of $\exp(-k_{DI}t)$ in eq 1, we write the amplitude of this term as

$$A_{DI} = \frac{DI_0 k_{DI}{}^3\phi_{RXN}{}^{T3}k\phi_{PH}}{k_{DI} - {}^3k}\left[\frac{\phi_F{}^1\phi_{RXN}(k_{DI} - {}^3k)}{\phi_{PH}({}^1\phi_{RXN} + {}^3\phi_{RXN}){}^3k} - 1\right] \quad (2)$$

Because a positive coefficient produces a falling exponential while a negative coefficient produces a rising one, we need only to evaluate the term in brackets to test the possibility of a nonradiating intermediate producing the observed fast decay. If we set $^1\phi_{RXN}/({}^1\phi_{RXN} + {}^3\phi_{RXN})$ to its maximum value of 1, use the known values of $\phi_F = 0.0012$[20] and $\phi_{PH} = 0.02$,[23] and use our experimental values for the fast decay, $k_{DI} = k_2 = 75$ ms^{-1} and $^3k = k_3 = 5.2$ ms^{-1} at 10 mtorr, the term in brackets is negative, in obvious conflict with the experimental results which show a decaying rather than rising contribution. The controlling aspects of this system are the known efficiencies of intersystem crossing in ^{1}A and of acetone phosphorescence compared to fluorescence. These require that k_{DI} exceed ^3k by substantially more than the ratio $\phi_{PH}/\phi_F \sim 17$ for the bracketed term to be a large positive quantity as the experiment demands. (The term in brackets is just the ratio of amplitudes of the fast and slow decay, A_{DI}/A_3, which is more than 20 in figure 1a.) *A dark intermediate having the observed lifetime of the fast decay is simply incompatible with acetone photophysics.* Any dark intermediate, such as the biradical, must have a much shorter lifetime than the species which we observe since the decay is the dominant feature in the measurement, and an additional *emitting* species must be present since the data are incompatible with emission from only the expected products, ^{1}A and ^{3}A.

Identifying the additional radiating molecule is more difficult than demonstrating its presence. The length of the measured

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lifetime eliminates ^{1}A as a possibility, and the prompt appearance of the emitter following electronic excitation at low pressures (see Figure 1a) rules out collisional production. Highly vibrationally excited ^{3}A, ^{3}A†, is also an unlikely candidate. Sufficient vibrational energy could shift the maximum in the emission to shorter wavelengths than the usual ^{3}A phosphorescence, but such a large shift, ~40 nm, which is independent of excitation energy seems improbable. In addition, the unimolecular decomposition of ^{3}A to $CH_3CO\cdot$ and $CH_3\cdot$ is an available loss mechanism which would be strongly energy dependent (contrary to the experimental results for k_2) and should yield a lifetime shorter than the 13 μs observed for the rapidly decaying component at 10 mtorr.[24] We also found no evidence of the fast decy in ^{3}A produced by excitation of acetone with 330-nm photons even though the energy content approaches the upper limit of that available to ^{3}A formed by decomposition of TMD excited to $v = 3$ of the CH stretch. These features along with the difficulty of rationalizing the relative amplitudes of the fast and slow decay in terms of ^{3}A† clearly show that the short-lived emitter is not acetone. An excimer of acetone, formed from the two parts of the decomposed TMD molecule, is consistent with our results, but the lack of data for comparison prevents any real test of this speculation. The short collisional lifetime of the emitter is certainly compatible with the absence of an observable excimer in solution.[25]

Our observation of an additional emitter in a single photon excitation experiment has consequences for the infrared multiphoton[13] and beam-gas measurements.[14] In their infrared multiphoton excitation study of TMD, Yahav and Haas[13] observe a component of the chemiluminescence signal which has a complicated pressure dependence, lasts a few microseconds after the laser pulse, and increases in duration with increasing signal intensities. As in our measurements, the spectrum during this time is neither that of ^{1}A nor that of ^{3}A, and they suggest it might be excimer emission or a mixture of acetone fluorescence and phosphorescence. A short extrapolation of our fast decay rate constant, k_2, to 70 mtorr (Figure 4), yields a 2.5-μs lifetime which is close to the value obtained by Yahav and Haas for their smallest signals at that pressure. They ascribe this component to additional decomposition which arises from collisional energy pooling between excited TMD molecules which individually lack the requisite decomposition energy. A slight variation in this scheme, in which the radiating molecule we observe is included as an energetic product, seems consistent with their results. Rapid infrared multiphoton pumping of the emitter (as well as TMD) to high levels where the decomposition is very fast produces the prompt signal which follows the laser pulse, and both the radiating molecule which we observe and collisional energy pooling give the slower signal. The distribution of excitation energies in TMD produced by its infrared multiphoton excitation and the subsequent multiphoton excitation of the products obscures the additional emitter which we find with single photon excitation. Similarly, Menzinger[14] analyzed the unresolved continuous emission produced by exciting TMD with a beam of translationally energetic Xe atoms as coming from ^{1}A and ^{3}A, in agreement with his available data. Perhaps including the additional radiating molecule which our experiments find in the reaction scheme would mitigate the requirement that a bimolecular reacton rate be 10 times the gas kinetic value in order to explain the quadratic pressure dependence of the emission intensity.

Laser excitation combined with time-resolved chemiluminescence detection reveals interesting aspects to the gas-phase kinetics of TMD which are not detectable in solution measurements. The observation of an emitting molecule in addition to excited singlet and triplet acetone and a measurement of its collisionless lifetime ($\tau \sim 50$ μs) as well as its collisional quenching efficiency (every other collision) are the principal results which should be considered in studies of TMD kinetics. Our approach is a sensitive probe of the chemiluminescence kinetics of dioxetanes which can be extended to include electronic and overtone vibration excitation at a variety of energies. Considering the sharp increase in the emission at 80 kcal mol^{-1} translational energy in the fast Xe beam excitation of TMD,[14] a measurement at larger electronic energy contents will be informative. For example, our data indicate that the relative contributions of the fast and slow decays change with excitation energy. Clearly, future experiments in which higher quality chemiluminescence spectra are extended to shorter wavelengths will help characterize and identify the additional emitting product indicated by our data.

Acknowledgment. We gratefully acknowledge support of this work by the Office of Basic Energy Sciences of the Department of Energy. Professors G. B. Schuster and W. E. Farneth provided helpful advice on the preparation and handling of TMD. We thank Professor R. S. Sheridan for an informative discussion and Professor J. C. Wright for generously loaning us the interference filters.

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