state is the most likely pathway.

(f) For the alkynes a similar series of pathways are feasible. All the rate constants fall in a narrow range, and oxygen heteroatom substituents do not result in significantly faster quenching rates. Indeed, one of the largest bimolecular quenching rate constants is found for diphenylacetylene, a quencher that can only realistically react by a diradical intermediate or by collisional deactivation of the triplet state.

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**Registry No.**  $Pt_2(pop)_4^{4-}$ , 80011-25-2;  $Pt_2(pcp)_4^{4-}$ , 114763-58-5; Pt<sub>2</sub>(pcp)<sub>4</sub><sup>3-</sup>, 114763-59-6; Pt<sub>2</sub>(pcp)<sub>4</sub><sup>5-</sup>, 114763-60-9; MeI, 74-88-4; EtI, 75-03-6; n-PrI, 107-08-4; (n-heptyl)I, 4282-40-0; i-PrI, 75-30-9; (CH2-Br)2, 106-93-4; PhCl, 108-90-7; PhBr, 108-86-1; PhI, 591-50-4; p-BrC<sub>6</sub>H<sub>4</sub>OH, 104-92-7; p-BrC<sub>6</sub>H<sub>4</sub>OMe, 104-92-7; 1-BrC<sub>6</sub>H<sub>4</sub>Bu-t-4, 3972-65-4; o-BrC<sub>6</sub>H<sub>4</sub>Me, 95-46-5; p-BrC<sub>6</sub>H<sub>4</sub>F, 460-00-4; p-BrC<sub>6</sub>H<sub>4</sub>CN, 623-00-7; p-BrC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, 586-78-7; p-ClC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, 100-00-5; o-ClC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, 88-73-3; C<sub>6</sub>F<sub>5</sub>Br, 344-04-7; C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH, 100-51-6; Ph<sub>2</sub>CHOH, 91-01-0; Ph<sub>3</sub>CH, 519-73-3; H<sub>3</sub>PO<sub>2</sub>, 6303-21-5; H<sub>3</sub>PO<sub>3</sub>, 13598-36-2; Et<sub>3</sub>SiH, 617-86-7; n-Bu<sub>3</sub>SnH, 688-73-3; MV<sup>2+</sup>, 4685-14-7; MeNO<sub>2</sub>, 4685-14-7; C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, 98-95-3; m-C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>, 99-65-0; NaCl, 7647-14-5; NaBr, 7647-15-6; NaI, 7681-82-5; isopropyl alcohol, 67-63-0; 1,4-naphthoquinone, 130-15-4; 1,2-naphthoquinone, 2066-93-5; anthraquinone-2,6-disulfonic acid, 84-50-4; ferrocene, 102-54-5; hydroquinone, 123-31-9; ascorbic acid, 50-81-7; 1-hexene, 592-41-6; 2-hexene, 592-43-8; trans-hexene-3, 13269-52-8; 1-heptene, 592-76-7; 1-octene, 111-66-0; cyclohexene, 110-83-8; cyclooctene, 931-88-4; cyclododecene, 1501-82-2; 1,5-cyclooctadiene, 111-78-4; 1,5-hexadiene, 592-42-7; trans-stilbene, 103-30-0; cis-stilbene, 645-49-8; fumaronitrile, 764-42-1; 3,4-dihydroxy-3-cyclobutene-1,2-dione, 2892-51-5; butadienol, 12542-32-4; trans, trans-1,4-diphenyl-1,3-butadiene, 538-81-8; 3-buten-2-one, 78-94-4; 1,3-cyclohexadiene, 592-57-4; 2,3-dimethyl-2-butene, 563-79-1; styrene, 100-42-5; 1,1-diphenylethylene, 530-48-3; ethyl vinyl ether, 109-92-2; bicyclo[2.2.1]hepta-2,5-diene, 121-46-0; norbornylene, 498-66-8; maleic acid, 110-16-7; allyl alcohol, 107-18-6; 1-hexyne, 693-02-7; butynediol, 11070-67-0; acetylenedicarboxylic acid, 142-45-0; C<sub>2</sub>(CMe<sub>2</sub>OH)<sub>2</sub>, 142-30-3; diphenylacetylene, 501-65-5; benzene, 71-43-2; toluene, 108-88-3; naphthalene, 91-20-3; anthracene, 120-12-7; phenanthrene, 85-01-8.

# High-Temperature Decomposition of Tetramethyldioxetane: Measurements of **Gas-Phase Chemiexcitation Yields**

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The yields of electronically excited acetone from high-temperature decomposition of gas-phase tetramethyldioxetane (TMD) are reported. High temperatures are achieved by using infrared-sensitized excitation of TMD. Emission studies are used to obtain the yield of excited singlet acetone,  $\Phi_{\rm S} = 0.017$  (±0.008). This value is approximately a factor of 2 higher than that reported in solution. A lower limit for the yield of triplet acetone is determined by using transient absorption studies,  $\Phi_T \ge 0.10$  (±0.03). This value is comparable to previous results in solution. The lifetime of triplet acetone observed in the present experiment is approximately 5 µs, almost 2 orders of magnitude shorter than the lifetime of thermalized triplet acetone at low pressures. The short lifetime is attributed to electronic quenching by the infrared-absorbing gas CH<sub>3</sub>F, with an estimated rate constant of  $5 \times 10^{-13} \text{ cm}^3/(\text{molecule s})$ .

### Introduction

The high yield of electronically excited products from the decomposition of tetramethyldioxetane (TMD) has stimulated extensive studies of this intriguing molecule. In addition to numerous studies in the gas phase<sup>1-10</sup> and in solution,<sup>11-20</sup> recent work has

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addressed the decomposition of solid-phase TMD as a possible source of a short-wavelength chemical laser.<sup>21</sup> These many studies have shown that decomposition of TMD results in the formation of two molecules of acetone, one of which may be electronically excited (reaction 1).

$$TMD \rightarrow A^* + A_0 \tag{1}$$

The chemiexcitation yields of singlet acetone, <sup>1</sup>A\*, and triplet acetone, <sup>3</sup>A\*, have previously been measured in solution at temperatures in the range 325-360 K.<sup>11</sup> The results indicate that 30-50% of the reactions lead to 3A\*, 0.04-0.08% of the reactions form  ${}^{1}A^{*}$ , and the remainder form only ground-state acetone, A<sub>0</sub>. The chemiexcitation yields have not been measured for decomposition of either solid-phase TMD or gaseous TMD at elevated temperatures (>500 K). This is unfortunate because these quantities are essential in assessing the possibility of a chemical

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Figure 1. Top: schematic diagram of the experimental arrangement. Bottom: schematic representation of the spatially averaged TMD concentration as a function of time during laser irradiation.

laser based on high-density TMD.<sup>21</sup> In the present study, we report quantitative chemiexcitation yields of  ${}^{1}A^{*}$  and  ${}^{3}A^{*}$  for the high-temperature decomposition of gas-phase TMD.

A previous study performed at moderate temperature (475 K) reported emission from infrared-sensitized excitation of TMD.<sup>8</sup> We have extended these studies to higher temperatures using the technique of laser-powered homogeneous pyrolysis (LPHP). The LPHP method not only results in very large temperature excursions but also allows a quantitative determination of the decomposition kinetics to be made. In the present study, we characterize the emission resulting from the high-temperature decomposition of gas-phase TMD. We report chemiexcitation yields, emission spectra, and photon yields for the decomposition at elevated temperatures.

Singlet-excited acetone is monitored directly by its fluorescence near 410 nm, and its fluorescence yield calibrated against laser-induced fluorescence of benzene. In previous studies,<sup>3,5</sup> triplet-excited acetone was observed through its phosphorescence near 460 nm. In the present investigation, no long-lived phosphorescence is detected. We measure the absolute density of  ${}^{3}A^{*}$ using transient absorption spectroscopy.

# **Experimental Section**

A detailed description of the LPHP technique may be found elsewhere,<sup>22</sup> and only a brief summary will be provided here. The LPHP flow system is indicated schematically in Figure 1, top. Infrared-absorbing gas mixtures (CH<sub>3</sub>F or 20% SF<sub>6</sub> in N<sub>2</sub>) are passed through a needle valve and over the TMD crystals held at constant temperature, giving a partial pressure of TMD of 0.3-1.0 Torr. The gas mixture then passes into a 17-cm diameter cylindrical reaction cell. Total pressures of 10-100 Torr are maintained in the reaction cell by using a second needle valve. The TMD crystals are synthesized by using a modified version of Kopecky's method.<sup>23</sup>

The gas mixture is irradiated at 0.25 Hz by using unfocussed light from a multimode TEA-CO<sub>2</sub> laser. The laser pulse duration is 1  $\mu$ s, and the fluence is varied between 0.2 and 1.2 J/cm<sup>2</sup>. Laser wavelengths of 10.6 and 9.5  $\mu$ m are used to vibrationally excite the infrared-absorbing gases SF<sub>6</sub> and CH<sub>3</sub>F, respectively. Collisional relaxation of the initially excited IR absorber (in 1-3  $\mu$ s) leads to rapid heating in the irradiated volume. A full discussion of the temperature and density profiles within the reaction cell as a function of time may be found elsewhere.<sup>22,24,25</sup>

Decomposition of TMD at elevated temperatures via reaction 1 is accompanied by blue chemiluminescence. As discussed below, the emission is due to  ${}^{1}A^{*}$  fluorescence. The emission is collected at right angles relative to the excitation beam, imaged onto the slit of a 0.25-m GCA/McPherson monochromator, and detected by using a 1P28 photomultiplier tube. The signal is averaged by using a Transiac transient digitizer controlled by a DEC LSI 11/23 microprocessor.

Dark intermediates of the decomposition of TMD ( ${}^{3}A^{*}$ ) are monitored by using absorption spectroscopy. The experimental arrangement for the measurement of transient absorption in our high-temperature LPHP cell is similar to that described above with several modifications. The infrared laser is aligned collinearly with a 40-W D<sub>2</sub> lamp or a 1000-W xenon lamp through the LPHP cell. A quartz window is used as a dielectric mirror to pass the UV light and reflect the IR radiation at 9.5  $\mu$ m. The Reststrahlen maximum for quartz occurs at 8.9  $\mu$ m,<sup>26</sup> and, therefore, a significant fraction of the incident IR light at 9.5  $\mu$ m is reflected. The transient absorption is measured by using a gated photomultiplier attached to the monochromator. Signals are collected and averaged as before.

For determination of the chemiexcitation yields for reaction 1, it is necessary to measure not only the  ${}^{1}A^{*}$  and  ${}^{3}A^{*}$  concentrations but also the amount of TMD that undergoes decomposition during each laser shot. Determination of this latter quantity is complicated by the fact that 20-100 laser shots are averaged to obtain better luminescence signal levels. A qualitative picture of the average TMD concentrations in the cell as it is sequentially irradiated with laser pulses is shown in Figure 1, bottom. Before laser irradiation, the TMD concentration is given by [TMD]<sub>0</sub>. During laser irradiation, the concentration decreases due to decomposition. This decrease is partially offset by replenishment of TMD from the incoming flow. After 5-20 laser shots, the TMD concentration reaches a steady-state value, [TMD]<sub>ss</sub>. At this point, decomposition by each laser shot is exactly replenished by the flow. In the present experiment, all measurements were made after steady state was achieved.

The chemiexcitation yields are obtained by determining the ratio of the concentration of excited (emitting) species to the number of TMD molecules that decompose on each laser shot at steady state. As shown below, under our experimental conditions, all of the TMD in the irradiated volume decomposes for each laser shot at steady state. The chemiexcitation yields are thus based on [TMD]<sub>ss</sub>. [TMD]<sub>ss</sub> is, in turn, measured by monitoring the time-averaged TMD absorption at 205 nm in situ during the decomposition. Plots of the absorption of TMD and of acetone at 205 nm as a function of pressure are linear. The UV-absorption cross sections obtained from the slopes of the lines are  $\sigma_{TMD} =$  $1.3 \times 10^{-19}$  cm<sup>2</sup> and  $\sigma_{acetone} = 9.8 \times 10^{-22}$  cm<sup>2</sup>. Measurement of the UV absorption at 205 nm thus allows the determination of

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Figure 2. Temporal profile of the 410-nm emission resulting from the high-temperature decomposition of TMD using SF<sub>6</sub> as the infrared absorbing gas (4 Torr of  $SF_6$ , 16 Torr of  $N_2$ , and 0.25 Torr of TMD).

the steady-state TMD concentration with little interference from acetone.

The fraction, F, of TMD molecules within the irradiated volume that undergo decomposition is given by  $2^{22}$  where  $V_{\rm T}$  and  $V_{\rm R}$  are

$$F = (([TMD]_0 / [TMD]_{ss}) - 1)(V_T / V_R)(\tau_1 / \tau_f)$$
(2)

the total and laser-irradiated volumes, respectively, and  $\tau_1$  and  $\tau_f$  are the time between laser shots and the flow lifetime of the gas in the cell, respectively. Typical values for these parameters are  $V_T = 1414 \text{ cm}^3$ ,  $V_R = 16 \text{ cm}^3$ ,  $\tau_1 = 4 \text{ s}$ ,  $\tau_f = 350 \text{ s}$ , and  $[\text{TMD}]_0/[\text{TMD}]_{\text{ss}} = 1.95$ . From 2, the fractional decomposition of TMD per shot is found to be unity over the temperature range studied.

One additional comment concerns the choice of path lengths of the LPHP cell for the various types of experiments. Most of the emission experiments were performed with a short-path-length cell (b = 1 cm) to minimize thermal gradients due to significant power absorption by the gas mixture. An exception is the experiment using SF<sub>6</sub> as the IR absorber, in which the average temperature of the gas was determined by using the measured IR-power absorption and the known heat capacity of the gas mixture (b = 14 cm). For the transient absorption measurements, a compromise between the absorption path length for monitoring the <sup>3</sup>A\* density by the white-light probe and the optical density of the gas mixture in the IR was achieved (b = 8 cm).

Product analysis (GC/MS) carried out after laser irradiation indicates that acetone is the only (>99%) product of the hightemperature decomposition of TMD.

#### **Results and Discussion**

Description of the Emission from TMD Decomposition. The decomposition of TMD at elevated temperatures is accompanied by blue luminescence. A typical emission profile is indicated in Figure 2, where an average of 100 shots is shown for a gas mixture of 20% SF<sub>6</sub> in  $N_2$  at a total pressure of 20 Torr. The emission rises fairly sharply after laser irradiation and then decays almost exponentially at a rate of  $1 \times 10^6$  s<sup>-1</sup>.

The temporal profile of the blue emission from TMD decomposition is a strong function of total gas pressure and incident laser fluence, variables that influence the gas temperature. Increases in either the infrared absorbing gas pressure or the laser fluence lead to increases in the reaction temperature.<sup>22</sup> The variation in emission profile with laser fluence is shown in Figure 3. It can be seen that both the rise and decay time of the emission are shorter at higher temperatures. Note, however, the areas under the curves in Figure 3 are the same. Thus, the same total amount of emission is occurring at medium and very high temperatures, even though the time scale for the emission is changing dramatically.

There are several ways of estimating the temperature excursions achieved in the present study. One method involves calculating an average temperature based on the laser power absorbed and



Figure 3. Variation in the temporal profile of the 410-nm emission with incident laser fluence using CH<sub>3</sub>F as the infrared absorbing gas. Gas pressures of 7.25 Torr of CH<sub>3</sub>F and 0.75 Torr of TMD were used in all three cases.

the heat capacity of the gas mixture, assuming fast and complete thermalization of the gas mixture. For example, the emission profile shown in Figure 2 was obtained by using a laser fluence of 1.0 J/cm<sup>2</sup>, a measured laser-power absorption of  $0.47 \text{ J/cm}^3$ , and a path length of 14 cm. The heat capacity of 20% SF<sub>6</sub> in  $N_2$  is 13 cal/(mol K) at 800 K.<sup>27</sup> With a total pressure of 20 Torr, these values result in a calculated temperature jump of 750 K

In previous LPHP work, the temperature of the hot irradiated region was determined by measuring the extent of decomposition of a temperature standard whose activation parameters were well-known.22 We obtain a crude estimate of the peak temperature under one set of experimental conditions using dicyclopentadiene (DCP) as a temperature standard. DCP decomposes to form two molecules of cyclopentadiene ( $A = 5.3 \times 10^{13} \text{ s}^{-1}$ ,  $E_a = 38.5$ kcal/mol).28 This reaction is followed by monitoring the real-time absorption of cyclopentadiene at 250 nm,<sup>29</sup> where DCP is transparent. With approximately 18 Torr of CH<sub>3</sub>F and 2 Torr of DCP, a peak temperature of 920 K  $(\pm 100 \text{ K})$  is determined. Unfortunately, we were unable to estimate temperatures significantly lower than this due to the low extent of decomposition, hence low transient absorption, of DCP on the microsecond time scale. Furthermore, other temperature standards with decomposition parameters closer to that of TMD were not readily available.

A final method of estimating the temperature utilizes TMD itself as the temperature standard. As discussed below, the observed emission profiles reflect the TMD density during decomposition. With the known activation parameters for TMD decomposition ( $A = 4 \times 10^{13} \text{ s}^{-1}$ ,  $E_a = 27.6 \text{ kcal/mol}$ ),<sup>12</sup> estimates of the temperature can be obtained from the emission decay times. For example, after correction of the activation parameters to account for falloff under our low-pressure conditions, the emission profiles in Figure 3 correspond to calculated temperatures in the range 750 (0.2 J/cm<sup>2</sup>) to 870 K (0.7 J/cm<sup>2</sup>).

Although all three methods indicate that large temperature excursions are occurring in the present work, they differ somewhat in their detailed evaluation of the temperature and in precisely how it varies with incident laser fluence. Additional studies are required to obtain this information. However, for the present study, it is sufficient to realize that quite high temperatures, as high as  $950 \pm 100$  K, are achieved.

The emission observed in the present study is much shorter lived (microsecond time scale) than the emission observed in previous sensitization studies at 475 K (millisecond time scale).<sup>8</sup> Due to

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Figure 4. Luminescence spectra of the emission resulting from the decomposition of TMD for high-incident laser fluence  $(0.7 \text{ J/cm}^2)$ ,  $\Box$ , and low-incident laser fluence  $(0.2 \text{ J/cm}^2)$ , O. All data were taken by using CH<sub>3</sub>F as the infrared absorbing gas with pressures and decay curves as in Figure 3. Acetone fluorescence (---) and phosphorescence (---) spectra are shown for comparison.

the higher temperature achieved in the present study, the rate of decomposition (reaction 1) is expected to be much faster than in previous work at 475 K.8 For example, using the known Arrhenius parameters, <sup>12</sup> we calculate rate constants of 9.7 and  $1.3 \times 10^6$  $s^{-1}$  at 475 and 800 K, respectively. In the present experiment, the rise and fall of the fluorescence is observed on the microsecond time scale, comparable to the calculated unimolecular decomposition rates. As will be discussed below, this argues that the observed emission is from a short-lived radiator.

The high-temperature luminescence spectrum obtained in the present experiment is indicated in Figure 4. This point-by-point spectrum was obtained by integrating the areas under the emission profiles as a function of detection wavelength. Also shown in this figure are the spectra of acetone fluorescence and phosphorescence normalized to the same peak intensity.<sup>30-32</sup> It can be seen that the present emission is due to acetone fluorescence. The effective lifetime of acetone fluorescence has been shown previously to be 2 ns.<sup>33,34</sup> Thus, the observed emission provides an instantaneous profile of the TMD density during the decomposition reaction. No acetone phosphorescence was observed in the present experiment (as concluded from the spectrum and the fast time scale of the observed emission).

Determination of the High-Temperature Photon Yield and Singlet Yield. The photon yield,  $\Phi$ , is defined as the number of photons emitted per decomposition event. The photon yield was measured by comparing the observed emission from reaction 1 with emission from benzene, whose fluorescence quantum yield is well-known. Benzene excited at 252 nm has been shown previously to have a fluorescence quantum yield  $\phi = 0.22$  for pressures in the range 0.5-20 Torr.<sup>35,36</sup> The excitation and detection geometries used to measure benzene fluorescence were identical with those described previously for fluorescence from TMD decomposition. The benzene pressure was varied between 0.3 and 1.0 Torr. Excitation at 248 nm was achieved by using a KrF eximer laser. The point-by-point spectrum for benzene is shown in Figure 5. The photon yield for reaction 1 was obtained by comparing the two emission signals after correcting them for the number of molecules excited in each case by using eq 3, where

 $\Phi = 0.22(Fl(TMD) / [TMD^*])([C_6H_6^*] / Fl(benzene))$ (3)

Fl is the fluorescence signal, [TMD\*] is the number of TMD molecules that undergo dissociation per shot, and  $[C_6H_6^*]$  is the



Figure 5. Determination of the photon yield for reaction 1. Emission spectrum from the decomposition of TMD, O, compared to the benzene fluorescence spectrum,  $\diamond$ , at 0.3 Torr, shown on the same intensity scale. The TMD curve was obtained by using an incident laser fluence of 0.7  $J/cm^2$  and  $CH_3F$  as the sensitizing agent.



Figure 6. Transient absorption signal at 300 nm following infrared excitation of a gas mixture consisting of 1.0 Torr of TMD and 11.5 Torr of CH<sub>3</sub>F. The absorption was measured by using (a) a high-pressure xenon lamp (1000 W) and (b) a deuterium lamp (40 W). The relative transmission scale corresponds to part a. The transmission signals before and after the peak transient signal are given by  $I_1$  and  $I_0$ , respectively.

number of excited benzene molecules per shot. The fluorescence signals were corrected for the different detection sensitivities at the two fluorescence wavelength maxima.

It was previously shown that all of the TMD molecules within the irradiated volume undergo decomposition at steady state, yielding  $[TMD^*] = [TMD]_{ss} = 1.8 \times 10^{16}$  molecules/cm<sup>3</sup> for the data in Figure 5. The number of benzene molecules excited per shot can be calculated by using the absorption cross section for benzene at 248 nm,  $\epsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}$ ,<sup>37</sup> and the incident laser fluence. Comparing the emission curves for TMD and benzene by using eq 3 results in a calculated photon yield of  $\Phi = 3.4 \times$  $10^{-5} \pm 1.5 \times 10^{-5}$  with use of the benzene fluorescence quantum yield of 0.22 determined at 252 nm. The largest source of error in this determination is the steady-state concentration of TMD, measured with an estimated error of  $\pm 25\%$ . Note that over the temperature range studied, the photon yield is independent of temperature.

The decomposition of TMD in solution has previously been shown to result in a yield of 0.0004-0.008 for  ${}^{1}A^{*,11}$  The fluorescence quantum yield for acetone is reported to be 0.002.33,34 This predicts a maximum theoretical photon yield of  $0.008 \times 0.002$ =  $1.6 \times 10^{-5}$  for <sup>1</sup>A\*, which is close to, although smaller than, our measured value. Conversely, our measured photon yield predicts a singlet yield of  $0.017 \pm 0.008$ , about 2 times larger than the yield observed in solution.

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Figure 7. Absorption spectrum of the peak transient signal due to triplet excited acetone using experimental conditions as in Figure 6. Also shown are previous spectra of triplet acetone in solution. The present spectrum and those of Porter et al. $^{38,39}$  have been normalized to the absolute cross sections of Kasama et al.  $^{\rm 40}$ 

Determination of the Triplet Yield Using Transient Absorption. Because <sup>3</sup>A\* does not measurably emit under our experimental conditions, it was not possible to determine the triplet yield from emission studies. Triplet excited acetone was therefore studied by using absorption spectroscopy. A transient absorption signal at 300 nm obtained during the decomposition of TMD is shown in Figure 6A. This figure displays the xenon lamp intensity through the LPHP cell as a function of time before and after the decomposition and displays a maximum of about 5% attenuation of the monitoring light beam at 300 nm. Any species created that absorbs light at 300 nm causes the lamp intensity to decrease. The observed signal in Figure 6a suggests a transient species is formed rapidly after infrared irradiation and decays in approximately 5  $\mu$ s. The much larger signal decrease occurring at 95  $\mu$ s corresponds to gating off the photomultiplier tube, thus providing a zero level enabling quantitative transmission measurements. Part B in this figure is a similar experiment shown on an expanded scale obtained by using the  $D_2$  lamp.

The spectrum of the observed transient absorption signal is indicated in Figure 7. The general shape and position of the observed signal are similar to those reported previously for triplet acetone in solution<sup>38-40</sup> (also shown in Figure 7). We have therefore assigned the observed transient as <sup>3</sup>A\*. Note that there is a large variation in the shapes of the reported <sup>3</sup>A\* spectra in the 300-350-nm region. The origin of this discrepancy is not clear but may be related to secondary photolysis of <sup>3</sup>A\*. The present values agree with the most recent ones obtained in solution by Kasama et al.40

Solution-phase spectra of triplet acetone have not been obtained at wavelengths below 300 nm due to interference from groundstate acetone absorption. We also have a small interference for  $\lambda$  < 300 nm due to acetone that is formed via reaction 1. The data shown in Figure 7 were obtained by assuming that at the absorption peak, the TMD had completely decomposed, and thus any absorption signal was due to the sum of  ${}^{3}A^{*}$  and ground-state A<sub>0</sub>. The contribution from ground-state acetone was subtracted out by using the known absorption coefficients for acetone<sup>41</sup> and the concentration of acetone expected from total decomposition of TMD within the irradiated volume (as discussed below). The resulting spectrum is that shown in Figure 7.

An important point to notice in Figure 6b is the base-line shift before and after laser excitation. More UV light is passing through the cell after irradiation than before. This shift is due to decomposition of TMD ( $\epsilon = 25 \text{ M}^{-1} \text{ cm}^{-1} \text{ at } 300 \text{ nm}^{23}$ ) to form ground-state acetone ( $\epsilon = 7.7 \text{ M}^{-1} \text{ cm}^{-1}$  at 300 nm<sup>41</sup>). Thus, the measured base-line shift,  $-\log (I_1/I_0)$  (Figure 6), is due to the difference between absorption by TMD (before laser irradiation) and by ground-state acetone (well after laser irradiation). To a first approximation, the final concentration of acetone is simply twice the steady-state concentration of TMD. However, the actual acetone concentration measured 50  $\mu$ s after laser excitation is much lower due to shock-wave expansion of the irradiated gas mixture.<sup>25</sup> It can be shown<sup>25</sup> that for a peak temperature of 950 K, the gas density in the irradiated region decreases by a factor of 2.7 for reaction times longer than 30  $\mu$ s. Thus, the acetone concentration at 50  $\mu$ s can be estimated as (2/2.7)[TMD]<sub>ss</sub>. The base-line shift can therefore be expressed as in 4, where b is the

$$-\log (I_1/I_0) = [\epsilon_{\text{TMD}} - (2/2.7)\epsilon_{\text{acetone}}]b[\text{TMD}]_{\text{ss}} \quad (4)$$

UV absorption path length. With use of this equation and known values for  $\epsilon_{TMD}$  and  $\epsilon_{acetone}$ , the base-line shift gives the steady-state concentrations of TMD during the decomposition. The steadystate concentration of TMD determined in this way agrees quantitatively to within 30% with that determined from UV absorption at 205 nm discussed above.

Triplet acetone in solution has a fairly strong absorption at 300 nm with  $\epsilon = 600 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>40</sup> With use of this value and the absolute absorption at the peak of the transient signal, the peak concentration of <sup>3</sup>A\* during TMD decomposition can be determined. Knowledge of both [TMD]<sub>ss</sub> and the peak concentration of <sup>3</sup>A\* allows the chemiexcitation yield for <sup>3</sup>A\* from reaction 1 to be calculated.

A lower limit to the yield of  ${}^{3}A^{*}$  formation is given by eq 5

$$\Phi_{\rm T} \ge [{}^{3}{\rm A}^{*}]_{\rm peak} / [{\rm TMD}]_{\rm ss}$$
 (5)

by using the fact that all of the TMD in the irradiated volume undergoes dissociation. The data in Figure 7 for wavelengths between 300 and 320 nm result in a lower limit for the triplet yield of  $\Phi_T \ge 0.10 \ (\pm 0.03)$ . As was the case in the <sup>1</sup>A\* yield, the largest source of uncertainty in the <sup>3</sup>A\* yield was in the determination of [TMD]<sub>ss</sub>. Over the range of UV wavelengths used, the measured chemiexcitation yield for <sup>3</sup>A\* was independent of wavelength. Equation 5 results in a lower limit to the chemiexcitation yield because only the peak concentration is measured, not the total production of <sup>3</sup>A\* integrated over time. Furthermore, if any  ${}^{3}A^{*}$  has left the irradiated region in the 10  $\mu$ s before the peak signal (due to shock-wave expansion), then the true chemiexcitation yield could be up to 2.7 times higher than the value reported here. The measured lower limit to the chemiexcitation yield is comparable to the triplet yield reported for TMD decomposition in solution (0.3-0.5).<sup>11</sup> The lifetime of the transient signal and the calculated triplet yield were independent of TMD pressure over the range studied,  $[TMD]_{ss} = 0.35-0.70$  Torr.

The temporal profile of the transient absorption signal indicates that the <sup>3</sup>A\* population is relatively short lived. The exact temporal profiles observed depend on the temperature of the laserirradiated gases. Higher temperatures result in slightly faster transient rise and decay times. Exponential fits of the absorption decay data at a total pressure of 12.5 Torr (in essentially pure CH<sub>3</sub>F) yield an average lifetime for  ${}^{3}A^{*}$  of  $5 \oplus 3 \mu s$ . This is much shorter than the lifetime of gas-phase vibrationally relaxed triplet acetone, 200  $\mu$ s, measured in the milliTorr and Torr pressure range.<sup>42,43</sup> Note, however, that this time scale is similar to that observed for  ${}^{3}A^{*}$  in solution (values ranging from 2-50  $\mu$ s).<sup>38-40,44</sup>

One possible explanation of the shorter lifetime of <sup>3</sup>A\* observed in our high-temperature experiment is that further decomposition of hot  ${}^{3}A^{*}$  is occurring. This possibility, however, can be ruled out by the product analysis carried out after laser irradiation, which indicates that acetone is the only product formed in the decomposition. Another possible reason for the shortened lifetime

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of TMD is electronic quenching by the CH<sub>3</sub>F buffer gas. The data in Figure 6 were obtained by using 11.5 Torr of CH<sub>3</sub>F. Thus, if quenching is the mechanism for depletion of  ${}^{3}A^{*}$  population, the quenching rate constant is approximately  $5 \times 10^{-13}$  cm<sup>3</sup>/ (molecule s). This value can be compared to previously measured acetone triplet quenching rates in solution and in the gas phase. Rate constants in the range  $10^{-16}$ - $10^{-12}$  cm<sup>3</sup>/(molecule s) have been measured for a variety of quenchers in solution.<sup>38-40</sup> In the gas phase, O<sub>2</sub> has been shown to quench  ${}^{3}A^{*}$  with a rate constant of 7.5 × 10<sup>-13</sup> cm<sup>3</sup>/(molecule s).<sup>45</sup> Further tests of the quenching postulate under our experimental conditions are difficult because variations in the CH<sub>3</sub>F pressure cause variations in the temperature of the reacting system. We have been unable to perform absorption studies using  $SF_6$  as the heating gas due to the technical problem of low reflectivity of quartz at 10.6  $\mu$ m. Further studies

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of electronic quenching of directly excited gas-phase acetone would prove very useful.

#### Conclusion

The high-temperature decomposition of gas-phase TMD has been studied by using LPHP to obtain quantitative values for the chemiexcitation yields. The observed emission is due entirely to <sup>1</sup>A\*, whose yield is measured to be  $\Phi_s = 0.017 \pm 0.008$ . This value is somewhat higher than that observed at room temperature in solution. A lower limit to the triplet yield was found to be  $\Phi_{T}$  $\geq 0.10 \pm 0.03$ . This yield is comparable to that found previously in solution. The main difference observed in the present study is the very short lifetime of  ${}^{3}A^{*}$  under our experimental conditions. This is postulated to be due to electronic quenching by CH<sub>3</sub>F with an estimated rate constant of  $5 \times 10^{-13}$  cm<sup>3</sup>/(molecule s).

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# Sources of Excited Cyclohexane in the Radiolysis of Cyclohexane<sup>1</sup>

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Streak camera measurements of the relative yield of the excited state of cyclohexane (CH\*) as a function of electron scavenger concentration (perfluoro-n-hexane, CO<sub>2</sub>, and N<sub>2</sub>O) strongly indicate that less than 10% of the CH\* is formed by direct excitation. The effects of the scavenging of geminate electrons on the yield of CH\*, in terms of the formulation  $f_s = (\alpha[S])^n / (1 + \{\alpha[S]\}^n)$ , where  $f_s$  is the fraction of geminate electrons scavenged, [S] is the scavenger concentration, and  $\alpha$  and n are constants (parameters), can be described as follows: for perfluoro-*n*-hexane, n = 1 and  $\alpha = 35$  M<sup>-1</sup>; for CO<sub>2</sub>, n = 0.6 and  $\alpha = 50$  M<sup>-1</sup>; for N<sub>2</sub>O, n = 0.6 and  $\alpha = 40$  M<sup>-1</sup>. The effects of static quenching of CH\* by the electron scavenger are taken into account in the analysis and are estimated from the values measured for the quenching rate constants. We obtain quenching rate constants, corrected for the effects of time-dependent rates,  $2.4 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> for N<sub>2</sub>O and CO<sub>2</sub> (±20% estimated uncertainty) and  $0.71 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for perfluoro-*n*-hexane (±15% estimated uncertainty).

# Introduction

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When liquid hydrocarbons are subjected to ionizing radiation, excited states can be formed instantly by direct excitation and almost instantly (in ca. 100 ps) by geminate ion recombination. The overall efficiency of excited-state formation in cyclohexane, which has been a frequently studied liquid in this respect, can be stated in terms of the measured G value of  $1.45 \pm 0.15$  molecules per 100 eV absorbed<sup>2</sup> by the solution, or in other words, about one excited state for every three ionizations.

Experiments have shown that the excited state observed via its emission in the 200-nm region is formed rapidly (in less than 100 ps), but limitations on time resolution and interference from Cerenkov light have prevented the direct determination of the fractions of this excited state formed by direct excitation and recombination. Thus, the origin of the excited state has been determined by inhibiting the ion recombination reaction with additives which react with the electron, and thus determining the total yield of fluorescence as a function of electron scavenger concentration. However, an electron scavenger can affect the fluorescence by mechanisms other than electron capture; i.e., the fluorescence yield can be decreased by both static and dynamic quenching of the excited states by the electron scavenger. Since many parameters neeeded to determine the role of the concentration of an electron scavenger are not well-known, the interpretation of these measurements is fraught with difficulties. In fact, recent experimental results have led to opposite conclusions concerning the fraction of these excited states which are produced

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We have developed a streak camera technique to measure the emission induced by 30-ps pulses of electrons and have shown the importance of fast time resolution in determining the "initial yields" and rate constants of very rapid processes. The role of interfering Cerenkov radiation is difficult to determine if the time resolution is not about a factor of 10 faster than needed to determine the reaction rates. With our present equipment, it is possible to determine both the "initial yield" and the decay of the excited state. We can measure the rate of excited-state quenching and from those data estimate the reaction cross section for the quenching reaction. Using this cross section, we can also estimate the static (or Perrin) quenching volume. Thus, such experiments can determine all the parameters necessary to separate the important processes which lead to a decrease in the initial yield of excited states.

#### **Experimental Section**

The cyclohexane and isooctane (Burdick and Jackson distilled in glass grade) were purified by passage through columns of silica gel (Aldrich, grade 12, 28-200 mesh) which had been heated in a vacuum oven at 290 °C overnight. The absorbance at 206 nm was about 0.05 per cm for the purified deaerated solvents.

by ion recombination vs the fraction produced by direct excitation of the solvent.3-5

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