Communications to the Editor

Infrared Laser Multiphoton Dissociation of Tetramethyldioxetane: Direct Observation of Triplet Acetone

Sir:

The focused radiation of a high power infrared laser is now frequently used to initiate chemical reactions in the gas phase.[1] We recently used this technique to study the unimolecular dissociation of tetramethyldioxetane (TMD), utilizing the 10.2-μm line of a TEA CO_2 laser.[2] The thermal dissociation of dioxetane[3] has been of considerable interest for some time now, as it provides a means for "photochemistry without light". We have shown[2] that high power laser excitation leads also to production of electronically excited states. Furthermore, the resulting emission, peaking at 420 nm, is identical with that obtained by heating TMD in oxygen-free fluid solutions.

In a related experiment, Farneth et al. used a CO_2 laser to initiate TMD decomposition by energy transfer from CH_3F.[4] The spectrum observed was similar to that obtained under thermal conditions. In distinction from our experiment, the indirect excitation of TMD obviously involves collisions. Also, the pressure used was more than an order of magnitude greater than in our experiments. Thus, the observation of unimolecular decomposition by the laser[1] is essentially precluded.

In this communication we report the first direct observation of pure triplet acetone emission resulting from TMD dissociation in the gas phase. We also show that the reaction is, at least partly, unimolecular, and that the 420 emission, contrary to previous assignments,[5] cannot be due to triplet acetone only. Finally, we point out possible mechanisms for triplet formation, and correlate our low pressure gas phase results with those obtained in liquid solutions.

The experimental set-up is fully described elsewhere.[2,6] Two improvements over the previous set-up, leading to a substantial reduction in the ambiguity of our interpretation, should be mentioned. First, the time resolution was increased to ~5 ns by using a mode locked laser. Second, the sample in the cell was replaced after each shot, thus minimizing complications due to accumulation of product molecules. TMD pressure was ~0.1 Torr in all the experiments, with no buffer gas added.

The output of the mode locked laser consists of a train of ~3-ns-wide pulses, as shown in Figure 1. The same figure shows the chemiluminescence of TMD initiated by the laser, which is seen to be similarly modulated. A more detailed discussion of the temporal behavior of the chemiluminescence is beyond the scope of this communication and will be given elsewhere.[6] For now it suffices to say that Figure 1 clearly demonstrates the unimolecular character of the phenomenon (at 0.1 Torr a molecule suffers ~1/200 of a collision in 5 ns).

Figure 2 shows the temporal behavior of the chemiluminescence on longer time scales. As discussed in ref 2, the emission intensity follows roughly the laser profile (also shown in Figure 2), although its decay is somewhat slower than that of the laser pulse. Furthermore (see Figure 2b), the oscilloscope trace does not quite return to the baseline even after 20 μs, long after the laser pulse (see Figure 2d) is terminated. This phenomenon was noticed before,[2] but could be explained by energy transfer to acetone produced by previous shots. As we are now using a fresh sample for each shot, it can be safely ascribed to the products of one single laser pulse. Figure 2c shows this
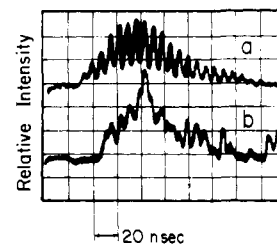

Figure 1. (a) Oscilloscope trace of mode locked laser intensity. (b) Chemiluminescence intensity resulting from same laser pulse. TMD pressure, 0.1 Torr; time scale, 20 ns/division.
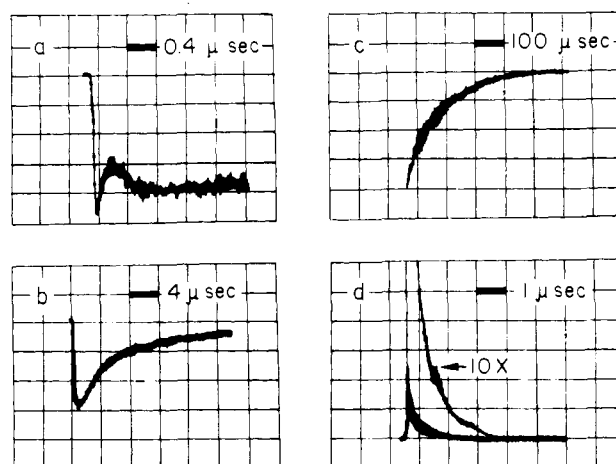

Figure 2. TMD chemiluminescence initiated by the IR laser: (a) 0.4 μs/division; (b) 4 μs/division; (c) 100 μs/division; (d) laser pulse shape at 1 μs/division.

"tail" on a longer time scale and bigger amplification. This part of the emission is seen to decay exponentially, with a (1/e) lifetime of 130 μs, very close to the reported lifetime[7] of triplet acetone in the vapor phase.

Figure 3, showing the spectral distribution of the emission, further supports the assignment of the "tail" to triplet acetone emission. Two distinct spectra emerge, depending on the time delay with respect to the laser pulse. The one peaking at 420 nm attains maximum intensity simultaneously with the laser pulse. The other one, peaking at 460 nm, is obtained 140 μs after the laser pulse. This latter spectrum is seen to closely agree with the reported triplet acetone spectrum.[8,9] The 420-nm emission is found to have a very short lifetime—it seems to follow closely the chemical reaction down to the nanosecond time scale (Figure 1). The possibility that it is due to singlet acetone fluorescence was discussed by us,[2] as this fluorescence is known to have a maximum at 405 nm.[10,11] This proposition was now further checked by measuring optically excited acetone fluorescence with the same set-up (monochromator plus photomultiplier) used in the chemiluminescence work. The light source was a nitrogen laser (10-ns pulse width) and the spectrum was measured only for light coincident with the laser pulse (i.e., fluorescence only). The spectrum of acetone vapor (with a little oxygen added[11]) was found to peak at 410 nm, distinctly to the blue of the infrared laser produced chemiluminescence.

The observation of pure triplet acetone phosphorescence (identified by its spectrum and by the decay time) is the first
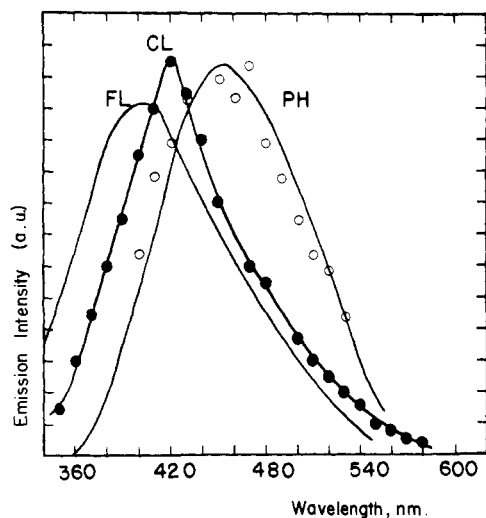
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Figure 3. Emission spectra of TMD dissociated by the laser: ● coincident with the laser; ○ 140 μs after the laser pulse. The left-hand curve is acetone fluorescence; the right-hand curve is acetone phosphorescence (from ref 8).

of its kind in TMD thermolysis. Previous workers,[5,12,13] detected the triplet mostly by indirect methods. The observed emission spectrum, even in oxygen free solutions, was always shifted to the blue relative to genuine triplet phosphorescence. The high time resolution afforded by the pulsed infrared laser technique is of crucial importance in our work, and allowed us to distinguish between the 420-nm emission, dominant at short time intervals, and the weaker 460-nm emission, that is fully developed only after $\sim 10^{-4}$ s.

We can thus conclude that the 420-nm emission cannot be due to either acetone phosphorescence or to acetone fluorescence. One possibility is that it is a mixture of the two.[14] Since on a 10^{-8}–10^{-7} time scale, all singlet states formed emit radiation instantaneously, whereas only a small fraction of triplet molecules have a chance to emit, this interpretation implies a strong preference for triplet production. The shift from 410 to 420 nm implies that the triplet accounts for $\sim 20\%$ of the total light yield. In order to produce that much light in a short time internal (say 10^{-7} s) initial triplet acetone concentration should be at least 10^3 times that of the excited singlet. Indeed, triplet acetone formation is reported to be dominant in TMD thermal decomposition.[12] The quantitative aspects of our observations obviously require further investigation.

Another possibility that was previously suggested by us[2] is that the 420-nm emission is due to a third, different species. The involvement of an intermediate chemical species (leading to triplet formation) in dioxetane thermolysis has often been indicated in the literature.[15] The nature of this species is far from being clarified, and in particular it may not be emissive. We tentatively proposed acetone excimer as a candidate,[2] but this assignment is rather dubious as this species has not been observed inspite of considerable effort. We are now using energy transfer methods in an attempt to further elucidate this point.

The mechanism of TMD decomposition by direct absorption of a large number of infrared photons appears to be complex, and a full discussion is beyond the scope of this communication. Figures 1 and 2 indicate that both uni- and bimolecular processes are involved. The ambiguity concerning the identity of the 420-nm emission precludes detailed mechanistic interpretation at this stage. However, the fact that it appears within 20 ns of laser pulse onset, and that it partially follows laser intensity modulations to ~ 5 ns, strongly suggests the involvement of a unimolecular process. In fact, many multiphoton dissociation reactions are believed to be dominated by uni-

molecular decomposition,[1] so that TMD would be no exception in this respect. As Figure 2 clearly shows, the 420-nm emission persists a few microseconds after laser pulse termination. The source of this emission must be collisional activation and the fact that the spectrum of the product of this bimolecular process is indistinguishable from that of the unimolecularly formed species may help in resolving the mechanism.

In conclusion, we have shown that the high sensitivity and excellent time resolution provided by the infrared laser dissociation method make it a powerful tool for mechanistic studies of reactions of electronically ground state molecules. In view of these properties, this method will probably be utilized in the elucidation of many other complex organic reactions.

References and Notes

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**Synthesis of *P*-Mesityldiphenylmethylenephosphine:
A Stable Compound with a Localized P=C Bond**

Sir:

It is well known that second and higher row elements are in general reluctant to form multiple bonds in which they are involved in a pπ-hybridized state.[1] Thus, simple compounds containing multiple phosphorus–carbon bonds, such as methylidynephosphine (HC≡P)[2] and methylenephosphine (H$_2$C=PH),[3] are not stable at room temperature.

Three approaches have been applied to stabilize double bonds involving phosphorus in the pπ-hybridized, two-coordinate state. The first one, delocalization, involves thermodynamic stabilization and has been particularly successful as exemplified by the phosphamethinecyanines[4] and by phosphabenzene and its derivatives.[5] The second one involves generation of positive charge on phosphorus to give contracted 3p orbitals which can overlap with 2p orbitals more effectively. Besides being an additional factor in the aforementioned phosphamethinecyanines,[4] this effect is clearly demonstrated in the amidophosphinium cations;[6] the stabilization thus achieved is also thermodynamic in nature. The third approach, kinetic stabilization of more or less isolated double bonds by steric hindrance, has so far been limited to a few cases of P=N[7] and heterosubstituted P=C[8] bonds. We wish to report the synthesis of *P*-mesityldiphenylmethylenephosphine (**1a**), the first thermally stable compound with a localized, all-car-