of cobalt hydride and readdition in the opposite sense, or by some equivalent interchange of cobalt and γ-hydrogen. The final position of cobalt would be attachment to the γ-carbon resulting in deuterium incorporation at that position, following hydrolysis. This more complex scheme cannot be ruled out in the absence of a carbon labeling experiment (synthetic efforts directed toward that end are in progress). However, the absence of any detectable amount of deuterium attached to the β-carbon, the potential complexity of the elimination–addition sequence and the precedent provided by the enzyme catalyzed rearrangement reactions (eq 1 and 2) have led us to a preference for acrylate as the migratory group, as suggested in the body of the text.

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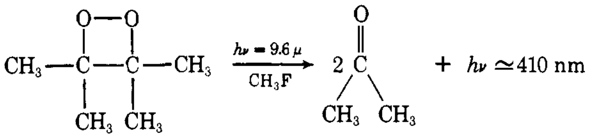
Time Resolved Infrared Laser Photochemistry and Spectroscopy: the Methyl Fluoride Sensitized Decomposition of Tetramethyl-1,2-dioxetane. An Example of Infrared Laser Induced Electronic Excitation

Sir:

The enhancement of chemical reactivity by infrared light absorption has been demonstrated in a variety of systems.[1] Efforts to date have fallen characteristically into one of two domains: (1) bimolecular reactions involving selectively excited small molecules (two, three atoms) in which the goal was to obtain detailed information on the dynamic course of the reaction,[2] (2) bulk reaction studies in which product identities and yields have been used to demonstrate the potential of IR laser excitation for production of unusual, or at least enhanced, chemical reactivity.[3] The competition between collisional energy transfer processes and chemical reaction, which plays a crucial role in determining the mechanism of a laser initiated chemical reaction, can be probed using pulsed infrared excitation followed by time resolved detection of the reaction and energy transfer coordinates. We report here initial studies on a system that is capable of yielding this type of information, the pulsed CO_2 laser-enhanced decomposition of gas phase tetramethyl-1,2-dioxetane (**1**) in a methyl fluoride bath. Methyl fluoride is a "sensitizer" for the CO_2 laser induced decomposition of tetramethyl-1,2-dioxetane (**1**) (eq 1). Some unique features of this system are: (1) the observed infrared photochemistry is extremely clean, acetone being formed quantitatively; (2) the IR laser induced decomposition of **1** is accompanied by the emission of blue light ($\lambda_{max} \simeq 410$ nm); (3) the thermochemistry of reaction 1 is well established and



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(1)

is such that acetone may be produced in an electronically *excited state*;[4] (4) the reaction dynamics can be probed after excitation by monitoring time-resolved visible emission from acetone, time-resolved spontaneous infrared emission from CH_3F, and time-resolved translational temperature changes (probed by the thermal lensing opto-acoustic technique);[5,6] (5) energy transfer processes in CH_3F are well understood[7,8] and serve as a benchmark for rate measurements in the mixture.

Irradiation of mixtures of CH_3F (2–30 Torr) and **1** (vapor pressure $\simeq$ 1 Torr at 25 °C) with an unfocused CO_2 TEA laser (1 μs pulse duration; 300 mJ per pulse) operating on the P_{20} (9.6 μ) line is accompanied by blue luminescence from the reaction cell and results in a smooth conversion of **1** to acetone. Laser radiation at this frequency excites only CH_3F although the luminescence is observed only when both CH_3F and **1** are present in the cell. Thus, CH_3F is a true photosensitizer of reaction 1. The thermochemistry of this "up-conversion" of photon energy is displayed in Figure 1. Typical blue luminescence, detected broadbanded with a photomultiplier (RCA 31034) through a sapphire window (which completely blocks laser scatter) is displayed in Figure 1a. The signal decays back to the baseline on a millisecond timescale (not shown). Addition of several Torr of other bath gases, such as Kr, O_2, N_2, and $(CH_3)_2CO$ effectively quenches the luminescence. Attempts to generate luminescence using other CO_2 absorbers as sensitizing agents (SF_6, CO_2, OCS, COF_2) failed in every case except SF_6, which generates luminescence at least as effectively as CH_3F.

In two other experiments using different experimental configurations the 3 μ infrared emission emanating from the C–H stretches in CH_3F was monitored using the laser induced fluorescence technique,[9,10] and the translational temperature rise was monitored using the thermal lensing technique.[5,6] Typical results performed under conditions identical with those of the luminescence experiment are also displayed in Figures 1b and 1c, respectively. These results show clearly that reaction is initiated by IR absorption into CH_3F and that the visible light generated by decomposition of **1** is produced on an energy transfer timescale. The following mechanism serves as a model to explain these observations.

$$CH_3F + h\nu(\mathrm{IR}) \longrightarrow CH_3F^{\dagger} \quad \text{absorption of infrared light} \tag{2}$$

$$CH_3F^{\dagger} + 1 \rightleftharpoons CH_3F + \mathbf{1}^{\dagger} \quad \text{vibrational (V–V) energy transfer} \tag{3}$$

$$\left.\begin{array}{ll} CH_3F^{\dagger} + \mathbf{1} \longrightarrow 1(T') + CH_3F(T') & (4) \\ \mathbf{1}^{\dagger} + CH_3F \rightleftharpoons \mathbf{1}(T') + CH_3F(T') & (5) \\ 1^{\dagger} + 1 \rightleftharpoons 21(T') & (6) \end{array}\right\} \begin{array}{l}\text{vibration to translation} \\ \text{(V–T) energy transfer}\end{array}$$

$$1^{\dagger} \text{ and/or } 1(T') \longrightarrow A^* + A \quad \text{chemielectronic excitations} \tag{7}$$

$$A^* \longrightarrow A + h\nu(\text{visible}) \quad \text{emission of visible light} \tag{8}$$

$$\text{heat diffusion} \tag{9}$$

In this mechanism, daggers refer to vibrationally hot, translationally cold molecules and asterisks refer to electronically excited acetone, while T′ refers to species whose translational temperature T′ is above the ambient equilibrium temperature of the gas mixture. The thermal decomposition of **1** is known to be chemiluminescent due to the efficient formation of A*. According to our mechanism, the blue luminescence should therefore correspond to electronic emission of acetone. Indeed, the blue emission produced in reaction 1 was shown to be experimentally identical with acetone *fluorescence.*[11]

The rapid rate of deactivation of vibrationally excited CH_3F (Figure 1b) is probably due to a combination of processes 3, 4, 5, and 6. Process 4 should not significantly contribute to the overall rate of decay based upon vibrational deactivation studies in CH_3F-rare gas mixtures[7b] and in pure CH_3F.[7a] In the latter case *the overall deactivation rate is two orders of magnitude slower than the rate observed here.* On the other hand, vibrational energy transfer processes like eq 3 are known to be rapid in many cases,[12] and eq 5 and 6 should also be efficient based upon the number and level spacing of states in **1**. In support of these assumptions we note that the rapid fall to the baseline in Figure 1b and the observation of greatly diminished 3 μ fluorescence intensity upon addition of **1** to pure CH_3F indicate negligible back-coupling in eq 3 implying eq 5 and 6 compete effectively with rapid V-V processes in pure CH_3F.[8]

Thermal lensing data in pure CH_3F[5] and CH_3F/O_2 mixtures[13] conclusively show that rapid V-V processes in pure CH_3F ($\simeq$2 μs at 5 Torr) are overall endothermic (translations cool), and that laser energy is stored in CH_3F vibrations on this V-V timescale. In contrast to this, the rapid rise in translational

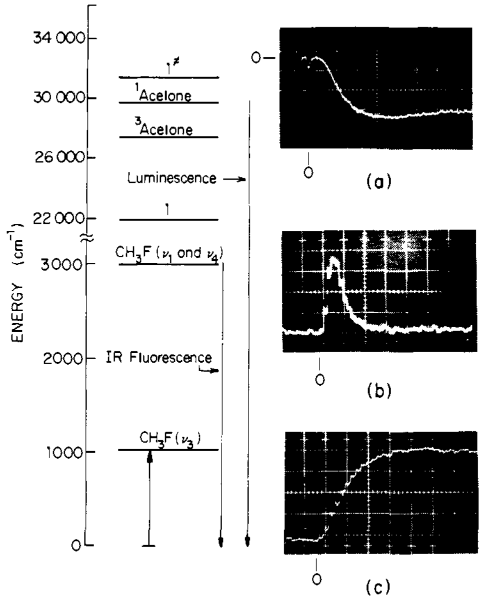

Figure 1. A partial energy level diagram for CH_3F, **1**, and acetone up to about 32 000 cm^{-1}. Energy scale referenced to CH_3F and acetone both in ground vibrational state. $1^{\ddagger}$ denotes the transition state for the decomposition of **1**. Also displayed are: (a) Time resolved visible luminescence ($\lambda_{max} \simeq 410$ nm). Signal is inverted with respect to (b) and (c). The small spike at short time is an instantaneous spark reflected off of the front of the reaction cell. Zero on the abscissa represents the initiation of the laser pulse. Zero on the ordinate represents the ambient signal level. (b) Time resolved 3 μ infrared fluorescence. Zero on the abscissa represents the initiation of the laser pulse. (c) Time resolved translation heating. Zero on the abscissa represents the initiation of the laser pulse. Time base is 5 μs per major division along the abscissa in (a), (b), and (c) measured with $P_{CH_3F} = 5$ Torr and $P_{C_6H_{12}O_2} \simeq 1$ Torr.

temperature (Figure 1c) in CH_3F-**1** mixtures indicates that on this same timescale, energy transfer is overall highly exothermic (translations heat). These results are consistent with and support the idea that eq 3, 5, and 6 rapidly drain laser energy into heat. The buildup rate of acetone luminescence should be governed both by these processes and eq 8. Based on Figures 1a and 1c, which show comparable risetimes for visible luminescence and translational heating, the rate of production of acetone is apparently limited only by the translational heating rate. This observation is indicative of a "laser temperature jump" mechanism; the rate of product formation occurs on a timescale comparable to (or slower than) the rate of ambient temperature rise.[14]

The millisecond long decay of luminescence mentioned previously is consistent with the transport of heat over a distance comparable to the reaction cell size.[15] The temperature rise due to laser heating was estimated to be 100–150 K based upon the measured laser pulse energy and percent absorption in pure CH_3F and an estimate of the heat capacity of the gas mixture.[16] Using this result and the known Arrhenius parameters[17] for the thermal decomposition of **1** yields a decomposition rate which is consistent with the observed decomposition rate measured as a function of successive laser shots. In addition, the quenching of the luminescence by added bath gases can be related to smaller translational temperature jumps as the heat capacity increases.

In summary, reaction 1 is the first example of an infrared photosensitized chemiluminescent organic reaction. A combination of measurements of infrared fluorescence from the photosensitizer, of visible luminescence from the primary product and of the translational temperature reequilibration are consistent with a predominant "temperature jump" mechanism (eq 2–7) wherein any contribution from $1^{\dagger}$ in eq 7 is dominated by the contribution from **1**(T′). These studies are being extended to 1,2-dioxetanes which directly absorb the laser pulse and to other systems in which a high energy content reaction possesses the potential of infrared laser induced electronic excitation.

Acknowledgments. The authors wish to thank Mr. Irwin Shamah for many useful suggestions and discussions. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR-74-2589), by the Joint Services Electronics Program (U.S. Army, U.S. Navy, and U.S. Air Force) under Contract DAABO7-74-C-0341, by the National Science Foundation (Grants NSF-MPS70-02165 and NSF-MPS73-04672 and NSF-MPS75-04118), and in part by the Advanced Research Projects Agency of the Department of Defense monitored by the Office of Naval Research under Grant N00014-75-C-1106.

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Salt-Type Complexes of Porphyrins: Monocation Octaethylporphinium Tri-μ-halogeno-hexacarbonyldirhenate(I)

Sir:

Porphyrins have been reported as the free base, the dicationic species, and, recently, as the monocationic species.[1] It has been suggested that in the biosynthesis of porphyrins the cationic species plays a role in the final stages of oxidation from porphyrinogen to porphyrins.[2] Recently out-of-plane bimetallic porphyrin complexes[3-6] have received considerable attention. However, bimetallic salt complexes[7,8] of porphyrin acids are rare.