of cobalt hydride and readlision in the opposite sense, or by some equiv-
alent interchange of alkyl and a-hydrogen. The final position of alkyl
would be attachment to the w-carbon resulting in deutelium incorporation
at that position, following hydrolysis. This more complex scheme cannot
be ruled out in the absence of a carbon labeling experiment (syntethic ef-
forts directed toward that end are in progress). However, the absence of
any detectable amount of deutelium attached to the a-carbon, the potential
complexity of the elimination-addition sequence and the precedent pro-
vided 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 re-
action,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 exci-
tation 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 CO2 laser-enhanced decomposition of gas phase
tetramethyl-1,2-dioxetane (1) in a methyl fluoride bath.
Methyl fluoride is a "sensitizer" for the CO2 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 (λmax ≈ 410 nm);
(3) the thermochemistry of reaction 1 is well established and

\[
\text{CH}_3\text{COOCH} \quad + \quad + h\nu \approx 410 \text{ nm} \quad (1)
\]

is such that acetone may be produced in an electronically ex-
cited 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
CH3F, and time-resolved translational temperature changes
(probed by the thermal lensing opto-acoustic technique)5,6
(5) energy transfer processes in CH3F are well understood;7,8
and serve as a benchmark for rate measurements in the mix-
ture.

Irradiation of mixtures of CH3F (2-30 Torr) and 1 (vapor
pressure ≈ 1 Torr at 25 °C) with an unfocused CO2 TEA laser
(1 μs pulse duration; 300 mJ per pulse) operating on the P20
(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 CH3F although
the luminescence is observed only when both CH3F and 1 are
present in the cell. Thus, CH3F is a true photosensitizer of
reaction 1. The thermochemistry of this "up-conversion" of
photon energy is displayed in Figure 1. Typical blue lumines-
cence, 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). Addi-
tion of several Torr of other bath gases, such as Kr, O2, N2, and
(CH3)2CO effectively quenches the luminescence. Attempts
to generate luminescence using other CO2 absorbers as sen-
sitizing agents (SF6, CO2, OCS, COF2) failed in every case
except SF6, which generates luminescence at least as effectively
as CH3F.

In two other experiments using different experimental
configurations the 3 μ infrared emission emanating from the
C-H stretches in CH3F was monitored using the laser induced
fluorescence technique9,10 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 CH3F 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.

CH3F + hν(IR) → CH3F* absorption of infrared light

CH3F* + 1 ≡ CH3F + 1° vibrational (V-V) energy transfer

CH3F* + 1 → 1(T′) + CH3F(T′)

1° + CH3F ≡ 1(T″) + CH3F(T″)

1° + 1 → 21(T″)

1° and/or 1(T″) → A* + A chemiluminescent excitations

A* → A + hν(visible) emission of visible light

heat diffusion

In this mechanism, daggers refer to vibrationally hot,
translationally cold molecules and asterisks refer to electroni-
cally excited acetone, while T′ refers to species whose trans-
lational 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 for-
mation of A*. According to our mechanism, the blue lumines-
cence should therefore correspond to electronic emission
of acetone. Indeed, the blue emission produced in reaction 1
was shown to be experimentally identical with acetone fluo-
rescence.11

The rapid rate of deactivation of vibrationally excited CH3F
(4 ps) is probably due to a combination of processes 3,
4, 5, and 6. Process 3 would not significantly contribute to the
overall rate of decay based upon vibrational deactivation
studies in CH3F-rare gas mixtures12 and in pure CH3F.13 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 ef-
fficient 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 di-
minished 3 μ fluorescence intensity upon addition of 1 to pure
CH3F indicate negligible back-coupling in eq 3 implying eq
5 and 6 compete effectively with rapid V-V processes in pure
CH3F.8

Thermal lensing data in pure CH3F5 and CH3F/O2 mix-
tures5,13 conclusively show that rapid V-V processes in pure
CH3F (≈ 2 μs at 5 Torr) are overall endothermic (translations
cool), and that laser energy is stored in CH3F vibrations on this
V-V timescale. In contrast to this, the rapid rise in translational
temperature (Figure 1c) in CH₃F–I 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 retsimes 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 CH₃F and an estimate of the heat capacity of the gas mixture.¹⁶ Using this result and the known Arrhenius parameters¹⁷ for the thermal decomposition of I 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 I' in eq 7 is dominated by the contribution from I(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.

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References and Notes

(11) CO₂ laser excited emissions of reaction 1 was compared to an emission spectrum of a gas mixture of acetone, 1, and CH₃F excited at 300 nm with a xenon lamp using the identical detection system in both cases. Approximately 10⁶ CO₂ photons must be absorbed per visible photon emitted in the CO₂ laser initiated reaction.
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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 complexes³–⁵ have received considerable attention. However, bimetallic salt complexes⁶–⁸ of porphyrin acids are rare.