Cr(III) can be used as an energy-transfer acceptor in proteins. CrATP and related complexes are inert species that bind to proteins.[45] The low-temperature lifetime of CrATP is 50 ns, but the lifetime of $Cr(NH_3)_4ADP$ is several microseconds. CrATP contains several H_2O ligands. When one or more Cr–O bonds is involved in a complex, thermal quenching will be significant. If Cr(III)–nucleotide complexes are bound to proteins in proximity to tyrosine and/or tryptophan residues, emission from the latter will be quenched by resonance transfer and the Cr(III) emission will be sensitized as has been observed for bound rare-earth ions.[46] In favorable circumstances, Cr(III)–nucleotide complexes can be used to estimate the distance between the binding site and an aromatic chromophore, but the protein will have to be dissolved in a low-temperature glycerol–H_2O glass.

Summary and Conclusions

Although variation in k_6^0 with ligand may be associated with changes in the accepting mode frequency within a group of closely related complexes, the absence of a correlation between $\Delta E/\nu_M$ and k_6^0 (Table II) indicates that the effect of ligand on the electronic factor cannot be ignored. The change of k_6^0 with ligand in the β-diketonates serves to underscore this conclusion.[32]

Estimation of intramolecular thermal relaxation rates for complexes dissolved in glassy media is risky. It is best to employ a solvent with the highest possible softening temperature. Also, the effective symmetry in a rigid glass is much lower than in a crystalline host. Consequently, symmetry arguments are not useful in discussing k_6^0 for complexes in glassy solvents.

The substitution of NH_3 by H_2O provides a facile thermal quenching channel, which is probably $^2E \rightsquigarrow {}^4T_2$.

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[45] W. W. Cleland and A. S. Mildvan, *Adv. Inorg. Biochem.*, 1, 163 (1979).

[46] W. deW. Horrocks, Jr., and D. R. Sudnick, *J. Am. Chem. Soc.*, 101, 335 (1979).

Multiple Infrared Photon Dissociation and Kinetics of CF_3O Radicals

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The multiple infrared photon dissociation of CF_3O radicals generated from bis(trifluoromethyl) peroxide has been investigated. Infrared fluorescence from $HF^{\dagger}$, formed by reaction of the liberated F atom with HI, was used to monitor the dissociation over a range of infrared fluences. A simple rate equation model has been used to interpret the multiphoton excitation and dissociation of the CF_3O species. The kinetics of the recombination reaction, $CF_3O + F \rightarrow CF_3OF$, have been investigated by scavenging the F atoms with added HI. The rate constant for this reaction at 300 K is determined to be $(3.5 \pm 0.5) \times 10^{10}$ L mol^{-1} s^{-1}.

Introduction

We have recently reported results on the multiple infrared photon dissociation (IRMPD) of bis(trifluoromethyl) peroxide (BTMP) by CO_2 laser radiation.[1] We found that the primary dissociation product is CF_3O, and that substantial secondary dissociation of these radicals occurred in focussed beams, forming F atoms and CF_2O. Little is presently known about the pumping and dissociation dynamics of transient species such as CF_3O. In addition, the potential use of these species in laser-induced etching of silicon surfaces[2] necessitates a knowledge of the relative yields of the different reactive fragments under various excitation conditions.

When BTMP is subjected to infrared radiation in the 9–10-μm region, at fluences above a few mJ/cm^2, symmetric cleavage occurs at the O–O bond:

$$CF_3OOCF_3 \xrightarrow{nh\nu} 2CF_3O \tag{1}$$

The CF_3O produced may continue to absorb infrared photons and further dissociate:

$$CF_3O \xrightarrow{mh\nu} CF_2O + F \tag{2}$$

The F atoms then combine with the remaining CF_3O to give the product, CF_3OF:

$$F + CF_3O \xrightarrow{k_3} CF_3OF \tag{3}$$

The recombination rate constant k_3 has been estimated at 3×10^9 L mol^{-1} s^{-1} from analysis of thermal data,[3,4] but a direct measurement of k_3 has not been carried out.

The production of F atoms in reaction 2 may be monitored by scavenging with HI according to the reaction

$$F + HI \xrightarrow{k_4} HF^{\dagger} + I \tag{4}$$

The HF is produced vibrationally excited, and thus may be monitored by its infrared fluorescence. The room-temperature rate constant k_4 has been measured[5] to be 2.4×10^{10} L mol^{-1} s^{-1}. The remaining CF_3O radicals which do not react via (3) recombine to form BTMP

$$2CF_3O \xrightarrow{k_5} CF_3OOCF_3 \tag{5}$$

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(1) J. S. Francisco, M. A. Findeis, and J. I. Steinfeld, *Int. J. Chem. Kinet.*, 13, 627 (1981).

(2) D. Harradine, F. R. McFeely, B. Roop, J. I. Steinfeld, D. Denison, L. Hartsough, and J. R. Hollahan, "Reactive Etching of Semiconductor Surfaces by Laser-Generated Free Radicals", Proceedings of the SPIE Symposium on High-Power Lasers and Applications, Hollywood, CA, 1981, Vol. 270, pp 52–60.

(3) R. C. Kennedy and J. B. Levy, *J. Phys. Chem.*, **76**, 3480 (1972).

(4) B. Descamps and W. Forst, *J. Phys. Chem.*, **80**, 933 (1976).

(5) E. Würzberg, A. J. Grimley, and P. L. Houston, *Chem. Phys. Lett.*, 57, 373 (1978); E. Würzberg and P. L. Houston, *J. Chem. Phys.*, **72**, 5915 (1980).

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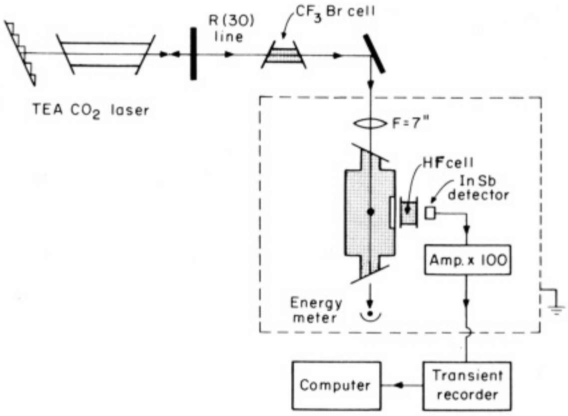

Figure 1. Schematic arrangement of the infrared fluorescence experiment.

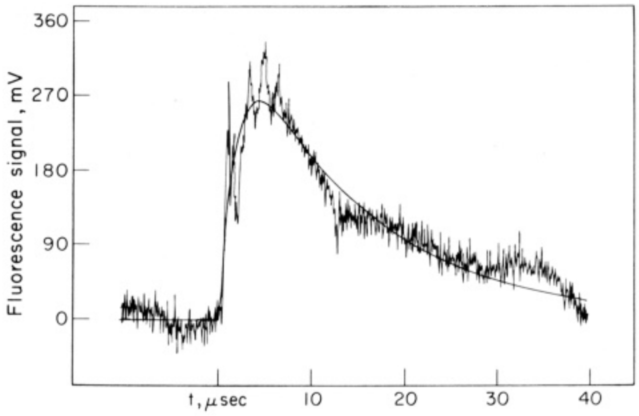

Figure 2. Infrared fluorescence signal from 0.045 torr of BTMP plus 0.655 torr of HI photolyzed with 0.43 J/pulse at the CO_2 $R_2(30)$ laser line. The smooth curve is a fit to eq 6.

The possibility of direct reaction of CF_3O with HI (presumably to form CF_3OH) was considered and ruled out in ref 1, on the basis of the lack of variation of CF_2O yield with added HI.

The questions which remain to be answered regarding the sequence of reactions 1–3 and 5 are, first, the yield of secondary dissociation (step 2) and the rate of the recombination process 3. Both of these are addressed via the scavenging reaction 4. The production of $HF^\dagger$, as determined by its infrared fluorescence, is used as a measure of the F atoms produced by secondary dissociation. The net yield of CF_3OF is used, in conjunction with a kinetic model, in order to determine k_3.

Experimental Section

The experiments may be divided into two sorts: first, infrared fluorescence measurements and, second, collection and analysis of CF_3OF product following photolysis with 4000 CO_2 laser pulses.

The experimental arrangement is shown schematically in Figure 1. The output of a Tachisto 215G TEA–CO_2 laser was focussed by an AR-coated Ge lens of fl 18 cm into a reaction cell, and the infrared emission from the vibrationally excited HF was observed at right angles to the laser beam. The CO_2 laser line used in these experiments was $R_2(30)$ at 9.219 μm, nearly single mode, with a maximum output energy of 1.1 J/pulse. An attenuation cell containing CF_3Br was inserted between the laser output mirror and the focussing lens, by means of which the laser pulse energy entering the reaction cell could be varied between 0.15 and 1.1 J/pulse.

The stainless steel sample cell was 7.4 cm in diameter by 20.3 cm long, with a total volume of 930 cm^3. The end windows were NaCl flats, while the fluorescence was observed through a LiF side window having a long-wave cutoff of 7 μm, which eliminated scattered laser light. The infrared fluorescence was viewed with an InSb photovoltaic detector (Infrared Industries Type 6800) having a peak $D^* \sim 1 \times 10^{11}$ at $\lambda = 5$ μm. Signals from the detector were amplified by a Tektronix 1121 amplifier, recorded on a transient recorder (Biomation 820), and then transmitted to a MINC laboratory computer for averaging and subsequent analysis.[6]

In the fluorescence experiments, the total pressure (BTMP + HI) in the cell was varied between 0.4 and 1.1 torr, maintaining a constant composition of [HI]/[BTMP] = 15. The cell was emptied and refilled after no more than 10–20 laser pulses, so that very little decomposition had a chance to take place. Since CF_2O, which is one of the products of reaction 2, has a characteristic band near 2.6 μm,[7] and may be expected to be born "hot" and thus to emit in this region, we carried out several checks on the identity of the fluorescing species. First, in the absence of HI, no fluorescence signal could be observed. Using standard experimental conditions, we inserted a gas filter cell containing HF between the observation window and the InSb detector (see Figure 1). When the cell was filled with 40 torr of HF, essentially 100% of the fluorescence signal was eliminated. We thus conclude that the observed emission is from $HF^\dagger$ produced in reaction 4, which is fully relaxed to its $v = 1$ state by rapid V–V relaxation processes occurring under our experimental conditions.

For the CF_3OF yield measurements, a mixture of 2 torr of BTMP with 0–3 torr of added HI was photolyzed with the CO_2 $R_2(30)$ line for 4000 pulses. The resulting product mixture was transferred to an infrared analysis cell, and characteristic absorptions of CF_3OF[8] known to be linear in concentration[1] were used to determine the yield of that product.

Gas purity was particularly important in these experiments. The BTMP, obtained from PCR Research Chemicals, contained a small amount of CF_3OF as an impurity.[1] This was removed by immersing the bulb containing BTMP in a −94 °C (hexane/liquid N_2) bath and pumping. The HI, obtained from the Matheson, is contaminated with H_2 and I_2 due to decomposition of HI on the iron wall of the cylinder. The presence of H_2 would be particularly troublesome, since this could initiate a chain reaction with F atoms; this may have been a source of error in previous measurements of HI inhibition of CF_3OF formation.[1] The H_2 was removed by several freeze–pump–thaw cycles of the HI, using a liquid N_2 bath. All the gases, once purified, were stored in glass bulbs at dry-ice temperature.

Results and Discussion

Secondary Photolysis of CF_3O. We have investigated directly the IRMPD of CF_3O radicals resulting from BTMP photolysis in the presence of HI by monitoring the spontaneous emission from $HF^\dagger$ produced in reaction 4. The HF emission was observed from the focal region of the laser beam, over a range of pulse energies between 0.1 and 1.1 J. No measurable fluorescence was observed with the laser unfocussed, or in the absence of HI. A typical fluorescence signal is shown in Figure 2. In these experiments, the time development of the observed

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(6) C. Reiser, *Rev. Sci. Instrum.*, **51**, 1727 (1980).

(7) A. P. Modica and R. R. Brochu, *J. Quantum Spectrosc. Radiat Transfer*, **9**, 1105 (1969).

(8) R. T. Lagemann, E. A. Jones, and P. J. H. Woltz, *J. Chem. Phys.*, **20**, 1768 (1952).

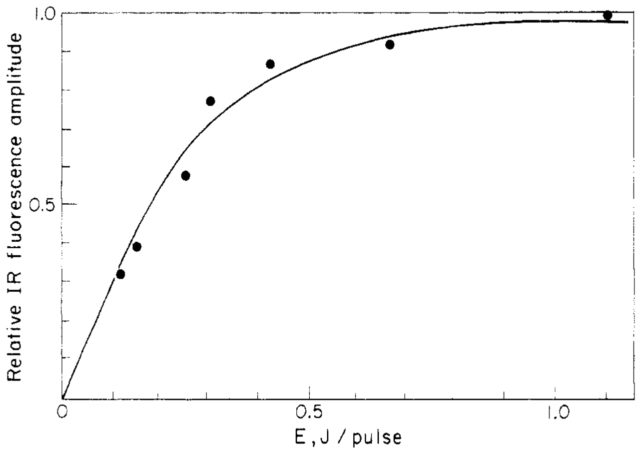

Figure 3. Relative IR fluorescence amplitude vs. CO_2 laser pulse energy. Solid curve is the F atom yield from IRMPD of CF_3O calculated from the model described in the text and depicted in Figure 4.

fluorescence signals could be fit to a simple three-parameter expression:

$$I_{fl}(t) = A[\exp(-t/\tau_d) - \exp(-t/\tau_r)] \tag{6}$$

If reaction 4 is the only source of $HF^\dagger$ and vibrational relaxation is exponential, then the amount of vibrationally excited HF present at a time t following the CO_2 laser pulse is given by

$$[HF^\dagger]_t = \frac{k_4[HI]_0[F]_0}{k_4[HI]_0 - 1/\tau_d}[\exp(-t/\tau_d) - \exp(-k_4[HI]_0 t)] \tag{7}$$

where the signal rise time is just $\tau_r^{-1} = k_4[HI]_0$ and the decay time, τ_d, is the vibrational relaxation time of HF(v=1) in the gas mixture being used. Since the relaxation of the $v = 1 \rightarrow 0$ fluorescence is due to a combination of slow V–T,R relaxation and diffusion out of the observation region, we have $k_4[HI]_0 >> 1/\tau_d$ under our experimental conditions (by at least a factor of ten), so that the maximum value of $[HF^\dagger]$ is nearly equal to $[F]_0$, the initial concentration of F atoms produced in reaction 2. Thus, the amplitude parameter A in eq 6 is directly proportional to $[F]_0$, which is the quantity of interest.

The rise time τ_r gives us an independent measurement of the rate of reaction 4. This rate constant has been previously determined by Würzberg et al.[5] using SF_6 + HI mixtures as (1.34 ± 0.03) × 10^6 torr^{-1} s^{-1}, which is in reasonable agreement with our lower limit of 9.0 × 10^5 torr^{-1} s^{-1}. The peak amplitude of the infrared fluorescence, which is proportional to the yield of F atoms, is shown in Figure 3. The yield rises linearly with pulse energy, as is characteristic of the IRMPD of a molecule already in a quasicontinuum regime,[1] and then appears to saturate at pulse energies $\gtrsim$1 J. We do not have an absolute calibration of the infrared fluorescence signal in terms of F atom concentration, and so we normalize this yield curve by assuming that the saturation corresponds to 100% dissociation of the available CF_3O.

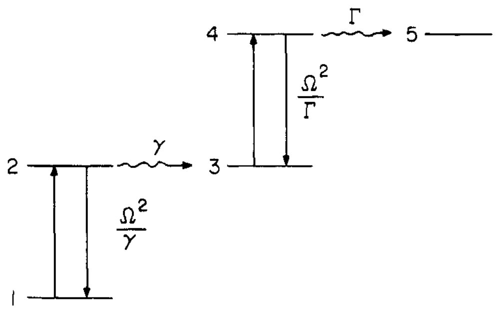

Figure 4. Five-level model for production of F atoms by secondary IRMPD CF_3O radicals.

In order to gain some insight into the process whereby CF_3O is driven to dissociation, following the IRMPD of the parent BTMP molecule, we have used a simple set of rate equations to model the system. From its IRMPD behavior, BTMP itself displays the characteristics of a molecule already in its vibrational "quasi-continuum" at room temperature.[1] Thus, the dynamics of the parent molecule can be adequately represented by a set of rate equations which described the incoherent pumping of BTMP to dissociation. The fragments resulting from IRMPD are also frequently produced with sufficient excess vibrational energy to be in the quasicontinuum; this is the case, for example, with SF_5 produced by IRMPD of SF_6.[9] Accordingly, we assume that CF_3O is produced in its quasi-continuum, and that its IRMPD dynamics can also be modeled by a set of incoherent rate equations. Since none of the details of the intermediate states of the pumping processes of these species are known, we have modeled the system with the ultrasimplified five-level model depicted in Figure 4, which is based on the more detailed treatments of Galbraith et al.[10] In this picture, we consider pumping from level 1, which represents all of the lower vibrational levels of BTMP, to level 2, which is the activated $BTMP^\dagger$ molecule, with a rate given by the effective Rabi frequency

$$\Omega^2 = \frac{8\pi I \mu^2}{h^2c^3} \tag{8}$$

where I is the laser power density, μ is the transition dipole moment matrix element, and h and c are Planck's constant and the speed of light, respectively. The unimolecular dissociation of the $BTMP^\dagger$ is represented by an effective decay rate γ from level 2 to level 3, which is the CF_3O radical. This species is in turn pumped to level 4 (activated CF_3O) with the same effective Rabi frequency Ω; this level in turn decays to level 5, which represents CF_2O + F atom, with a rate Γ. This model leads to a set of equations for the population in each level ρ_i (i = 1–5), viz:

$$\dot{\rho}_1 = -\frac{\Omega^2}{\gamma}(\rho_1 - \rho_2) \tag{9a}$$

$$\dot{\rho}_2 = \frac{\Omega^2}{\gamma}(\rho_1 - \rho_2) - \gamma\rho_2 \tag{9b}$$

$$\dot{\rho}_3 = -\frac{\Omega^2}{\Gamma}(\rho_3 - \rho_4) + \gamma\rho_2 \tag{9c}$$

$$\dot{\rho}_4 = \frac{\Omega^2}{\Gamma}(\rho_3 - \rho_4) - \Lambda\rho_4 \tag{9d}$$

$$\dot{\rho}_5 = \Gamma\rho_4 \tag{9e}$$

The value of the transition moment required in eq 8 was estimated from the infrared absorption coefficient of BTMP at the wavelength of the $R_2(30)$ line. Since no information exists about the spectroscopy of CF_3O, the same value of Ω was used in eq 9a–d. The effective decay rates, γ and Γ, were varied in the calculation; the curve shown in Figure 3 was calculated with the values γ = 2.1 × 10^{13} s^{-1} and Γ = 1.3 × 10^7 s^{-1}. The value for γ is equivalent to a thermal unimolecular decay rate[3] with a

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(9) E. R. Grant, M. J. Coggiola, Y. T. Lee, P. A. Schulz, Aa. S. Sudbø, and Y. R. Shen, *Chem. Phys. Lett.*, **52**, 595 (1977).

(10) H. W. Galbraith and J. R. Ackerhalt in "Laser-Induced Chemical Processes", J. I. Steinfeld, Ed, Plenum, New York, 1981, pp 1–44.

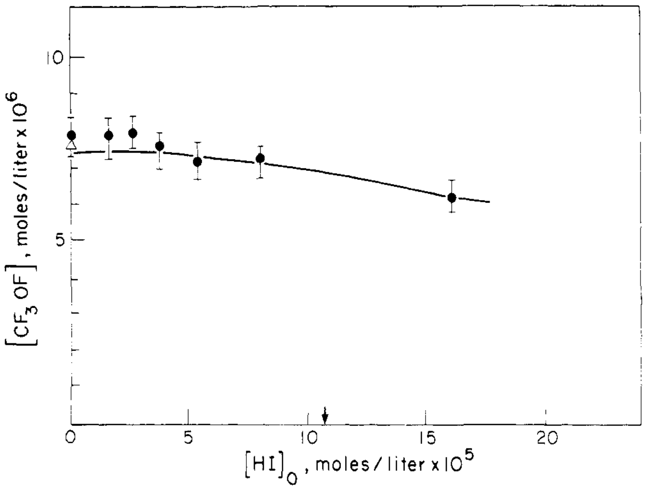

Figure 5. Yield of CF_3OF from IRMPD of BTMP as a function of added HI concentration. The arrow on the horizontal axis indicates the fixed initial concentration of BTMP. The open triangle is the data point for CF_3OF yield in the presence of added 2 torr (1.0×10^{-4} mol L^{-1}) of Ar. The solid curve is the calculated yield function on the basis of the kinetic model described in the text, using the rate constants $k_3 = 3.9 \times 10^{10}$ L mol^{-1} s^{-1} and $k_4 = 2.4 \times 10^{10}$ L mol^{-1} s^{-1}.

mean excitation in the activated BTMP molecule of 9.2 kcal/mol; the much smaller value of Γ probably reflects less efficient pumping of the CF_3O by the laser line used in the experiment, leading to a lower level of vibrational excitation, and thus a smaller decomposition rate, for that species.

CF_3O + F Recombination Reaction. So that the rate of the recombination of trifluoromethoxy radicals with fluorine atoms could be determined (eq 3), experiments were carried out in which varying amounts of HI were added to a cell containing 2 torr of BTMP, and the mixture was photolyzed at a constant infrared wavelength and fluence. The net amount of CF_3OF formed, measured as a formation of initial HI concentration, it shown in Figure 5. The effect of the HI is to suppress the formation of CF_3OF, as a result of the competition for F atoms due to reaction 4.

Once initial amounts of CF_3O, CF_2O, and F atoms are generated by primary and secondary IRMPD, the subsequent evolution of the species concentrations is governed by a set of kinetic equations derived from reactions 3–5. These are

$$\dot{X}_1 = -k_3X_1X_3 - k_5X_1^2 \tag{10a}$$

$$\dot{X}_3 = -k_3X_1X_3 - k_4X_3X_5 \tag{10b}$$

$$\dot{X}_4 = k_3X_1X_3 \tag{10c}$$

$$\dot{X}_5 = -k_4X_3X_5 \tag{10d}$$

$$\dot{X}_6 = k_4X_3X_5 \tag{10e}$$

with $X_1 = [CF_3O]$, $X_2 = [CF_2O]$, $X_3 = [F]$, $X_4 = [CF_3OF]$, $X_5 = [HI]$, and $X_6 = [HF]$. It is the term which is second-order in X_1, appearing in eq 10a, resulting from the recombination reaction 5, which makes the derivation of an integrated analytic rate expression exceedingly difficult. The system of equations can be easily integrated numerically, however, with a modified Euler differential analysis method.[11]

It remains only to specify the initial conditions on the concentrations of the radical species, X_1 and X_3. This can most easily be done in terms of the concept of reaction volume,[1,12] which is a volume U_R surrounding the focal region of the laser beam within which all of the parent molecules (BTMP, in this case) are assumed to be dissociated. The amount of starting material dissociated by each laser pulse is then a fraction of the total amount in the cell, given by

$$f = U_R/V_{cell} \tag{11}$$

so that, after K laser pulses have been applied to the sample

$$[BTMP]_K = [BTMP]_0e^{-fK} = e^{-fK}X_0 \tag{12}$$

and, since each peroxide molecule dissociates to form two trifluoromethoxy radicals, the initial concentration of these radicals in the volume U_R is

$$[CF_3O]_{K,0} = (X_1)_{K,0} = 2e^{-fK}X_0 \tag{13}$$

If a known fraction q of the CF_0O species are further dissociated to form CF_2O + F, we have

$$[F]_{K,0} = (X_3)_{K,0} = 2qe^{-fK}X_0 \tag{14}$$

The values given by eq 13 and 14 provide initial values for the integration of eq 10a–e for the Kth laser pulse. The incremental amount of CF_3OF formed after that pulse, $\Delta(CF_3OF)_K$, is found by integrating eq 10c to a stationary value. The total amount of CF_3OF formed after K pulses (K = 4000 in our case) is given by

$$[CF_3OF]_{total} = f\sum_{i=1}^{4000} \Delta(CF_3OF)_i \tag{15}$$

The value of f for our experimental conditions, found by applying eq 12 to the total amount of BTMP decomposed, is $f = 0.74 \times 10^{-4}$. Since the cell volume is 930 cm^3, this gives a reaction volume U_R = 0.069 cm^3. This may be compared with a value of $U_R \simeq 0.2$ cm^3 found for this fluence in our previous work;[1] since a 30-cm focal length lens was used in that work, the U_R is proportional to the focal length,[12] these two measurements are self-consistent. The foregoing treatment is based, of course, on the assumption of complete mixing of the cell contents between each laser pulse; for a characteristic reaction-zone dimension of 4 mm, and an interval between pulses of ~1 s, this is an entirely reasonable assumption.

The F + HI reaction rate constant, k_4, is known from the work of Würzberg et al.[5] to be 2.4×10^{10} L mol^{-1} s^{-1} at 300 K. Since the fit shown in Figure 5 is relatively insensitive to the value chosen for the CF_3O recombination rate constant, was take Kennedy and Levy's[3] estimate for $k_5 \simeq 2.5 \times 10^9$ L mol^{-1} s^{-1}, and vary k_3 to obtain a fit to the data. A value of $k_3 = (3.5 \pm 0.5) \times 10^{10}$ L mol^{-1} s^{-1} gives the yield dependence shown as the solid curve in Figure 5. Using Kennedy and Levy's[3] earlier value of $k_3 = 3 \times 10^9$ L mol^{-1} s^{-1} predicts a yield of $[CF_3OF]$ which is a factor of 2 too low; a significantly larger value of k_3 would not reproduce the falloff with added [HI]. Other data for this system, such as the variation of CF_3OF yield with initial BTMP pressure, are also consistent with the stated value for k_3. We are therefore led to infer the value of k_3 stated above, which is comparable to rates known for other similar association reactions.[13]

An estimate of the critical impact parameter for bimolecular association can be made[14] by assuming that there

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(11) K. L. Nielsen, "Methods in Numerical Analysis", 2nd ed, Macmillan, New York, 1964.

(12) D. R. Keefer, J. E. Allen, Jr., and W. B. Person, *Chem. Phys. Lett.*, **43**, 394 (1976).

(13) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1976, p 164.

(14) Reference 13, p 86 *ff*.

is no barrier in the entrance channel other than that arising from centrifugal energy, and that the F atom approaches the O atom along a Lennard-Jones potential curve. This gives

$$\left(\frac{r_m}{r_0}\right)^2 \simeq \left(\frac{6D_0}{kT}\right)^{1/3} \tag{16}$$

where r_m is the critical distance between the F and the CF_3O centers of mass, r_0 is the equilibrium F–O bond distance, and D_0 is the F–O bond dissociation energy. We find that the critical distance between the two centers, and hence the effective reactive impact parameter, is 4.0 Å from eq 16. This gives a gas-kinetic collision rate at 300 K which is the upper limit for the rate of recombination of CF_3O with F, equal to 1.7×10^{11} L mol^{-1} s^{-1}. The value found for k_3, which is 4–5 times smaller than this, suggests that a modest orientational requirement exists for the collision to be reactive, similar to (but less restrictive than) that observed in the recombination of CF_3 radicals.[15]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Grant No. AFOSR-78-3725. We thank Dr. H. W. Galbraith for helpful discussions concerning the model for secondary IRMPD of CF_3O.

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(15) M. Rossi and D. M. Golden, *Int. J. Chem. Kinet.*, 11, 775 (1979).

Deazaflavin Photocatalyzed Methyl Viologen Reduction in Water. A Laser Flash-Photolysis Study

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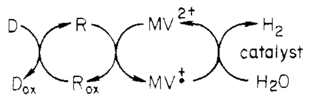
Photosensitized reduction of methyl viologen, MV^{2+}, by 2×10^{-4} M 10-methyl-5-deazaisoalloxazine-3-propanesulfonic acid, dF, in the presence of 1×10^{-3}–10×10^{-3} M EDTA has been investigated in aqueous solutions by nanosecond laser flash photolysis. At substoichiometric concentrations of MV^{2+}, the reactions ${}^1dF \xrightarrow{h\nu} {}^1dF^* \xrightarrow{isc} {}^3dF^*$; ${}^3dF^* + EDTA \rightarrow {}^2dF\cdot + EDTA^+$; ${}^2dF\cdot + MV^{2+} \rightarrow {}^1dF + MV^{+}\cdot$ have been discerned; thus dF acts as an electron relay. At higher MV^{2+} concentrations additional modes of dF catalyzed $MV^{+}\cdot$ formation become available.

Introduction

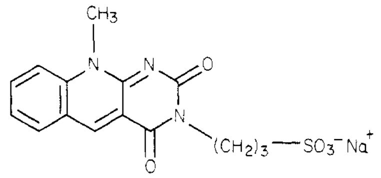
Photochemical solar energy conversion is an important and highly active area of research.[2-14] Much attention has been focussed upon the photosensitized reduction (by an electron relay, R) of methyl viologen, MV^{2+}, since the oxidized relay, R_{ox}, can be regenerated by a suitable electron donor, D, and since reduced methyl viologen, $MV^{+}\cdot$, in the presence of a suitable catalyst is reoxidized to MV^{2+} with concurrent water splitting



(1)

Hydrogen is, therefore, photogenerated from water at the expense of a sacrificial donor (eq 1).

Flavins, particularly proflavin, appear to be attractive relays because they have high quantum yields for MV^{2+} reduction.[13-18] Deazaflavins have the additional advantage of being able to be regenerated from their photooxidized form by such a large variety of electron donors as amines and carboxylic and amino acids.[19] They are also powerful photoreductants for many different redox enzymes and proteins.[19] As part of our overall investigations of electron transfer processes we have examined a water-soluble 7,8-unsubstituted 5-deazaflavin, 10-methyl-5-deazaisoalloxazine-3-propanesulfonic acid (dF) as a potential photocatalytic electron relay. Using nanosecond laser flash photolysis mechanisms for photosensitized EDTA and MV^{2+}, reductions have been elucidated.



dF

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(1) Agricultural University, Wageningen, The Netherlands.

(2) Kiwi, J.; Kalyanasundaram, K.; Grätzel, M. "Visible Light Induced Cleavage of Water into Hydrogen and Oxygen in Colloidal Microheterogeneous Systems"; Springer-Verlag: Heidelberg, 1981.

(3) Porter, G.; Archer, M. V. *ISR Interdiscip. Sci. Rev.* **1976**, *1*, 119.

(4) Calvin, M. *Acc. Chem. Res.* **1978**, *11*, 4701.

(5) Hautala, R. R.; King, R. B.; Kutal, C. "Solar Energy, Chemical Conversion and Storage"; The Humana Press: Clifton, NY, 1979.

(6) Bolton, J. R. "Solar Power and Fuels"; Academic Press: New York, 1977.

(7) Archer, M. D. In "Photochemistry, Specialists Periodical Report"; The Chemical Society: London, 1978; Vol. 9, p 603; 1977; Vol. 8, p 570; Vol. 7, p 567; 1976; Vol. 6, p 736.

(8) Claesson, S.; Engström, M. "Solar Energy—Photochemical Conversion and Storage"; National Swedish Board for Energy Source Development: Stockholm, 1977.

(9) Barber, J. "Photosynthesis in Relation to Model Systems"; Elsevier: New York, 1979.

(10) Gerischer, H.; Katz, J. J. "Light Induced Charge Separation in Biology and Chemistry"; Verlag Chemie: Berlin, 1979.

(11) Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chim. Acta* **1979**, *62*, 1345.

(12) Krasna, A. I. *Photochem. Photobiol.* **1979**, *29*, 267.

(13) Krasna, A. I. *Photochem. Photobiol.* **1980**, *30*, 75.

0022-3654/82/2086-2406$01.25/0