The Infrared Photodissociation of CH_3OHF^-

Sir:

We report here the infrared photodissociation of the ion CH_3OHF^- under conditions such that the photochemical and collisional time scales are separated by several orders of magnitude. The development of IR multiphoton absorption as an activation technique of general utility requires that the chemistry associated with both regimes be well characterized. While experiments done under conditions where collisional processes are important[1] can provide data on intermolecular relaxation and energy pooling, studies under collision-free conditions[2] are required to characterize photochemical energy deposition and its subsequent *intramolecular* relaxation (including unimolecular decomposition). Isolated molecule chemistry cannot, in general, be inferred from experiments where the mean time between collisions is on the same order as molecular activation and decomposition, since an insufficient experimental or theoretical basis exists for deconvoluting the effects of collisional deactivation and energy pooling. Experimental constraints typically pose other problems. The use of tightly focused laser beams may introduce undesired (or uncharacterized) effects, and small fractional conversions suggest that the ensemble of reactant species may not be uniformly sampled.

Ion photodissociation spectroscopy constitutes an experimental approach that can, in principle, circumvent these difficulties. The utility of this method has been established in a variety of cases using ultraviolet or visible light sources.[3] Beauchamp and co-workers[4] have recently demonstrated that a relatively low power CW infrared laser can be used to induce the dissociation of some ions under conditions where collisions are competitive with photochemical processes. Our results indicate that extensive infrared multiphoton dissociation can be achieved in the absence of collisions using an unfocused laser beam. Additionally, we find that IR photodissociation spectroscopy may provide a useful probe of collisional relaxation of internal energy and suggest that, in the present case, relaxation may be less efficient than previously thought.[5]

Experiments are carried out in a pulsed ion cyclotron resonance spectrometer[6] in which ions are trapped for 1 s. The sequence of events is:

(i) Electron-beam pulse

$$NF_3 + e^- \rightarrow F^- + NF_2 \qquad (1)$$

(ii) Reaction

$$F^- + HCO_2CH_3 \rightarrow CH_3OHF^- + CO \qquad (2)$$

(iii) Laser pulse, photodissociation

$$CH_3OHF^- + nh\nu \rightarrow CH_3OH + F^- \qquad (3)$$

(iv) Detect CH_3OHF^-

The multimode output of a CO_2 TEA laser[7] is directed longitudinally through the cell and reflected out, approximately collinearly with the incoming beam. The laser fluence was typically 2-4 J/cm^2 in a beam about 1 cm^2. Reaction 2 is reported to be exothermic[8] by ca. 15 kcal/mol if the reactants are thermalized; however, dissociative attachment of an electron to NF_3 has been reported[9] to produce translationally hot F^-. We assume, based on the relative densities of states of the two product species, that a significant fraction of the reaction exothermicity is coupled into vibrational modes of CH_3OHF^-. (See below. Tests of this assumption are currently in progress.) Following the electron beam pulse the CH_3OHF^- signal rises exponentially as the F^- signal decays. Irradiation of the CH_3OHF^- at some time after the electron beam pulse (typically 300 ms but variable between 100 and 900 ms) results in a decrease in the CH_3OHF^- signal which is faster than the millisecond time resolution of the ICR. This decrease, which can be as large as 80%, is attributable[10] to reaction 3 and represents a conversion per pulse which is much larger than those typically observed in the multiphoton dissociation of neutrals. The threshold for (3) is reported[8] to be 24 kcal/mol. Other higher energy photoprocesses, for example, dissociation to CH_3O^- and HF, or photodetachment of an electron, are not observed. This is in accord with the estimated lifetime[11] for dissociation of CH_3OHF^- at threshold, $\tau_d(E_0) \approx 10^{-10}$ s. The relative cross section[12] is approximately independent of wavelength from 930 to 1090 cm^{-1} over the pressure range examined. With a laser delay of 300 ms, the fraction of CH_3OHF^- decomposed was found to decrease from 80% at about 1×10^{-6} Torr to a limiting value of 50% at 7×10^{-6} Torr. At a given pressure,[13] increasing the delay between the electron beam and laser pulses (from 100 to 900 ms) resulted in similar behavior. Control experiments indicate that this effect does not result from changes in the ion cloud–laser beam overlap. The simplest alternative explanation is collisional cooling of vibrationally hot ions during the trapping period prior to irradiation. We find that the extent of photodissociation decreases as the number of collisions before irradiation is increased from 10 to ca. 100. Increasing the number of collisions beyond this point results in no further change in the photodecrease, indicating that the ions are vibrationally thermalized after about 100 collisions. The collision frequency was calculated using the appropriate ADO collision rate constants[14a] and the absolute pressure of the gases.[14b]

The experimental approach outlined here constitutes an attractive alternative to the methods commonly used in studying multiphoton chemistry in neutrals. The time regimes for collisional and photochemical events differ by more than five orders of magnitude, so that the chemistry associated with either can be identified and studied. Additionally, a collimated, rather than focused, laser beam is used. Thus the energy density across the beam can be well characterized, and the relatively large beam diameter employed allows thorough sampling of the reactant population so that the "averaging" associated with the experiment is well defined and complete.

The approximate wavelength *independence* observed in this work may be associated with long-lived vibrational excitation in CH_3OHF^- so that absorption occurs from a quasi-continuum of ro-vibrational states populated by chemical (rather than laser[15]) activation. Alternatively, these results may arise from excitation of a continuous unstructured background observed for proton-bound species in condensed phases.[16]

It is generally assumed that internal energy in ions is collisionally equilibrated by ion-neutral collisions with cross sections that can approach the Langevin-ADO limit.[14] Some recent results suggest that vibrational relaxation via collisions can, in some cases, be quite inefficient.[17] In particular, Kim and Dunbar[18] have shown that, depending on the bath gas, 50 or more collisions may be required to remove 1.3 eV of internal energy from $C_6H_5Br^+$. Our results suggest that on the order of 100 collisions are required to cool CH_3OHF^- when it is vibrationally hot by ca. 15 kcal/mol even though the bath gas, methyl formate, should be an efficient collider (relative to, e.g., helium). Our results, in conjunction with those of Kim and Dunbar,[18] suggest that long-lived internal excitation may be a more pervasive phenomenon in ion chemistry than previously thought. This finding may have important implications for experiments designed to measure equilibrium and threshold-type quantities.

In summary, we have demonstrated the unambiguous, collisionless IR photodissociation of a negative ion in the gas phase. This technique is found to be a useful method for studying internal energy effects in multiphoton absorption and collisional energy transfer. The large (ca. 80%) fractional

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decreases observed here ensure that the ensemble of reactant ions is well sampled. Our initial results indicate that the collisional cooling of vibrationally hot ions may be a surprisingly inefficient process requiring on the order of 100 collisions.

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(7) Lumonics TEA-103-2. The pulse consisted of a 150-ns spike containing ca. 50% of the total energy, followed by a tail out to ca. 3 μs. Appreciable self-mode locking was evident when the pulse was viewed with a fast pyroelectric detector.

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(9) Harland, P. H.; Franklin, J. L. *J. Chem. Phys.* **1974,** *61,* 1621–1636, report that F^- formed from NF_3 may be translationally hot by 9 kcal/mol. The coupling of this translational energy to vibrational modes of CH_3OHF^- is currently being studied in our laboratory.

(10) During an experiment, thermal electrons are continuously removed by trapping plate ejection. F^- ion is routinely ejected by a double resonance pulse turned on simultaneously with the laser pulse. If F^- is not ejected, a transient decrease is observed followed by a full recovery of the initial CH_3OHF^- signal amplitude. This occurs since photochemically formed F^- reacts with methyl formate via eq 2 to regenerate CH_3OHF^-

(11) Estimated using quantum-RRK theory. See Robinson, P. J.; Holbrook, K. A. "Theory of Unimolecular Reactions"; Academic Press: New York, 1972.

(12) Calculated assuming ln $(I/I_0) = -\sigma F$ where I/I_0 is the ratio of signal heights with and without the laser and F is the number of photons per unit area. We anticipate that this will be a valid approximation in the limit where photodissociation is extensive.

(13) Pressure measured using an ionization gauge calibrated against a capacitance manometer.

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Early Events and Transient Chemistry in the Photohomolysis of Alkylcobalamins[1]

Sir:

Photoinduced metal-ligand homolysis is well established as a characteristic kind of reaction of transition metal complexes.[2,3] However, many features of such reactions have continued to be controverisal despite extensive investigations. Major points at issue have been the elucidation of the roles of geminate radicals trapped by a solvent cage and their excited state precursors.

Photochemical studies of complexes of cobalt have been relatively extensive and have been the basis of most of the discussions of photohomolysis in transition metal complexes.[2,3] The observed photochemical behavior[4-9] may be most simply described by the sequence of events: (1) absorption of radiation produces a Franck-Condon excited state (Y*), which (2) rapidly loses its excess vibrational energy ($k_v > 10^{11}$ s^{-1}) to form the thermalized excited state Y_0, followed by (3) product formation and internal conversion to the ground state from Y_0. At present, little can be said about whether or not additional excited states mediate product formation. Models which attribute all the details of variations of ϕ_R and product distributions to the behavior of radical pair species[2d,e] seem less in accord with observations.[2b,3] Heretofore, there have been no direct observations on the behavior of excited state or radical-pair precursors to the homolysis products in transition metal systems.

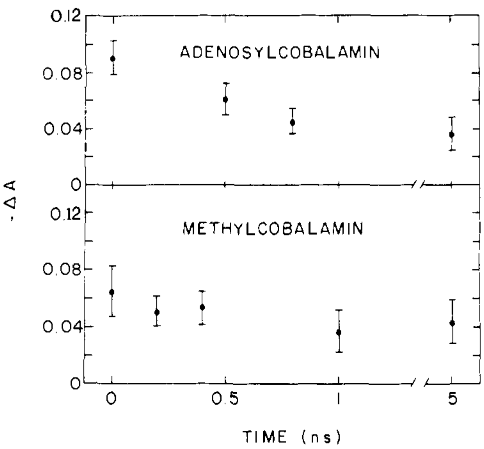

Figure 1. Time dependence of the substrate bleaching at 565 nm for both compounds studied. See ref 18 for experimental details.

Photohomolyses of organocobalt complexes are qualitatively similar to the patterns noted above.[9-12] The biological functioning of adenosylcobalamin (coenzyme B_{12}) is very often described in terms of thermal Co-L homolysis and complex free-radical reactions in the enzymatic environment.[13] Photohomolyses of organocobalamines or organocobaloximes are often studied to elucidate the chemistry of appropriate intermediate species.[14] Recently, in such a study of homolysis of adenosylcobalamin in aqueous propane-1,2-diol, Lowe and co-workers[15] found a several-fold increase in the cobalt (II) EPR signal when the irradiated frozen solutions were warmed; this was interpreted as indicating a precursor to the homolysis step and parallels were drawn to the free-radical mechanism proposed for function of the coenzyme.[13] However, a long-lived precursor stands in contrast to the interpretation of photohomolysis patterns[2b,3] outlined above.

In this paper we report our studies of the transient intermediates generated following irradiations of methyl- and adenosylcobalamin. For the study of primary homolysis fragments, we used a picosecond flash photolysis technique[16] employing 3-4-mJ, 527-nm pulses of ~6 ps duration and a visible continuum probe beam generated by pulsing CCl_4 with the 1054-nm laser fundamental.[17,18] These experiments were performed in aqueous solutions, approximately millimolar in the organocobalamin with 2-mm path length cells. The photolysis cross section was about 4.5 mm^2. Flash photolyses of aerated or deaerated aqueous and ~90% 2-propanol (~10% water) solutions were performed using techniques described previously.[3,11] The cobalamin substrates were obtained from Sigma Chemical Co. and solutions and compounds were handled in darkened rooms. Fresh samples were substituted after about 25 laser shots. No more than a few percent change in the photolyzed samples' absorbancy was noted under these conditions.

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