

from the d_{π} orbitals will decrease the amount of equatorial π -back-bonding to the porphyrin ring and, thus, diminish the increase in energy of the (π, π^*) states due to equatorial π -back-bonding. However, the axial π -back-bonding will result in increased stabilization of the d_{π} , maintaining the increased energy of the $(d_{\pi}, e_g(\pi^*))$ CT state over its position with no π -back-bonding interaction. A change from equatorial-to-axial π -back-bonding, then, should decrease the energy of the ${}^3T(\pi, \pi^*)$ state while leaving the energy of the $(d_{\pi}, e_g(\pi^*))$ CT state relatively unchanged.

Therefore, the model suggests that whether the lowest excited electronic state in the Ru^{II} porphyrins is the ${}^3T(\pi, \pi^*)$ or the $(d_{\pi}, e_g(\pi^*))$ can be modulated by the use of different axial ligands.^{1,2} Absorption and emission measurements and IEH calculations on a series of Ru^{II} porphyrins support this view,^{1,2} as do similar studies^{1,2} and picosecond experiments^{3,4} on Os^{II} porphyrins. The results of the picosecond investigations reported here for several Ru^{II} complexes also are in agreement with the predictions of the π -back-bonding model.

The effects of π -back-bonding on the photophysical behavior are most readily illustrated by comparing the assignment of the lowest excited states for the $Ru^{II}(\text{OEP})(\text{CO})(\text{L})$ complexes vs. $Ru^{II}(\text{OEP})(\text{P-}n\text{-Bu}_3)_2$. The π -back-bonding between Ru and the axially bound CO will have two effects: (1) It will reduce equatorial π -back-bonding between the metal and the porphyrin ring. This should lower the energy of the $e_g(\pi^*)$ orbitals and hence the ${}^3T(\pi, \pi^*)$ excited state. (2) Good Ru-CO axial π -back-bonding will push down the d_{π} orbitals in energy, thus maintaining or raising the energy of the $(d_{\pi}, e_g(\pi^*))$ CT state. The net effect of the Ru-CO back-bonding is a lowering of the ${}^3T(\pi, \pi^*)$ relative to the metal-to-ring (d, π^*) CT. We have assigned absorption difference spectra of Figure 1 (solid and inset) to the ${}^3T(\pi, \pi^*)$ in the three $Ru^{II}(\text{OEP})(\text{CO})(\text{L})$ complexes, L = EtOH, py, or 1-MeIm. The $\sim 75 \mu\text{s}$ relaxation kinetics measured by decay of room temperature absorption changes and emission are consistent with the ${}^3T(\pi, \pi^*)$ as the lowest excited state. The same conclusion has been drawn previously from photophysical studies on these or similar Ru^{II} porphyrins, as mentioned above.^{2,6,13,15}

Compared to CO, P-*n*-Bu₃ is a weaker π -acceptor and much stronger σ -donor.²³ Thus removal of CO as an axial ligand and

the concomitant change in importance from axial-to-equatorial π -back-bonding at the metal has the effect of raising the energy of the ${}^3T(\pi, \pi^*)$ relative to the (d, π^*) CT. The absorption difference spectrum observed upon excitation of this complex has the characteristics of a porphyrin metal-to-ring CT, as discussed above. The 12-ns lifetime also is consistent with the assignment of the (d, π^*) CT as the lowest excited state of this molecule.

Considering now $Ru^{II}(\text{OEP})(\text{NO})(\text{OMe})$, the nitrosonium ion, NO^+ , is an even stronger axial π -back-bonding ligand than is CO. The additional effect from the σ -donating OMe ligand establishes a push-pull bonding stabilization for the complex,² and a red shift of the ${}^1Q(\pi, \pi^*)$ ground-state absorption band (compared to the CO complexes) results from this bonding scheme. The Q bands for the $(\text{NO})(\text{OMe})$ complex are at 532 and 572 nm, while they are at 517 and 548 nm for the $(\text{CO})(\text{L})$ complexes studied here, as discussed in the Results section. Therefore, we expect that that for $Ru^{II}(\text{OEP})(\text{NO})(\text{OMe})$ the ${}^3T(\pi, \pi^*)$ will be lower in energy relative to the (d, π^*) as compared to $Ru^{II}(\text{OEP})(\text{CO})(\text{L})$. We assign the $<50 \text{ ps}$ and $\geq 5 \text{ ns}$ decays in the absorption changes (Figure 2A) to ${}^1Q(\pi, \pi^*) \rightarrow {}^3T(\pi, \pi^*)$ and ${}^3T(\pi, \pi^*)$ relaxation, respectively. This interpretation is similar to that given for the analogous Os^{II} complex.^{3,4} However, as pointed out above, the previous absorption measurements and the lack of 77 K emission provide evidence that predicted¹ $[(\pi, d_{\pi} + \text{NO}(\pi^*))]$ CT states may be involved in the triplet decay.¹

Finally, the $Ru^{III}(\text{OEP})(\text{P-}n\text{-Bu}_3)(\text{Br})$ complex has a half-filled d_{π} orbital, giving the possibility of a low-energy ring \rightarrow metal (π, d_{π}) CT excited state. This state may be responsible for the weak 710-nm band observed in the ground-state absorption spectrum. The presence of this low-energy quenching state appears to dominate the photophysical behavior, and it results in rapid relaxation in $\leq 35 \text{ ps}$.

Acknowledgment. This work was supported in part by the U.S. National Institutes of Health (AM 17989 and BRSG S07RR07054-17) and the Canadian Natural Sciences and Engineering Research Council. The U.S. National Science Foundation Chemical Instrumentation Program (CHE-8306587) provided partial support for the nanosecond apparatus. We thank Dr. Martin Gouterman for helpful discussion and Johnson Matthey Ltd. for the loan of ruthenium used for the present studies and the previous work described in ref 7.

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Product Branching in Infrared Multiple Photon Decomposition of Gas-Phase Ions. Mechanistic Implications for Proton-Transfer Reactions

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Abstract: Negative ions that lie on potential surfaces for proton-transfer reactions have been photolyzed in the gas phase with an infrared laser. The relative photodissociation yields of reactants and products of the proton-transfer reactions as well as the kinetics of the reactions themselves have been measured. The results provide details about the potential surfaces, mechanisms, and thermochemistry of these reactions.

Reactive intermediates are highly elusive,¹ but a complete understanding of a reaction mechanism necessitates knowledge of the structure and energetics of such species. Chemically activated intermediates such as those which occur in low-pressure,

gas-phase, ion-molecule reactions are especially interesting, because very little is known about them. The purpose of this work has been to probe potential surfaces of ion-molecule reactions (in particular, proton-transfer reactions) by means of infrared pho-

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tolysis of presumed intermediates.

Intermediates in ion-molecule reactions lie lower in potential energy than reactants and products, due to the long-range ion-dipole and ion-induced dipole forces between the discrete species. They are not observed in solution because the separated reactants and products are better stabilized by solvation than is the intermediate. In the gas phase, however, it is possible to form and trap such ionic species at energies below that of their lowest dissociation channel. Infrared laser radiation can, in principle, be used to activate such intermediates rapidly to energies comparable to those they possess during chemical reactions, and the competition between unimolecular reactions and further up-pumping may be directly observed.²

In this paper, experiments are described in which several putative proton-transfer intermediates are prepared in the gas phase and then decomposed rapidly with an infrared laser, producing either one or two sets of products. The systems studied include hydrogen-bonded complexes between alcohols and anions as well as covalently bound ions that could be formed by addition of nucleophiles to carbonyl compounds. The results suggest that even when reaction via an addition-elimination mechanism is conceivable, proton transfers proceed through hydrogen-bonded intermediates.

Experimental Section

Experiments were performed on a pulsed ion cyclotron resonance spectrometer modified for infrared photochemical measurements as previously described.³ The output of a Lumonics TEA 103-2 CO₂ laser was effectively collimated with a 5 m focal length gold-plated copper mirror, directed through the analyzer cell, reflected off a mirror behind the cell, and sent back out colinearly through the cell and entrance window to a beam stop. Duty cycles of 1–2 s were used to accommodate the laser recharge time. A variable-delay TTL pulse was used to trigger the laser. Removing the nitrogen component of the gas mixture eliminated the 3 μs pulse tail, leaving a 200 ns pulse of 1 J. The average intensity (flux) was thus increased by this procedure, but the fluence was decreased. Placing CaF₂ or polyethylene attenuators in the beam before the ICR cell reduced both fluence and intensity. Judicious choices of gas mixtures and attenuators therefore allowed the production of pulses with similar fluences but different intensities.

Photolysis products were determined in two different ways. First, mass spectra could be taken 20–50 ms after the laser pulse and compared to scans taken before irradiation. This method gave reliable branching fractions when no product ions reacted with any of the neutrals in the cell, as in the methyl acetate experiments. For the other systems, at least one product ion reacted with some neutral species to replenish the reactant ion supply, so that the second method was used. Double resonance ejection of each product ion after the laser pulse prevented the ensuing reaction, so that the difference between the reactant ion signal with and without double resonance ejection was equal to the size of the signal of the product ion of interest.

In all cases, the observed branching fractions were independent of wavelength. The extent of decomposition varied a great deal, so measurements were made with laser lines that effected the greatest signal decreases.

During the course of this work, the ICR detection system was changed from a marginal oscillator^{4,5} to a capacitance bridge detector.^{6,7} A Hewlett-Packard Model 3325A synthesizer/function generator replaced the marginal oscillator as the primary detection (ω_1) radio frequency source. A Wavetek Model 171 synthesizer/function generator was used as a double-resonance (ω_2) source. Experiments that had been performed with the marginal oscillator were repeated with the capacitance bridge detector, and identical results were obtained.

Ketene was produced by distilling diketene over a hot wire coil. Dimethyl peroxide was prepared according to the procedure of Hanst and Calvert.⁸ Neopentyl formate was prepared from neopentyl alcohol and

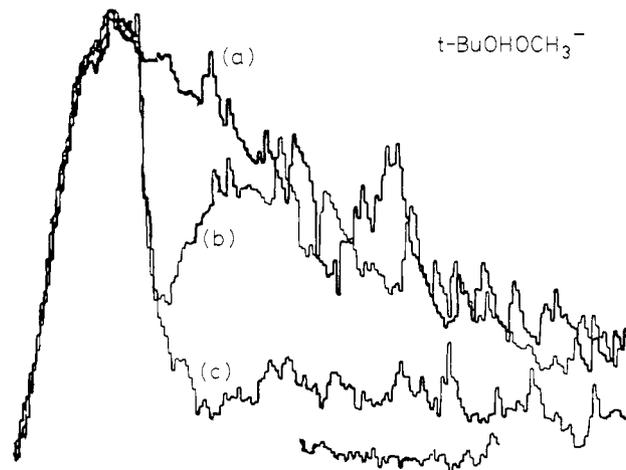
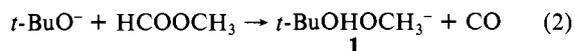
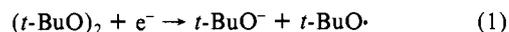


Figure 1. Time scans (1 s) of ion 1: (a) no laser, decay is nonreactive ion loss; (b) laser fired at 200 ms; (c) laser fired and *tert*-butoxide ejected afterwards by double resonance. The total pressure for these scans was 2.6×10^{-6} torr; laser fluence was about 1.5 J/cm^2 .

a formic/acetic anhydride reaction mixture by the procedure of Stevens and van Es.⁹ The esterification was allowed to proceed for 3 days. All other compounds were obtained commercially.

Results

t-BuOHOCH₃⁻. When the following reaction sequence was used, the complex ion *t*-BuOHOCH₃⁻ (**1**) was produced:



Analogues of reaction 2 may be carried out with a variety of anions and formate esters.^{10–12} This proton-bound complex between the methoxide and *tert*-butoxide ions is presumably the intermediate in the following proton-transfer reaction:



Substitution reactions of ions ROHOR⁻ have shown that the two alkoxide groups are chemically equivalent, and isotopic labeling experiments have shown that no hydrogen scrambling occurs between the two alkyl groups within the complex ion.¹⁰ A hydrogen-bonded ROHY⁻ structure has therefore been proposed for the products of reactions of anions Y⁻ with formate esters HCOOR. Since proton transfer between Y⁻ and RO⁻ must proceed through such a configuration, it is reasonable to conclude that these ions are in fact intermediates in proton-transfer reactions.

The enthalpy change for reaction 3 is the difference between the heats of deprotonation of methanol and *tert*-butyl alcohol. According to the standard table of gas-phase acidities,¹³ this reaction is exothermic by 6 kcal/mol.

Significant decomposition of ion **1** was achieved with the P(20), 9.6 μm line of the laser; about 65% of the ions were dissociated. After a steep drop at the laser pulse, the dimer signal always recovered to the level shown on time scans during which the laser was not fired. When *tert*-butoxide ion was ejected after the laser pulse, the signal did not recover (Figure 1). These observations

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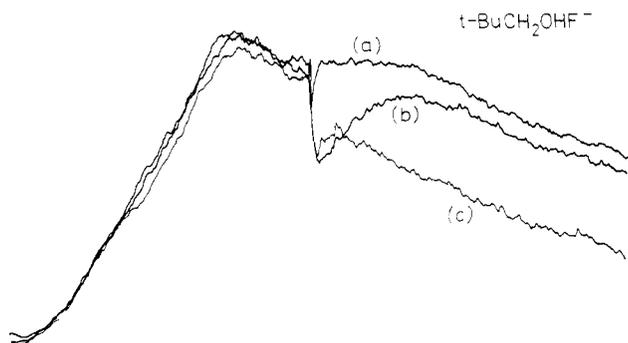
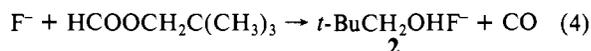


Figure 2. Time scans (1 s) of ion **2**: (a) no laser; (b) laser at 500 ms; (c) laser fired and fluoride ejected afterwards by double resonance. The difference between signals in parts a and b at 700 ms is the amount of neopentoxide formed; the difference between signals in parts b and c is the amount of fluoride formed. The pressure was 9.0×10^{-7} torr.

showed that *tert*-butoxide was the sole product of the decomposition and that complete regeneration of dimer **1** via reaction **2** occurred unless the *tert*-butoxide ions were ejected by double resonance.

The rate constant reaction **3** was measured; the best set of data yielded a rate constant of $1.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; compared to an ADO collision rate constant¹⁴ of $2.0 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, this rate constant corresponds to a reaction efficiency of 55%.

***t*-BuCH₂OHF⁻**. Since neopentyl alcohol and HF were believed to have gas-phase acidities that differ by less than 1 kcal/mol, according to literature values,¹³ the proton-bound complex between neopentoxide and fluoride was a logical candidate for branching upon photolysis. Consequently, neopentyl formate was prepared and allowed to react with fluoride ion (eq 4) to yield *t*-BuCH₂OHF⁻ (**2**), the likely intermediate in a nearly thermoneutral reaction (eq 5).



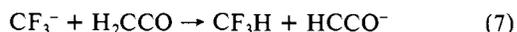
Fluoride ion was formed by the following reaction:



The best results for decomposition of ion **2** were achieved with the P(20), 10.6 μm laser line. More than 80% of the ions could be dissociated at fluences of about 3 J/cm². Both fluoride and alkoxide were formed in the decomposition. Although the alkoxide + HF product pair was believed to be lower in free energy, the fluoride + alcohol pair was the major product at all fluences used.² No intensity effect and only a modest fluence effect on the branching ratio was observed. The branching fractions were determined as above; fluoride was ejected after the laser pulse to prevent recovery of the dimer signal and to show the extent of decomposition; the difference between the recovered signal and the signal obtained without firing the laser gave the alkoxide yield, and the difference between the recovered signal and the fluoride ejection signal gave the fluoride yield (Figure 2).

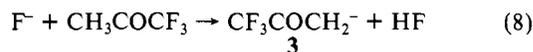
The rate constant for reaction **5** was also measured and found to be $2.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Dividing by the collision rate constant of $2.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ yields a reaction efficiency of about 12%.

CF₃COCH₂⁻. The infrared multiple photon decomposition of ion **3**, trifluoroacetone enolate, was also performed, because **3** is a possible proton-transfer intermediate. It must lie somewhere on the hypersurface containing the reaction coordinate of the following proton transfer reaction:

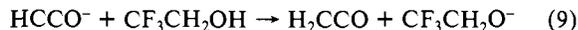


Ion **3** was prepared by deprotonation of the ketone by fluoride

ion (reaction 8). F⁻ was formed from NF₃ as before.



The thermochemistry of reaction **7** was not known, so a study of the acidity of ketene was carried out. Double-resonance experiments showed that the following reactions occur:



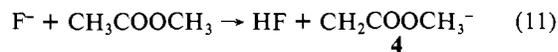
These results place the gas-phase acidity of ketene between those of the two alcohols,¹³ leading to an estimated heat of deprotonation of $365.7 \pm 1.5 \text{ kcal/mol}$. Ellison and co-workers have recently published¹⁵ the results of their bracketing studies of the acidity of ketene, which agree quite well with the above value. They report a heat of deprotonation of $365 \pm 2 \text{ kcal/mol}$, measured in a flowing afterglow apparatus.

It should be possible to determine the thermochemistry of the infrared multiple photon decompositions of ion **3**, because the enolate is the conjugate base of a molecule whose gas-phase acidity is known. There seems to be some controversy, however, about the heat of formation of 1,1,1-trifluoroacetone. Benson and O'Neal¹⁶ gave a value of -200.2 kcal/mol ; Dewar and Rzepa¹⁷ subsequently calculated the heat of formation to be -189.9 kcal/mol ; and Bartmess and McIver¹³ listed a value of -193.9 kcal/mol . The first and third values were estimated by group addivities; the second was a MNDO calculation with an uncertainty of 8.8 kcal/mol assigned by the authors. Because the MNDO calculation has a larger uncertainty than the additivity-based values, and because Bartmess and McIver cite an updated value for the contribution of the C-(F)₃(CO) group to the heat of formation, we use their value as given in ref 13. This leads to a heat of formation of -210.8 kcal/mol for ion **3**. Decomposition to $\text{HCCO}^- + \text{CF}_3\text{H}$ is therefore endothermic by 31 kcal/mol (11 photons), and dissociation to $\text{CF}_3^- + \text{H}_2\text{CCO}$ is endothermic by 41 kcal/mol (14 photons). Reaction **7** is thus exothermic by about 10 kcal/mol.

Up to 70% of the ions could be decomposed with the P(20), 9.6 μm laser line. The branching fraction, like that from **2**, was determined from the extent of enolate signal recovery; after photolysis, both CF_3^- and HCCO^- deprotonate trifluoroacetone to regenerate the enolate in a manner analogous to those described above. Representative data are depicted in Figure 3. In this case, branching fractions for the higher energy products of up to 40% could be obtained at high fluences, and these branching fractions showed a significant intensity dependence; more CF_3^- was produced at higher intensities.²

The kinetics of reaction **7** were also investigated. Again, the measured rate constant was rather slow: $4.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Since the collision rate constant for this system is $1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the reaction efficiency is approximately 31%. Ion **3** was not observed as a side product of the reaction. For the kinetic experiments, CF_3^- was formed by deprotonation of fluoroform by methoxide ion. Methoxide ion was prepared by electron impact on dimethyl peroxide.

CH₂COOCH₃⁻. A similar ion, $\text{CH}_2\text{COOCH}_3^-$ (**4**), was prepared by deprotonation of methyl acetate by fluoride ion (eq 11). The corresponding proton transfer here (eq 12) is exothermic by 16 kcal/mol.



Reaction **11** is only one of three reactions between fluoride ion and methyl acetate observed by José and Riveros.¹⁸ In addition

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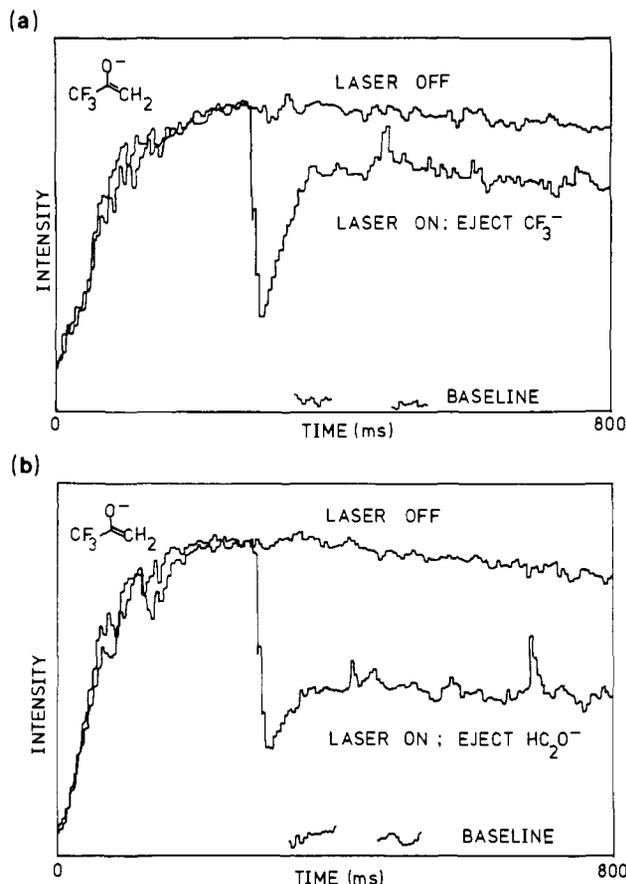
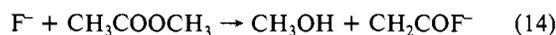


Figure 3. (a) Time dependence of the 1,1,1-trifluoroacetone enolate signal in the presence and absence of irradiation with CF_3^- ejected. (b) Time dependence of the 1,1,1-trifluoroacetone enolate signal in the presence and absence of irradiation with HC_2O^- ejected.

to proton transfer, $\text{S}_{\text{N}}2$ displacement (eq 13) and addition-elimination (eq 14) were also observed. Nucleophilic substitution



is exothermic by 19 kcal/mol, but it was not observed to occur in our experiments. Addition-elimination was observed and is exothermic by 5 kcal/mol. Proton transfer occurred although it is exothermic by only 0.5 kcal/mol.

An explanation for Riveros' observation of a reaction pathway undetected in our experiments is suggested by the different methods of forming F^- used in the two laboratories. The neutral precursor used here, as mentioned above, was NF_3 . Harland and Franklin¹⁹ have shown that at the resonance maximum of 1.7 eV, F^- formed from NF_3 has only 0.78 eV excess translational energy. José and Riveros, on the other hand, produced fluoride by impact of 4.2-eV electrons on sulfonyl fluoride. It has been shown²⁰ that fluoride ions formed from SO_2F_2 at this electron energy have about 2.8 eV excess energy. Apparently, the additional energy enables the ions to react via a pathway not accessible to thermalized ions.

In any case, the addition-elimination product, the enolate of acetyl fluoride, did not absorb the infrared radiation enough to cause decomposition on any laser line, as confirmed by separate experiments on that ion alone. The photochemistry of **4** was therefore unaffected by side reaction 14.

Decompositions of up to 50% were observed at the laser pulse, with the P(22), 9.6 μm laser line; there was no signal recovery after the pulse occurred (Figure 4). HCCO^- is not basic enough

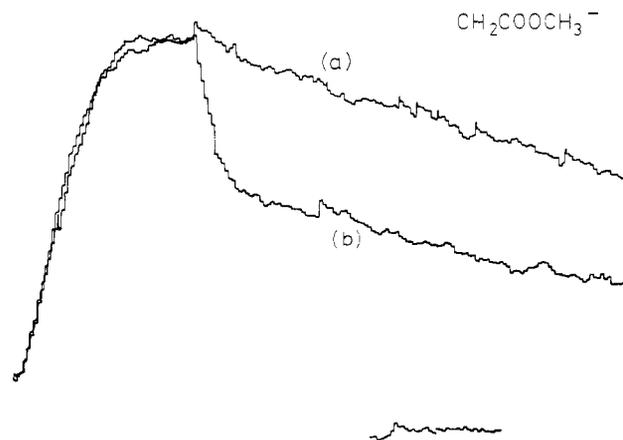


Figure 4. Time scans (1 s) of ion **4**: (a) no laser; (b) laser at 300 ms. The pressure for these scans was 7.7×10^{-7} torr; fluence was about 2 J/cm^2 .

Table I. Proton-Transfer Reaction Rates

reaction	ΔH° (kcal/mol) ^a	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	ϵ (%)
$\text{CH}_3\text{O}^- + t\text{-BuOH}$	-6	1.1×10^{-9}	55
$\text{F}^- + t\text{-BuCH}_2\text{OH}$	+2.5	2.9×10^{-10}	12
$\text{CF}_3^- + \text{H}_2\text{CCO}$	-10	4.2×10^{-10}	31
$\text{CH}_3\text{O}^- + \text{H}_2\text{CCO}$	-18	1.4×10^{-9}	83

^a Tabulated values from ref 13 and ref 29.

to abstract a proton from methyl acetate; that reaction is endothermic by 5.3 kcal/mol. Methoxide, however, is sufficiently basic; deprotonation of methyl acetate is exothermic by 8.2 kcal/mol. The lack of signal recovery demonstrates that no methoxide ion reacted with methyl acetate by either proton transfer or addition-elimination. No acetate ion appeared after the laser pulse, so no methoxide ion reacted by nucleophilic substitution either. Mass scans showed only HCCO^- as a photolysis product, so ion **4** does not exhibit branching upon decomposition.

The thermochemistry of the two lowest dissociation pathways is known for this system. When the heat of deprotonation of ketene discussed above is used, decomposition to methoxide + ketene is estimated to be 49 kcal/mol uphill, while decomposition to methanol + HCCO^- is endothermic by 33 kcal/mol. At least 11 infrared photons are required to decompose ion **4**.

The rate of reaction 12 was found to be quite fast. Deprotonation of ketene by methoxide ion proceeds with a rate constant of $1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The collision rate constant for this ion-molecule pair is estimated to be $1.7 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, so the efficiency was determined to be 83%.

CH_3OHF^- . Infrared photolysis of the CH_3OHF^- ion, **5**, which has been previously described,²¹⁻²³ is relevant to the results discussed above. Like ions **1** and **2**, it is a proton-bound complex between two anions; as such, it is an obvious proton-transfer intermediate. In this case, the proton transfer is described by the reaction



This reaction is exothermic by about 10 kcal/mol.

Ion **5** was formed by reaction of fluoride ion with methyl formate; F^- was prepared from NF_3 as described above (eq 6). Infrared photodissociation of **5** produced fluoride as the only ionic product; methoxide was never observed, even at the highest fluences and intensities possible with our apparatus. These results are certainly consistent with the photolysis of **1**, since no branching was observed in that system either. The kinetics of reaction 15

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Table II. Decomposition Pathways for Putative Proton-Transfer Intermediates

reactant	products	ΔH° (kcal/mol)	obsd? ^a
1. <i>t</i> -BuOHOCH ₃ ⁻	<i>t</i> -BuO ⁻ + CH ₃ OH	+18.9 ^b	yes
	CH ₃ O ⁻ + <i>t</i> -BuOH	+24.8 ^b	no
2. <i>t</i> -BuCH ₂ OHF ⁻	F ⁻ + <i>t</i> -BuCH ₂ OH	+34 ^c	yes
	<i>t</i> -BuCH ₂ O ⁻ + HF	+36.5 ^c	yes
3. CH ₂ COOCH ₃ ⁻	HCCO ⁻ + CH ₃ OH	+33	yes
	CH ₃ O ⁻ + H ₂ CCO	+49	no
4. CF ₃ COCH ₂ ⁻	HCCO ⁻ + CF ₃ H	+31	yes
	CF ₃ ⁻ + H ₂ CCO	+41	yes
5. CH ₃ OHF ⁻	F ⁻ + CH ₃ OH	+30 ^c	yes
	CH ₃ O ⁻ + HF	+40 ^c	no

^aOnly the ionic product was observed. ^bCaldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660–4667. ^cEstimate based on Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944–2950 and ref 29.

were not studied, because our ICR vacuum system is not equipped to handle HF.

The proton-transfer pathways, kinetics (where known), and possible photochemical pathways are summarized in Tables I and II.

Discussion

Product branching is one possible result of the kinetic competition between a unimolecular decomposition and absorption of infrared photons. In general, a molecule at a given internal energy level has three collisionless pathways out of the level: absorption of another photon, stimulated or spontaneous emission of a photon, and dissociation (if the internal energy is above the threshold for reaction). Electron autodetachment is also a possibility for some systems.²⁴ While the rate constant for further absorption is proportional to the light intensity and the cross section for absorption,^{25,26} the rate constant for unimolecular decomposition is a rapidly increasing function of energy above threshold, corresponding to the increasing sum of quantum states for the transition state of the decomposition reaction. Up-pumping will continue until decomposition occurs faster than further absorption. A typical cross section for absorption of a photon is 10⁻¹⁹ cm², while a typical intensity value is 10²⁶ photons cm⁻² s⁻¹. An average rate constant for pumping from one level to the next is therefore about 10⁷ s⁻¹.

The requirements for observation of multichannel decomposition are the following: (1) the pumping rate constant must be large enough, (2) the thresholds must be close enough in energy, and (3) the decomposition rate constants for the lower channel must be small enough so that the reactants have a chance of being energized past a second threshold. Since most species do not show branching even upon excitation with a high-power pulsed CO₂ laser,²⁷ observation of products of a secondary reaction channel implies either that the two thresholds are close in energy or that the rate constant for the first channel is relatively small. Most of the known examples of branching involve a lower channel whose rate constant is significantly smaller than that of an upper channel (above both thresholds) due to a difference in transition-state tightness.²⁷

For the proton-bound dimers **1**, **2**, and **5**, each possible decomposition channel is a simple cleavage reaction (Figure 5). The tightness of the transition states for these channels is quite similar, so the branching is controlled by the thermochemistry. The product ratios therefore give a good indication of how far above the lower threshold the ions can be pumped before decomposing.

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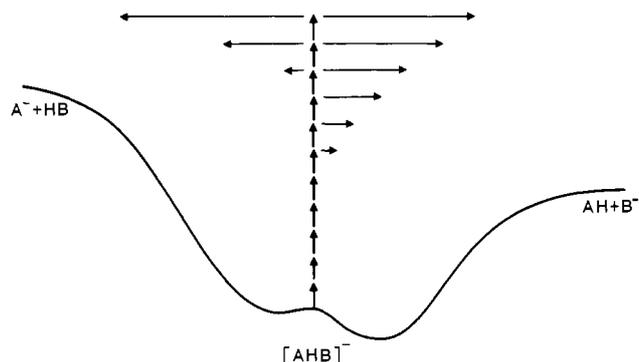
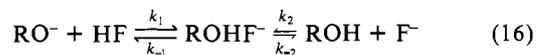


Figure 5. Generalized branching scheme for the proton-transfer intermediate. Vertical arrows represent photon absorption rate constants; horizontal arrows represent unimolecular decompositions of the intermediate. In this example, the upper decomposition channel has a looser transition state; the rate constant for dissociation increases faster with energy than does the rate constant for the lower channel.

In the case of **1**, the ion is sufficiently large and the channels are sufficiently far apart that one would not expect branching to be observed. For **5**, however, the ratio of the sums of states in the product channels suggests that branching might be measurable if the threshold energy for the second channel were exceeded. Thus, the lack of observed branching of **1** and **5** shows that decomposition must complete favorably with further pumping at energies below the onset of the second threshold (i.e., less than three photons above the lower threshold). This conclusion is in accord with known rates of decomposition at threshold for molecules of this size as compared with the estimated optical absorption rate constant of ca. 10⁷ s⁻¹.

The decomposition of **2** is in good accord with this picture. Absorption of one photon past the lower threshold drives the internal energy past the upper threshold as well. Consequently, we see branching, although the lower energy fluoride product always dominates, particularly at low fluence.² Low-power continuous-wave CO₂ lasers have in fact been previously used in positive ion systems to determine conclusively which of several channels has the lowest threshold.²⁸ In the case of **2**, the photochemical results suggest that not only is the fluoride-producing channel lower in enthalpy but also it is lower in free energy as well. (We base this conclusion on the assumption that since formation of the complex appears to be essentially barrier free, the transition-state energetics are a good reflection of those of the final product.) This observation led us to question²⁹ the thermochemistry¹³ of alcohol acidities relative to that of HF. Measurement of the rates of proton transfer from F⁻ to neopentyl alcohol and benzyl alcohol suggests that HF is indeed more acidic than neopentyl alcohol,²⁹ a result which also resolves a long-standing problem in the area of O–H bond strengths in alcohols. Other plausible explanations have been advanced² for both the branching fraction of ion **2** and the slow rate of reaction **5**, but we feel that both of the results are more easily explained if a revision is made in the thermochemistry. The observed branching fraction varies from 100% to 80% fluoride ion depending on fluence. For a reaction involving an intermediate (or rapidly converting intermediates), one can write



where k_1 and k_2 are the collision rate constants. At chemical equilibrium, $K = k_1 k_{-2} / k_2 k_{-1}$. On the basis of an estimated equilibrium constant²⁹ of 18 and $k_1/k_2 = 0.6$, we expect $k_{-2}/k_{-1} = 29$, or a branching fraction of 97%, in good agreement with the observed infrared induced result.

The results of the photolyses of **1**, **2**, and **5** are consistent with rates of cleavage reactions that increase rapidly enough with

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increasing energy so that almost no reactant ions exist at energies corresponding to three or more photons above threshold. The substantial branching of **3**, on the other hand, implies that the rate constant for reaction via the channel of lowest energy is significantly slower than the corresponding decompositions of the proton-bound dimers. This observation is consistent with a reaction that is not a simple cleavage. Direct formation of $\text{HCCO}^- + \text{fluoroform}$ is a four-center elimination process which would be expected to be slow compared to cleavage reactions for both energy and entropy reasons. Such eliminations in neutral systems³⁰ exhibit activation energies of about 50 kcal/mol and A factors of approximately $10^{13.5}$. Thus we expect that the elimination of fluoroform from the enolate ion is kinetically less favorable than the cleavage to CF_3^- and ketene at all energies, despite being more favorable thermodynamically.

If the elimination is indeed slow, we would expect that it would not be able to compete with the kinetically favored cleavage reaction. Elimination should be so slow as to be unobservable, or at least the minor pathway. Neither of these predictions is borne out by the data. The well-defined intensity effect on the branching ratio² indicates that decomposition at higher energies increasingly favors CF_3^- formation over HCCO^- formation, whereas a competition between the two direct reactions would be expected to result in exclusive production of CF_3^- at energies below the activation energy for the elimination process, with a gradually increasing but always minor branching fraction for HCCO^- at energies above that second threshold.

Supportive evidence against the direct elimination of fluoroform from ion **3** comes from the unimolecular reactions of trifluoroacetone itself.¹⁶ The neutral species does not undergo four-center elimination in either of its two lowest decomposition pathways; rather, it cleaves to yield CF_3 or CH_3 radicals with activation energies greater than 80 kcal/mol. Any concerted elimination pathway would have to have an even larger activation energy. The appearance of elimination products in preference to cleavage products in the ion photolysis suggests strongly that an alternative mechanism for decomposition is available to the isoelectronic ion.

These considerations suggest that the branching of **3** is not due to competing photochemical reactions as is the decomposition of **2**. The data are consistent with photochemical formation of a single vibrationally excited intermediate which can react to give either set of products. Although the intermediate could conceivably absorb additional photons and itself branch photochemically, ion **3** does not. The intensity dependence of the branching fraction is accounted for if the process leading from the intermediate to HCCO^- has a lower threshold energy but a tighter transition state than that for decomposition to CF_3^- . The photochemical intermediate, like ion **3**, must be lower in potential energy than both the reactants and products of reaction 7.

We propose that the photochemically formed intermediate is the $(\text{CF}_3 \cdots \text{H}_2\text{CCO})^-$ proton-bound complex that would correspond to the first of the two wells in a standard proton-transfer potential surface.³¹ This complex has two reaction pathways: the reactant channel (CF_3^-) and the product channel (HCCO^-). The former is a simple dissociation with a higher threshold energy but a looser transition state. The latter pathway has a lower threshold but a tighter transition state, since it involves passage over the tighter proton-transfer barrier. (The existence of this barrier is consistent with the relative inefficiency of reaction 7 despite its exothermicity; see below.) Once having crossed the barrier, the resulting complex dissociates rapidly to products.

McDonald and Chowdhury³² have also observed decomposition of an enolate ion to a CF_3^- -neutral complex which then follows a standard proton-transfer reaction coordinate. In their chemical activation system, the $\text{CH}_2=\text{CHCH}_2\text{C}(\text{CF}_3)\text{COOCH}_3^-$ ion did not have sufficient energy to branch upon dissociation. The

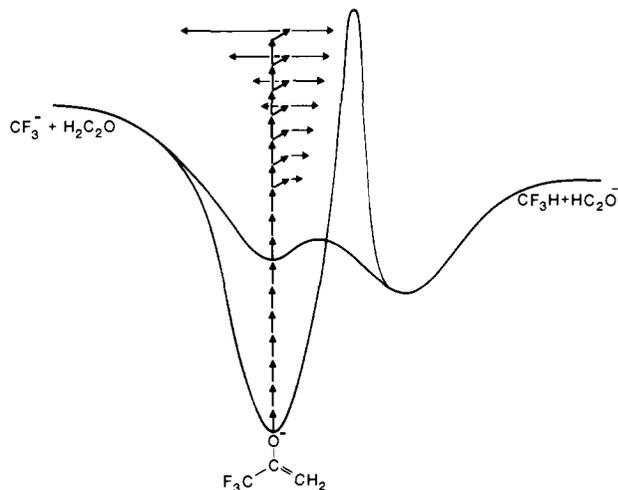
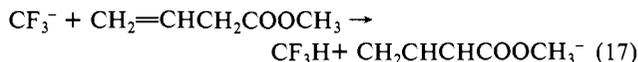


Figure 6. Proposed potential surface for $\text{C}_3\text{H}_2\text{OF}_3^-$. The double-well curve represents the reaction coordinate for proton transfer. Vertical arrows represent infrared pumping of ion **3**. Diagonal arrows represent rearrangement of ion **3** to hydrogen-bonded intermediate. Horizontal arrows represent unimolecular reactions of intermediate: dissociation to reactants (left) and proton transfer leading to products (right). The large peak represents a barrier to direct four-center elimination of fluoroform from the enolate.

corresponding proton-transfer reaction, eq 17, is exothermic by at least 15 kcal/mol. Even if a lower channel is hindered by some kind of barrier, branching is not observed in these systems if the corresponding proton-transfer reaction is sufficiently exothermic.



Evidence for a two-step decomposition in the IR photolysis of another anion has recently been advanced.³³ Deuterium isotope effect studies on the multiple photon dissociation of the *tert*-butoxide ion suggested that a C-C bond cleaves to form an ion-molecule complex, which then undergoes an internal abstraction reaction to form acetone enolate ion plus methane. A large secondary isotope effect with a large laser intensity dependence suggested that four-center elimination of methane does not occur.

At low enough pumping rates the photochemical intermediate is formed with energy sufficient only to give proton transfer. As the internal energy increases past the threshold for dissociation to $\text{CF}_3^- + \text{H}_2\text{CCO}$, the branching fraction for that pathway goes from zero (all proton transfer) to roughly equal amounts of both products. This occurs because the looser transition state for the dissociation channel causes that rate constant to increase much faster with energy than the rate constant for the proton transfer to give $\text{CF}_3\text{H} + \text{HCCO}^-$. The experimental efficiency of 31% observed in reaction 7 demonstrates that 69% of the complexes decompose back to reactants at thermal energies. Our maximum photochemical branching fraction, however, is about 40%. Therefore, the CF_3^- -ketene complex is prepared with less internal energy than it acquires by a capture collision between the two fragments at room temperature, even at our highest fluences. This is quite reasonable since the intermediate itself is much more stable than the reactants. The hydrogen-bonded complex consequently follows the same behavior as ions **1**, **2**, and **5**; it decomposes within several photons above threshold.

The photochemical results therefore provide insight into which mechanism the system in reaction 7 chooses to follow. Ion **3** lies along the addition-elimination reaction coordinate. When rapidly energized, it reacts to form an intermediate on the other reaction coordinate rather than undergoing the four-center elimination to yield products directly (Figure 6). The elimination step is so unfavorable as to outweigh the favorable addition step; the reaction proceeds through proton-bound complexes as the others do.

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Even though the proton transfer probably proceeds through hydrogen-bonded complexes, addition of CF_3^- to the carbonyl group may occur on some collisions, yielding enolate ion **3** directly. This is not a productive pathway, in the sense that it is simply reversible (at low pressure) formation of a nonreacting intermediate, so it cannot affect the apparent rate of reaction **7**. It may influence the dynamics, however, in that the total lifetime of all the intermediates will be greater than if the enolate were not a feature on the potential surface. One might therefore expect to observe a lower pressure onset for third-body stabilization reactions of $\text{CF}_3\text{COCH}_2^-$ than for intermediates of other proton-transfer reactions.

Given that trifluoroacetone enolate branches in these photochemical reactions, one might expect methyl acetate enolate to do the same, but it does not. This is probably caused by two factors. First, the resonant mode in **4** is probably a weaker absorption than the intense C-F stretching mode that is undoubtedly being pumped in the decomposition of **3**. The absorption rate constants are thus smaller, and decomposition occurs before the ion has been pumped far above threshold. Second, the difference between channels is 6 kcal/mol greater than that for dissociation of **3**. The results of the photolyses of **1** and **5** indicate how quickly the rate constant for decomposition may increase with increasing energy; it is not unreasonable that no branching occurs if this process also involves an intermediate whose lowest threshold energy decomposition pathway yields HCCO^- . Furthermore, if the large difference in reaction efficiency between reactions **7** and **12** does not simply reflect their relative exothermicities, then CF_3^- has a larger barrier to proton transfer from ketene than methoxide does and is therefore less likely to react via the lower decomposition channel.

The total dissociation yield, even in branching systems, should depend primarily on fluence rather than intensity,³⁴ and this holds true for the decompositions of **2** and **3**. Plots of $-\ln$ (fraction undecomposed) vs. fluence are linear if steady-state energy distributions are formed during irradiation;³⁵ data for ion **2** are linear when depicted in such a plot. This suggests that if ion **2** exists as two asymmetric hydrogen-bound isomers that interconvert extremely slowly,² the two complexes absorb infrared photons at identical rates. Subpopulations that are pumped at different rates

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yield bent fluence curves.^{22,23} A small intensity effect on total yield is observed in the photolysis of **3**, however. We infer that there is a modest bottleneck in the pumping process, so that the total energy absorption is slightly intensity dependent. Intensity effects on dissociation yield are strongly dependent on the particular molecules involved; some species show no effects³⁶ and some show large ones.^{37,38}

Conclusions

Insofar as the aforementioned results represent general phenomena, several conclusions may be drawn. First, on the basis of the observed photochemical behavior of ion **2** and on subsequent additional work, we conclude²⁹ that the currently accepted values of the relative gas-phase acidities of alcohols and HF are in error by approximately 2.2 kcal/mol. Second, on the basis of the observed branching behavior of ion **3** and available kinetic data on four-center elimination reactions, we conclude that proton transfers do not proceed by addition-elimination reactions even when the addition complex is a very stable species on the potential-energy surface. Finally, an ion decomposing to elimination products need not do so directly but can decompose to an ion-molecule complex and then transfer a proton within the complex. This mechanism has been previously suggested for positive ion systems.³⁹⁻⁴²

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Registry No. CH_3O^- , 3315-60-4; *t*-BuOH, 75-65-0; F^- , 16984-48-8; *t*-BuCH₂OH, 75-84-3; CF_3^- , 54128-17-5; H_2CCO , 463-51-4.

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Origin of the Temperature-Dependent Product Variation in Carbene Reaction with Alcohol

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Abstract: Extraordinarily temperature-dependent product variation in the reaction of carbene with alcohol has been investigated by ab initio MO theoretical calculations of the potential energy barrier along the IRC (intrinsic reaction coordinate) path on the hypersurface. The classical rate constants along the one-dimensional IRCs were calculated and compared with those including a quantum-mechanical tunneling effect. The extraordinary observation originates from the stable intermediate formation at low temperatures in the singlet carbene insertion reaction into the O-H bond of alcohols. The contribution of the triplet carbene is not important. The classical mechanism and the tunneling gave the same conclusion. The normal mode of vibration of imaginary frequency at the saddle point is approximately the displacement of a hydrogen atom only in all the reactions investigated. However, not only the hydrogen atom displacement but also the whole structure change along the IRC path contribute to the tunneling process.

I. Introduction

A few years ago, Tomioka and Izawa reported an extraordinarily temperature-dependent product variation in the reaction of carbene with alcohol; i.e., irradiation of phenyldiazomethane

(**1**) in degassed 2-propanol in a quartz tube at 20 °C gave 2-propyl benzyl ether (77%) as a main product (O-H insertion), but irradiation of **1** in frozen 2-propanol matrix at -196 °C gave the C-H insertion products in high yield (78%) with a sharply reduced