Ia   Ib

configuration is achieved, negative charge must localize on the α carbon for the proton transfer to proceed. These factors can act to raise the energy of the proton-transfer barrier E_1 for enolate ions with low oxygen basicities, and, as a result, addition (mainly through carbon) becomes competitive or even dominant. The implication here is that the proton transfers observed for all of the aldehyde enolates and acyclic or larger ring ketone enolates are occurring mainly through oxygen. Unfortunately, we cannot confirm this hypothesis directly since the neutral enol products cannot be detected directly in our experiments.

It is instructive to consider the differences in reactivity between DMFU and CH_3COCF_3 (eq 7) since their gas-phase acidities are similar and their structures are comparable. Trifluoroacetone does not yield an adduct with any type of enolate ion, despite the fact that addition to the carbonyl (through carbon) is estimated to be more exothermic than proton transfer for most enolates. This could imply the existence of an unusually high barrier to nucleophilic addition in CH_3COCF_3, but this is unlikely for several reasons. While the presence of barriers to carbonyl addition have been demonstrated experimentally,[3,55] computational studies have suggested that they are quite small when addition is exothermic.[53,54,56] Moreover, for certain dipole-aligned approach vectors of the anionic nucleophile and the carbonyl compound, no barrier at all is found in the calculations.[50] Thus, the absence of an observable adduct in the enolate ion/CH_3COCF_3 reactions is probably not due to a kinetic barrier preventing exothermic addition. Rather, it is more likely that it is due to facile reversion of the tetrahedral addition complex back to a hydrogen-bonded complex which readily undergoes proton transfer. That is, the tetrahedral adduct is not sufficiently long-lived for efficient collisional stabilization by the helium buffer gas. The analogous

barrier separating the adduct III and the hydrogen-bonded intermediate I in the anion/DMFU reactions is likely to be much higher. When the adduct III forms, charge is extensively delocalized in the aromatic cyclopentadienyl ring, and the localization of charge that is required to reform intermediate I is energetically unfavorable. Accordingly, the adduct is relatively long-lived and undergoes efficient three-body stabilization.

Conclusions

6,6-Dimethylfulvene is a sensitive probe of the relative nucleophilicity and kinetic basicity of gas-phase anions. Charge delocalization appears to be the most important intrinsic property controlling anion reactivity. Localized anions react exclusively by proton transfer, while the behavior of delocalized anions is determined by the nature of the charge stabilizing substituent. Delocalized carbanions such as allyl, benzyl, and cyanomethyl anion react as both Brønsted and Lewis bases; certain resonance stabilized carbanions such as the aldehyde enolates and acyclic ketone enolates react only as Brønsted bases. Amide enolates, ester enolates, and small-ring ketone enolates show a greater tendency to act as Lewis bases. The observed reactivity patterns strongly suggest that the Brønsted and Lewis acid–base channels arise from kinetically distinct intermediates. The initially formed intermediate is proposed to be an electrostatically bonded ion-molecule complex that can either undergo proton transfer or rearrange to an excited adduct. Subtle changes in the electronic configurations of the reactant ions can affect the relative heights of the potential energy barriers for these two channels, and the reaction-branching ratios are kinetically determined by the microscopic partitioning of each system over these barriers. The differences observed for the enolates are attributed to the relative basicities of the oxygen and carbon ends of the ambident ions. The kinetically preferred intermediate involves a hydrogen bond between the DMFU proton and the enolate oxygen. Proton transfer either occurs directly, or, if energetically unfavorable, rearrangement of the intermediate occurs followed by both proton transfer and addition.

Mechanistic Studies of Gas-Phase Negative Ion Unimolecular Decompositions. Alkoxide Anions
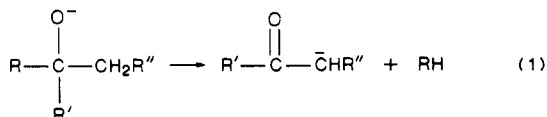
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Abstract: The unimolecular decompositions of 15 gas-phase alkoxide negative ions have been studied by infrared multiple photon photochemical activation in an ion cyclotron resonance spectrometer. Upon pulsed CO_2 laser irradiation, alkoxide anions undergo elimination of neutral molecules (e.g., alkanes RH) to yield enolate anions. The observed reactivity patterns and kinetic isotope effects further establish a stepwise decomposition mechanism involving initial heterolytic cleavage to an intermediate anion–ketone complex followed by proton transfer to give the ultimate products. A relative order of leaving group propensities $CF_3 > Ph > H > t$-Bu $>$ Me $> i$-Pr $>$ Et was observed. The apparent anomalous reactivity order for the alkyl groups can be rationalized by invoking a change in mechanism to one involving an intermediate in which an electron is not bound specifically by the eliminated alkyl group for R = t-Bu, i-Pr, and Et: either a radical–ketone radical anion complex produced by homolytic cleavage or an anionic cluster. This order also leads to the conclusion that methane elimination from alkoxide anions proceeds via the pathway involving heterolytic cleavage. The results of this study have implications for bimolecular ion–molecule reaction dynamics, since the photochemically generated intermediates are also intermediates in bimolecular proton transfer reactions.

Infrared multiple photon (IRMP) photochemical studies of gas-phase ions trapped in an ion cyclotron resonance (ICR)

spectrometer can provide insight into the mechanisms and dynamics of unimolecular ion decompositions.[1,2] This paper de-

Gas-Phase Negative Ion Unimolecular Decompositions

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scribes a general investigation of the unimolecular reactions of gas-phase alkoxide anions in which neutral molecular fragments (such as alkanes) are eliminated to produce enolate anions upon pulsed CO_2 laser activation.

$$R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-CH_2R'' \longrightarrow R'-\overset{\overset{\displaystyle O}{\|}}{C}-\bar{C}HR'' + RH \qquad (1)$$

Unimolecular reactions of gas-phase ions present very interesting mechanistic possibilities, in that ion–molecule complexes may intervene as intermediates. Since ions and neutrals have a large attraction due to ion–dipole and ion–induced dipole interactions, these complexes may be sufficiently long-lived that rearrangements and ion–molecule reactions, such as hydrogen transfers, may occur prior to their dissociation. Without careful studies, these interesting stepwise pathways cannot be distinguished from possible concerted reactions. There is now considerable precedent for the intermediacy of ion–molecule complexes in unimolecular reactions of positive ions.[3,4] We have recently reported a stepwise decomposition for a negative ion system as well. A stepwise mechanism involving initial cleavage to an intermediate ion–molecule complex was established for the IRMP-induced elimination of methane from *tert*-butoxide anion (to yield acetone enolate anion) through competitive isotope effect studies.[5,6] This mechanistic proposal was based on the magnitude and energy dependence of both primary and secondary hydrogen isotope effects. The observations could not, however, be used to distinguish whether the initial cleavage was heterolytic or homolytic.

Herein, we present results that provide further evidence for a general stepwise decomposition mechanism for alkoxide anions[7–9] and also address particular aspects of this mechanism. The product distributions from a number of alkoxide anions provide insight into the structure of the intermediate complex. The elucidation of a heterolytic stepwise mechanism, with some constraints, is reported. In addition, a general order of leaving group propensities has been assigned. One finding of this study is an apparent anomalous reactivity order for the simple alkyl groups. The implications and origins of this reactivity are discussed. Finally, the results from this study have implications for bimolecular ion–molecule reaction dynamics, since the photochemically generated intermediates are also intermediates in a class of bimolecular proton transfer reactions.

Experimental Section

Materials. Nitrogen trifluoride (Ozark Mahoning) was used as received. 2-Propanol (Aldrich) was distilled from sodium metal under an

atmosphere of nitrogen. 2-Phenyl-2-propanol (Aldrich) was purified by fractional vacuum distillation prior to use. The following alcohols were obtained commercially and used without further purification: 2,3,3-trimethyl-2-butanol, 2-methyl-3-ethyl-3-pentanol, and 3-methyl-2-pentanol (Wiley); 2,3-dimethyl-2-butanol, 2-methyl-2-butanol, 2-methyl-2-pentanol, 3-ethyl-3-pentanol, and 1-phenylethanol (Aldrich).

Several alcohols were prepared by Grignard reactions following standard literature procedures. 2-(Trifluoromethyl)-2-propanol was prepared by the addition of methylmagnesium bromide (Aldrich) to 1,1,1-trifluoroacetone (Aldrich) in ether. The trideuteriated alcohol, 2-(trifluoromethyl)-2-propanol-*1,1,1-d₃*, was prepared in an analogous manner with methyl-*d₃*-magnesium iodide generated from iodomethane-*d₃* (Aldrich, 99+ atom % D). Both alcohols were isolated in ca. 50% yield after fractional distillation at atmospheric pressure (bp 80–81 °C). Pure (by GC) 2-phenyl-2-propanol-*1,1,1-d₃* was prepared by the addition of methyl-*d₃*-magnesium iodide to acetophenone (Aldrich) and subsequent vacuum distillation (101–102 °C (17 Torr)).
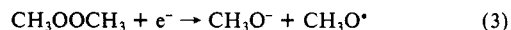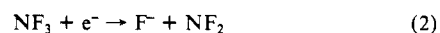
2,2-Dimethyl-3-ethyl-3-pentanol and 2,2,4-trimethyl-3-ethyl-3-pentanol were synthesized by the reaction of *tert*-butyllithium (Aldrich) with 3-pentanone (Aldrich) and 2-methyl-3-pentanone (Wiley) respectively following procedures detailed in the literature.[10] Under the reaction conditions, deprotonation of the starting ketone was competitive with addition to the ketone, so a significant amount of adducts resulting from subsequent aldol chemistry was also produced. The pure alcohols were isolated by preparative gas chromatography.

All of the synthesized alcohols were characterized by their NMR and IR spectra. Negative ion mass spectra measured in the ICR spectrometer permitted further characterization; only one signal which corresponded to the $(M - 1)$ ion was observed in each case.

The trimethylsilyl ether of 2-propanol was synthesized from 2-propanol and trimethylsilylacetamide (Petrarch) as described elsewhere[6] and purified by preparative gas chromatography of the crude reaction mixture just prior to use. The silyl ether was characterized by its negative ion–molecule chemistry. Only isopropoxide anion (m/e 59) was observed upon reaction with fluoride ion.

Instrumentation. All experiments were performed on a pulsed ion cyclotron resonance spectrometer which has been modified for infrared photochemical studies as described in detail elsewhere.[11,12] The optical setup and the commercial pulsed CO_2 laser (Lumonics TEA 103-2) which was run multimode with nitrogen in the gas mixture have also been previously described.[11] All samples were degassed by several freeze–pump–thaw cycles on the ICR foreline prior to use.

Ion Generation. Primary negative ions, fluoride ion and methoxide ion, were generated by low-energy electron impact on nitrogen trifluoride (2–3 eV electrons) and dimethyl peroxide (2.5–3.5 eV electrons), respectively. Alkoxide ions were then prepared by deprotonation of the corresponding alcohol with either one of these primary ions as a base, B⁻ (eq 4). Under typical operating conditions (ca. 10^{-6} Torr), reaction 4 went to completion within 100–200 ms. In one set of experiments, isopropoxide anion was generated by the reaction of fluoride ion with the trimethylsilyl ether of 2-propanol.[12]

$$NF_3 + e^- \rightarrow F^- + NF_2 \qquad (2)$$

$$CH_3OOCH_3 + e^- \rightarrow CH_3O^- + CH_3O^\bullet \qquad (3)$$

$$ROH + B^- \rightarrow RO^- + BH \qquad (4)$$

Photochemical Experiments. All experiments were carried out with a single laser pulse from the pulsed CO_2 laser which was fired at a designated time (using a laser trigger pulse) after the alkoxide ions to be studied were completely generated from the appropriate ion–molecule reaction (eq 4). The photodissociation yield of the reactant was determined by measuring the intensity of the anion in the presence and absence of laser irradiation. Since the extent of decomposition of a particular ion was often found to vary considerably with laser wavelength, measurements were done with laser lines that produced large photodecreases, although, in general, no effort was made to maximize these decreases. Photolysis products were determined from mass spectra taken immediately (10–25 ms) after the laser pulse. Due to the long duty cycles (1.5–2 s) necessarily employed to permit laser recharging, these mass spectra were accumulated by successive scans (frequency or magnetic field scans) limited to the mass ranges of interest. In addition, magnetic field scans were run over a small range near the maxima of each ion to

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Table I. Summary of Alkoxide Ion Decompositions

$$O^-$$
$$|$$
$$R_1 - C - R_3$$
$$|$$
$$R_2$$

alkoxide ion	R_1	R_2	R_3	neutral product	enolate ion product (m/e)
1	CH_3	CH_3	CH_3	CH_4	57
2	H	CH_3	CH_3	H_2	57
3	H	H	CH_3	H_2	43
4	Ph	H	CH_3	PhH	43
5	CF_3	CH_3	CH_3	CF_3H	57[20]
5-d_3	CF_3	CD_3	CH_3	CF_3H	60 (72%)[20]
					CF_3D 59 (12%)
6	Ph	CH_3	CH_3	PhH	57
6-d_3	Ph	CD_3	CH_3	PhH	60 (71%)
					PhD 59 (29%)
7	t-Bu	CH_3	CH_3	t-BuH	57 (66%)
					CH_4 115 (34%)
8	i-Pr	CH_3	CH_3	CH_4	85
9	n-Pr	CH_3	CH_3	CH_4	85
10	Et	CH_3	CH_3	CH_4	71
11	Et	Et	CH_3	CH_4	85
12	t-Bu	Et	Et	t-BuH	85
13	t-Bu	i-Pr	Et	t-BuH	99
14	i-Pr	Et	Et	i-PrH	85 (45%)
					EtH 99 (55%)
15	Et	Et	Et	EtH	85

check for resonance shifts or other artifacts upon photolysis. The time dependences of the reactant and the photoproduct abundances were monitored with and without laser irradiation by holding the laser trigger pulse constant in the duty cycle and scanning the detect pulse. Double resonance techniques[13] were used to verify all reaction pathways.

For those ions that produced multiple photoproducts, the fluence (and intensity) dependence of the product distribution was investigated. The laser fluence was attenuated by placing calcium fluoride flats in the optical train which also resulted in a commensurate decrease in the laser intensity. This procedure was also used to study the reactant photodissociation yield as a function of laser fluence for several ions.

Results

The pulsed CO_2 laser-induced decomposition of 15 different alkoxide anions was investigated. Upon IRMP activation, the alkoxide anions were found to undergo elimination of a neutral fragment to produce enolate anions; the results are summarized in Table I. Specific results are discussed below along with some general conclusions.

The general photochemical features were similar for all of the ions studied. Only one ion peak which corresponded to the deprotonated alcohol (M – 1) was present in the negative ion mass spectra of the *tertiary* alcohols with either fluoride ion or methoxide ion as a base. The reactant ion intensity decreased on a submillisecond (unimolecular and collisionless) time scale upon laser irradiation; a corresponding rise in the intensity of the product ion(s) was also observed. For most of the alkoxide ions investigated, the product enolate ions were less basic[14] than the reactant alkoxide anions so the reactant ion signal did not usually recover after the laser pulse. For those exceptions such as 2-(trifluoromethyl)-2-propoxide anion (see below), it was necessary to detect the photoproduct ions immediately after the laser pulse and prior to any bimolecular ion–molecule reactions. For most of the ions studied, the amount of product produced was nearly equal to the amount of alkoxide decomposed, indicating that vibrationally induced electron detachment[15a] was not occurring to any significant extent. The alkoxide ions of trialkylcarbinols were found to exhibit rather high threshold fluences (some greater than 500 mJ cm^{-2})

as determined from the fluence dependence of the photodissociation yield.[15b]

Isopropoxide and Other Secondary Alkoxides. In addition to the alkoxide ion signal (M – 1), another ion signal at (M – 3) which corresponds to the enolate ion that would result from formal 1,2-elimination of molecular hydrogen from the alkoxide anion was observed in the negative ion mass spectra of the secondary alcohols studied: 2-propanol, ethanol, 1-phenylethanol. For example, a signal for acetone enolate anion (M – 3) appears in the mass spectrum of 2-propanol along with the alkoxide ion (M – 1). The enolate signal (M – 3) was very small near the beginning of the duty cycle and slowly increased with time (with a corresponding decrease in the alkoxide signal). Such behavior is indicative of formation via a bimolecular ion–molecule reaction and has been reported previously.[16] This behavior has been attributed to subsequent ion–molecule reactions of the corresponding neutral ketones produced at fairly low partial pressures by pyrolytic oxidation of the neutral alcohols on the filaments (electron-beam filament and ionization gauge filament) in the high vacuum system of the ICR. These complications presented no problems in the photochemical experiments as long as the desired alkoxide ions were irradiated early in the duty cycle.
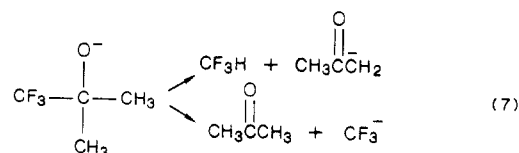
In a separate set of experiments, isopropoxide anion was cleanly generated from the reaction of fluoride ion and the trimethylsilyl ether of 2-propanol without any formation of the (M – 3) acetone enolate ion. This result further substantiates the proposal of pyrolysis of the neutral alcohol as the source of the (M – 3) ions typically encountered in such systems. As illustrated in Table I, isopropoxide ion, generated from the alcohol or the trimethylsilyl ether, exclusively eliminates H_2 to produce acetone enolate anion (m/e 57) upon infrared laser photolysis. No evidence for methane elimination which would lead to the production of acetaldehyde enolate (m/e 43) was observed.[17]

$$CH_3 - \underset{\underset{H}{|}}{\overset{\overset{O^-}{|}}{C}} - CH_3 \longrightarrow CH_3\overset{O}{\overset{||}{C}}CH_2^- + H_2 \qquad (5)$$
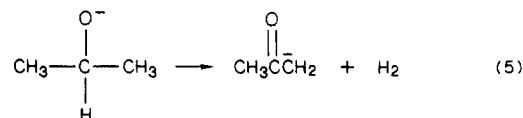
Ethoxide ion, **2**, did not undergo efficient laser-induced decomposition when irradiated with any of the available laser lines; however, with certain laser lines (e.g., R(24)/10.6 μ, 1081 cm^{-1}, at about 1.5 J cm^{-2}) a small signal decrease (<10%) could be observed along with a corresponding increase in the acetaldehyde ion signal (m/e 43) due to H_2 elimination. Deprotonated 1-phenylethanol (**4**) was found to undergo extensive decomposition resulting in the loss of benzene and the production of acetaldehyde anion. No photoincrease in the acetophenone enolate signal (m/e 119) arising from laser-induced H_2 elimination could be detected.

$$Ph - \underset{\underset{H}{|}}{\overset{\overset{O^-}{|}}{C}} - CH_3 \longrightarrow PhH + \overset{O}{\overset{||}{C}}H_2CH^- \qquad (6)$$
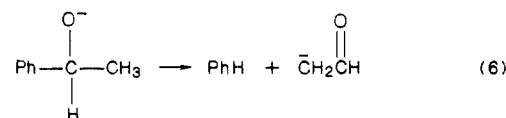
2-(Trifluoromethyl)-2-propoxide. Two photoproducts, trifluoromethyl anion (m/e 69) and acetone enolate ion (m/e 57), were generated in the pulsed laser photolysis of 2-(trifluoromethyl)-2-propoxide ion, **5**.

$$CF_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{O^-}{|}}{C}} - CH_3 \Big\langle \begin{array}{l} CF_3H + CH_3\overset{O}{\overset{||}{C}}CH_2^- \\ CH_3\overset{O}{\overset{||}{C}}CH_3 + CF_3^- \end{array} \qquad (7)$$

It was essential to detect these ions immediately after the laser pulse (within 10 ms), because each deprotonates neutral 2-trifluoro-2-propanol to regenerate the reactant alkoxide ion. The

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(17) CW CO_2 laser photolysis also resulted in the clean production of only acetone enolate anion.
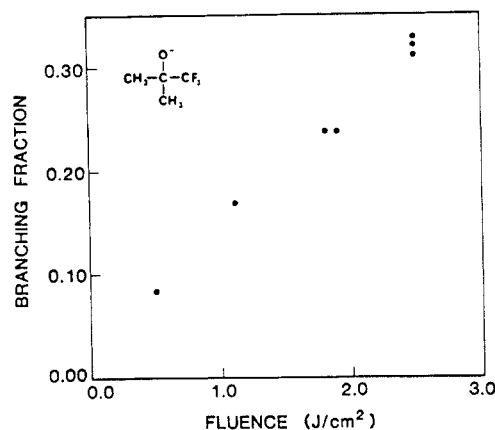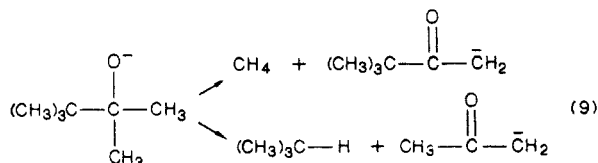
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Figure 1. Plot of branching fraction for 2-(trifluoromethyl)-2-propoxide anion (defined as the ratio of CF_3^- yield to the total yield: $[CF_3^-]/([CF_3^-] + [C_3H_5O^-])$) as a function of laser fluence.

reaction channel involving production of CF_3^- is 7 kcal/mol more endothermic than the channel producing acetone enolate ion.[18a] The branching fraction, defined as the yield of the higher energy channel product CF_3^- divided by the total product yield, was found to increase monotonically with increasing fluence (and thus intensity), indicating that the more endothermic reaction channel, CF_3^- production, also has a higher activation energy (Figure 1). Further substantiating evidence was found in preliminary results on the photolysis of 5 with a low-power continuous wave (CW) CO_2 laser. In these experiments, only products resulting from the lowest energy pathway are usually formed because ions activated with a CW CO_2 laser decompose very close to the reaction threshold.[19] Acetone enolate anion was the only detectable photoproduct when this mode of activation was employed.

2-Phenyl-2-propoxide. This ion was found to eliminate benzene to produce acetone enolate ion exclusively upon pulsed CO_2 laser photolysis. No methane elimination (i.e., production of acetophenone enolate anion) was detected.

$$Ph-\overset{\overset{O^-}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \longrightarrow PhH + CH_3\overset{O}{\overset{||}{C}}CH_2 \quad (8)$$
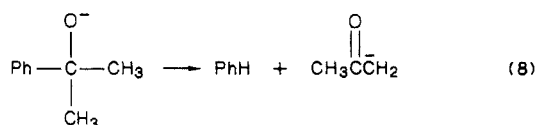
2,3,3-Trimethyl-2-butoxide. Deprotonated *tert*-butyldimethylcarbinol, 7, yielded two photoproducts in a ratio of ca. 2:1 (4:1 statistically corrected) which arise from overall elimination of isobutane and methane. This branching ratio is independent of laser intensity (and fluence, Figure 2) and therefore suggests that these two reaction channels are very close in energy.

$$(CH_3)_3C-\overset{\overset{O^-}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \underset{\searrow}{\overset{\nearrow}{}} \begin{array}{l} CH_4 + (CH_3)_3C-\overset{O}{\overset{||}{C}}-\overset{-}{C}H_2 \\ \\ (CH_3)_3C-H + CH_3-\overset{O}{\overset{||}{C}}-\overset{-}{C}H_2 \end{array} \quad (9)$$

Other Alkoxides. Alkoxide anions of a number of trialkylcarbinols were investigated in an effort to assess the relative leaving propensities of the simple alkanes. Methane elimination occurs to the exclusion of propane (originating from either an *i*-Pr or a *n*-Pr group) or ethane elimination as demonstrated by the results for ions 8 through 11. Analogously, elimination of isobutane (in
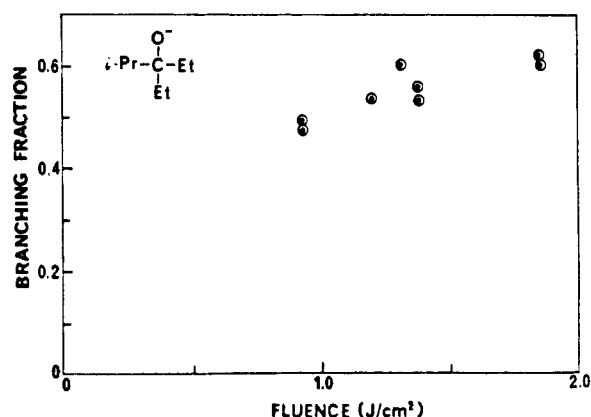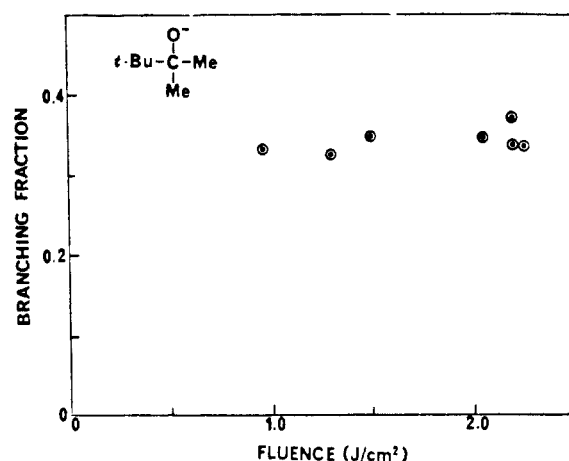

Figure 2. Branching fraction as a function of laser fluence for 2,2,3-trimethyl-2-butoxide anion (upper graph) and 2-methyl-3-ethyl-3-pentoxide (lower graph). The branching fractions are defined as the amount of the higher energy product formed divided by the amount of total photoproduct.
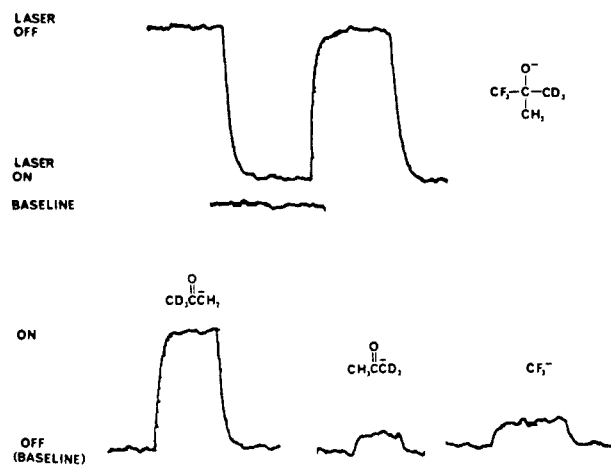

Figure 3. Signal intensities of the reactant 2-(trifluoromethyl)-2-propoxide-$1,1,1$-d_3 anion (upper trace) and the photoproducts acetone-d_3 enolate, acetone-d_2 enolate, and trifluoromethyl anions in the presence (ON) and absence (OFF) of pulsed CO_2 laser irradiation. The decreases in the reactant anion correspond to increases in the photoproduct signals.

(18) (a) Calculated from literature values for the gas-phase acidities of trifluoromethane (375.6 kcal/mol) and acetone (368.8 kcal/mol): ref 21. (b) The homolytic C–R bond dissociation energies are ca. 97 kcal/mol or greater for R = H, Ph, and CF_3, whereas the C–CH_3 BDE is only ca. 86 kcal/mol. The electron affinities of R• are much larger than that for methyl radical, so the heterolytic bond dissociation energy is less for C–R than for C–CH_3: EA(H•) = 17.6; EA(CF_3•) = 42; EA(Ph•) = 22; EA(CH_3) = 1.8 (all values in kcal/mol): ref 21.

(19) Preliminary results with the P(20)/9.6 μ line with 26 W cm^{-2}, 150–300 ms irradiation time.

the form of a *t*-Bu group) was found to predominate over ethane and propane elimination, as revealed by the observed products from 12 and 13. Both propane and ethane elimination were observed from 14 where only isopropyl and ethyl group cleavage is possible. A slight preference for propane formation (ca. 1.6:1, statistically corrected) was found. This branching ratio is only moderately dependent on laser fluence and thus intensity (Figure 2).
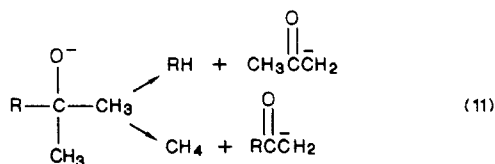
Competitive Primary Isotope Effects. Intramolecular primary kinetic isotope effects were measured from the observed product distribution in the pulsed laser photolysis of 5-d_3 (2-(trifluoromethyl)-2-propoxide-$1,1,1$-d_3) and 6-d_3 (2-phenyl-2-propoxide-$1,1,1$-d_3) (Figure 3). An isotope effect (k^H/k^D) of 6.0 ± 0.5 for 5 was calculated from the relative intensities of the d_3 and d_2 product acetone enolate ions which result from CF_3H and CF_3D elimination, respectively.[20] An isotope effect of 2.5 was determined for 6 in an analogous manner.
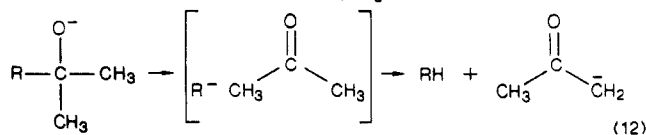
Discussion

We have established a stepwise mechanism involving initial cleavage to an intermediate ion–molecule complex followed by a hydrogen transfer reaction for the unimolecular decomposition of *tert*-butoxide anion[6] to acetone enolate ion and methane. This mechanism (eq 10) should be equally applicable to other alkoxide anions such as those studied here. Indeed, the results of this present study provide further evidence for a general stepwise mechanism for alkoxide ion decompositions and also address particular aspects of this mechanism.

$$(10)$$
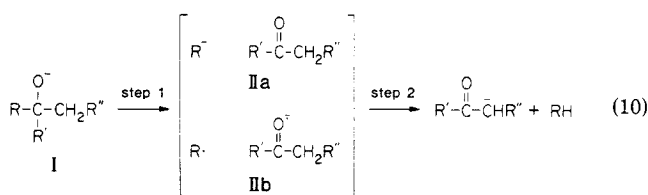
Nature of the Cleavage. The kinetic isotope effects measured in the *tert*-butoxide anion decomposition[6] did not provide any indication of the electronic nature of the cleavage in the first step of the multistep fragmentation reaction, i.e., whether the reaction proceeds through initial heterolytic cleavage (to produce intermediate Ia) and a subsequent proton transfer or through homolytic cleavage (to give intermediate Ib) followed by a hydrogen atom transfer. Studies on particular 2-substituted-2-propoxide anions such as **2, 5,** and **6** in which the C–R bond is weaker than the C–CH$_3$ bond relative to heterolysis but the C–R bond is stronger than the C–CH$_3$ bond with respect to homolysis allow us to probe this cleavage reaction.[18b,21] For these systems (R = Ph, H, and CF$_3$), the product distribution from the IR laser photolysis would reflect the nature of the initial cleavage; elimination of RH should predominate if a heterolytic mechanism were operative, whereas methane elimination should represent the major pathway in a homolytic scheme. All three of the alkoxide anions investigated yield acetone enolate as a result of RH elimination (Table I). No methane elimination was detected even though this channel is more exothermic overall.[21] These observations reveal a mechanism involving initial heterolytic cleavage where the reaction pathway is determined by the relative stability of the intermediates rather than that of the final products.

$$(11)$$

R=Ph,H,CF$_3$

$$(12)$$

The formation of CF$_3^-$ as an additional product in the CO$_2$ laser photolysis of **5** (eq 7) provides further verification for this mechanism; this photoproduct arises from simple dissociation of the intermediate anion–ketone complex. Additional evidence for a heterolytic stepwise pathway can be found in the primary kinetic isotope effects (k^H/k^D) determined from the photolysis of 2-(trifluoromethyl)-2-propoxide-$1,1,1$-d_3. The observed k^H/k^D of 6.0 is much larger than that for *tert*-butoxide ion (2-methyl-2-propoxide-$1,1,1$-d_3) for which a value of 1.6 was obtained.[5,6] It is difficult to account for such a large difference in primary isotope effects by invoking a concerted mechanism where the four-center transition states should be structurally similar. These isotope effects are, however, consistent with the intermediacy of an anion–ketone complex (Ia) in that k^H/k^D should decrease as the proton transfer reaction in step 2 becomes more exothermic.

Leaving Group Propensities. On the basis of the observed product enolate ions from IRMP activation of the alkoxide ions, Table I, a relative order of leaving group propensities can be assigned.[22]

$$CF_3 > Ph > H > \textit{t-Bu} > CH_3 > \textit{i-Pr} > Et$$

For most of the alkoxides studied, only one product was observed, so quantitative ratios could not always be assessed. DePuy and co-workers[23] have reported the same reactivity order for cleavage in an entirely different set of experiments involving gas-phase ion–molecule reactions of substituted trimethylsilanes with hydroxide ion.

$$(13)$$
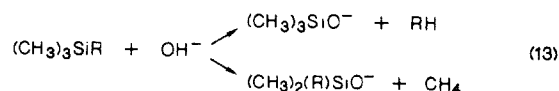
The relative reactivity order correlates with the gas-phase acidities of the conjugate acids (CF$_3$H > PhH > H$_2$ > CH$_4$) for those systems whose acidities have been measured or at least estimated.[21] This correlation is not surprising given that an anionic intermediate is formed along the reaction path. To the extent that the R–H and R–C homolytic bond dissociation energies follow each other, the gas-phase acidity (heterolysis of the R–H bond) will correlate with the heterolytic R–C bond energy which essentially determines the activation barrier in the first step of the alkoxide decompositions (see below). This correlation suggests, as also proposed by DePuy et al. for their system,[23] that the relative gas-phase acidities of molecules whose acidities are inherently difficult to measure by conventional equilibrium methods could be determined indirectly from studies on unimolecular decompositions of appropriate alkoxide ions that would undergo competitive elimination reactions. For example, the results for 1-phenylethoxide ion in which both phenyl and hydride ion ejection are possible indicate that benzene is more acidic than hydrogen, in agreement with estimates by others.[21] Of course, one must ensure that the same mechanism is operative for all groups under investigation.

There are several important ramifications of the results for 1-phenylethoxide, **4,** in addition to the confirmation of the relative gas phase acidity of benzene and molecular hydrogen. The preference for benzene elimination over hydrogen expulsion can be accounted for by the relative stabilities of the anions (Ph$^-$ and H$^-$) in the intermediate. This suggests that the elimination of molecular hydrogen also proceeds via the same heterolytic mechanism and argues against a unique concerted pathway for H$_2$ elimination from alkoxide anions. The observations in this study are entirely consistent with a stepwise mechanism for the elimination of molecular hydrogen from gaseous alkoxide ions.

(20) Trifluoromethyl anion was also observed as a photoproduct (Table I).

(21) Pertinent thermochemical information was taken from the following sources. Gas-phase acidities: ref 14. Electron affinities: Janousek, B. K.; Brauman, J. I. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979. Homolytic bond dissociation energies: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982,** *33,* 493. Heats of formation of neutral compounds: Benson, S. W. *Thermochemical Kinetics,* 2nd ed.; Wiley-Interscience: New York, 1976.

(22) In this study the relative stability of trifluoromethyl anion and phenyl anion (CF$_3$ > Ph) was deduced from the observation that CF$_3^-$ was formed via dissociation of the intermediate ion–molecule complex formed from **5** and the lack of any formation of free Ph$^-$ from **4** or **6.** The ordering H > *t*-Bu was deduced from the determined reactivity orders H ≫ Me and *t*-Bu ≥ Me.

(23) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984,** *106,* 4051. DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* **1987,** *20,* 127. A related reaction is discussed in: Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981,** *34,* 519.
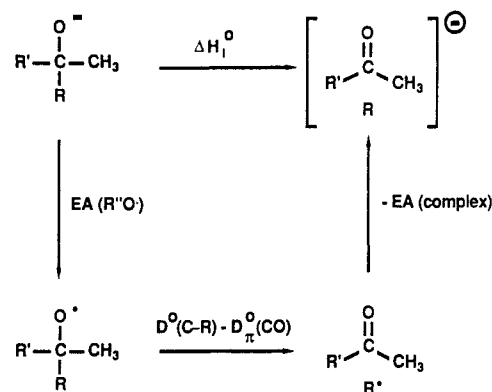
Bowie and co-workers have recently reported[24] an isotope effect study on the collisionally induced elimination of molecular hydrogen from partially deuteriated ethoxide anions. Competitive primary isotope effects of 2.9 and 1.6 were calculated from the product ion abundances obtained from collisionally activated ethoxide-*1-d* anion and ethoxide-*2-d* anion, respectively. These isotope effects can be readily rationalized in terms of the proposed stepwise mechanism.[25] The authors also carried out ab initio calculations on this system which they suggest confirm such a scheme. The relatively large effect for the *1-d* alkoxide (k^H/k^D = 2.9) arises from the competitive C–H and C–D cleavage in the first step to give a (hydride ion–acetaldehyde) complex. The other primary effect (1.6 for the ethoxide-*2-d*) is derived from the proton transfer reaction comprising the second, product-determining step. This last isotope effect is in line with our measurement of 2.5 for the primary isotope effect in the decomposition of 2-phenyl-2-propoxide-*1,1,1-d₃*. The exothermicity of the second step should be very similar for these two systems. Quantitative comparison is difficult because the energy distributions of the reacting ions are probably much different for the two activation methods, although the smaller effect in the collisional activation experiment does suggest that higher internal energies are accessed by this method than in the IRMP photochemical experiments.

The product distribution from photochemically activated 1-phenylethoxide anion also addresses the source of the (M − 3) enolate ions commonly observed in the negative ion mass spectra of secondary alcohols, in that it rules out the possibility of unimolecular decompositions of chemically activated alkoxide anions as the origin of these enolate ions. If such a process were the source of enolate ions under chemical ionization conditions, then enolate ions arising from the lower energy pathway, elimination of benzene (i.e., formation of acetaldehyde enolate ion), should also be present in the mass spectra of 1-phenylethanol. That no such ion signal is observed provides further evidence for pyrolysis of neutral alcohols and subsequent ion–molecule chemistry of neutral ketones as proposed in the literature.[16]

Alkyl Cleavage: Alkane Acidities. The elimination of the simple alkanes presents an interesting contrast to the results discussed above. If the heterolytic mechanism and the arguments presented above were extended to these systems, then, as we pointed out in our preliminary communication,[1] a natural conclusion would be that the observed reactivity order, *t*-Bu > CH₃ > *i*-Pr > Et, reveals an unusual acidity order[26] for the simple alkanes, namely, *t*-Bu-H > CH₃-H > *i*-Pr-H > Et-H. Such an order has been recently suggested by DePuy and co-workers[23] based on their observation of the same reactivity order in the reaction of gas-phase hydroxide ion with substituted trimethylsilanes (eq 13). This proposed scale of acidities implies an anomalous methyl substituent effect[27] that has no precedent in the gas phase. That is, substitution of one or two methyl groups for hydrogen in methane makes the central hydrogens less acidic, but addition of a third methyl group increases the acidity relative to methane.

The origins of this reactivity pattern for alkane elimination and the stability of the simple alkyl anions can be understood more thoroughly by thermochemical considerations. The activation barrier (E_a) for the simple cleavage reaction that comprises the first step in the multistep scheme (eq 10) can be approximated reasonably well by calculating the overall enthalpy change for

(24) Hayes, R. N.; Sheldon, J. C.; Bowie, J. H.; Lewis, D. E. *Chem. Commun.* **1984**, 1431.

(25) These effects alone could also be consistent with a concerted mechanism. Evidence for a stepwise pathway for this system would be found in a study of the energy dependence of these isotope effects analogous to our study of *tert*-butoxide anion. Unfortunately, we were not able to carry out such a study because ethoxide anion does not undergo efficient photodissociation upon CO₂ laser irradiation.

(26) Steric effects in the cleavage reaction may be partially responsible for the observed reactivity particularly for isobutane elimination; however, their relative importance cannot be ascertained given the available data.
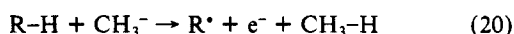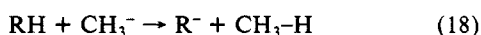
(27) Ab initio calculations suggest that methyl substituents destabilize alkyl carbanions: (a) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363. (b) Schleyer, R. v. R.; Spitznagel, G. W.; Chandrasekhar, J. *Tetrahedron Lett.* **1986**, 4411. (c) Jorgensen, W. L.; Briggs, J. M.; Gao, J. *J. Am. Chem. Soc.* **1987**, *109*, 6857.

Scheme I

$$\Delta H_1^o = EA(R''O^-) + D^o(C\text{-}R) - D_\pi^o(CO) - EA(\text{complex}) \qquad (14)$$

formation of the intermediate I, ΔH_1 which can be formally derived by using the thermochemical cycle[6] in Scheme I. In this scheme, EA(R′O•) is the electron affinity of the alkoxide radical, D(C–R) is the C–R homolytic bond dissociation energy (BDE), D_π(CO) is the strength of the C–O π bond that is formed upon cleavage of the alkoxyl radical, and EA(complex) is the total energy that would be released when an extra electron is formally added to the radical–molecule intermediate to generate the intermediate I.

For heterolytic cleavage, the term EA(complex) in eq 14 reduces to the sum of the electron affinity of the radical R (EA(R•)) and ϵ, which is the total ion–molecule interaction energy ("solvation" energy) due to ion–dipole and ion–induced dipole forces (i.e., the energy required to dissociate the intermediate complex I into completely separated R⁻ and ketone).[28] Equation 14 then becomes eq 15 for methyl cleavage and eq 16 for R′• cleavage where R′ = *t*-Bu, *i*-Pr, or Et. Subtracting eq 16 from 15 and rearranging yields an expression for EA(R′), eq 17.

$$E_a = EA(R''O) + D(C\text{-}CH_3) - D_\pi(C\text{-}O) - EA(CH_3) - \epsilon \qquad (15)$$

$$E_a' = EA(R''O) + D(C\text{-}R') - D_\pi(C\text{-}O) - EA(R') - \epsilon' \qquad (16)$$

$$EA(R') = [E_a - E_a'] + [D(C\text{-}R') - D_\pi(C\text{-}CH_3)] + EA(CH_3) + [\epsilon - \epsilon'] \qquad (17)$$

Our results indicate that the activation barrier for elimination of R′H is greater than or equal to that for CH₄ elimination, so the term $[E_a - E_a']$ is less than or equal to zero for all R′. The experimentally determined value for the methyl radical electron affinity is 1.8 kcal/mol.[29] The carbon–methyl bond is at least 1.8 kcal/mol stronger[21] than the C–R′ bond so [D(C–R′) − D(C–CH₃)] + EA(CH₃) is negative. If the solvation or ion-molecule stabilization term is assumed to be the same for all R (i.e., $\epsilon = \epsilon'$) *and* the cleavage is heterolytic, then we are left with the conclusion that the electron affinities of the ethyl, isopropyl, and *tert*-butyl radical are negative. Within this construct, our results permit us to estimate the value for the *tert*-butyl radical electron affinity. The observation that the branching ratio between methane and isobutane elimination for anion 7 is independent of laser fluence (Figure 3) implies that the activation barriers for these processes are very close in energy. Taking $E_a = E_a'$, $\epsilon = \epsilon'$, and[21,26] D(C–CH₃) − D(C–*t*-Bu) = 10 kcal/mol, the EA of *tert*-butyl radical would be calculated to be −8 kcal/mol with this formalism. DePuy and Schleyer have reported similar results based on experiment[23] and theory,[27] respectively. It is important to realize that a constant ion–molecule interaction energy or

(28) This stabilization energy could be as high as 10–15 kcal/mol in the intermediate and somewhat less in the transition state: Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

(29) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

"solvation" term is implicit in DePuy's analysis as well. These formal "electron affinities" represent alkyl anion stabilities within an intermediate complex given a constant solvation energy. It is not clear whether we can attach any physical significance to such numbers with respect to the relative stability of the isolated anions since the isolated species would not be thermodynamically stable.[30]

What do we know about the acidities of the alkanes or the stabilities of the simple alkyl anions? The gas-phase acidity ($\Delta H°_{acid}$) is defined[14] as the energy of ionization into R^- and H^+ and can be calculated from the R–H homolytic bond dissociation energy, the electron affinity of the corresponding radical $R^•$, and the ionization potential of the hydrogen atom: $\Delta H°_{acid} = D(R-H) - EA(R^•) + IP(H^•)$. The gas-phase acidity of methane can be calculated to be 416.6 kcal/mol from the experimental electron affinity[29] (0.08 eV) of $CH_3^•$ and the methane C–H bond dissociation energy.[21] The electron affinities of the other simple alkyl radicals are unknown. In fact, there is a growing body of evidence[23,27] (including this work) that isolated saturated alkyl anions other than methyl are incapable of existence as bound species in the gas phase. Relative acidities can be defined on the basis of proton transfer equilibria (eq 18), and relative anion stabilities can be based on electron transfer equilibria (eq 19); however, that the alkyl anions other than methyl are not bound presents a significant problem in discussing alkane acidities or alkyl anion stabilities. How does one discuss such thermodynamic properties when the products are not thermodynamically capable of existence? One could circumvent this issue by defining a free energy of deprotonation of an acid RH by some base such as methyl anion. Even if the electron affinities of the alkyl radicals were zero, the deprotonation reaction between methyl anion and $R'H$ would still be exothermic; however, the product would not be the conjugate base R'^- but rather a radical and a free electron (eq 20). Such a reaction would represent a nonadiabatic proton transfer and might be quite slow due to the necessary curve crossing. Regardless of the nature of the process, one could not use such a parameter to discuss the relative stabilities of these conjugate bases because they are not formed in the reaction since they are not bound.

$$RH + CH_3^- \rightarrow R^- + CH_3-H \qquad (18)$$

$$R^• + CH_3^- \rightarrow R^- + CH_3^• \qquad (19)$$

$$R-H + CH_3^- \rightarrow R^• + e^- + CH_3-H \qquad (20)$$

Due to the anomalous alkane reactivity order and the inherent problems associated with defining the alkane acidities and peculiar "electron affinities", we were interested in analyzing our system in a different fashion. The intermediate I (eq 10) is formally a neutral radical–molecule complex with an additional electron. The structure of this intermediate should depend on the absolute and relative values of the electron affinities of the radical $R^•$ and ketone, as well as the ion–molecule interaction energies. If the EA of the radical were greater than that of the ketone, then the intermediate should be an anion–ketone complex (Ia in eq 10). In this case, the reactivity pattern would correlate with the heterolytic bond strengths ($D(C-R) - EA(R)$) or acidities, and we are left with the conclusions discussed above. On the other hand, a radical–ketyl radical anion complex should result if the electron affinity were much larger for the ketone than the radical. If the EA of both species were comparable, then the intermediate might be a hybrid of Ia and Ib (eq 10) or involve an electron transfer equilibrium. If neither species had an appreciable EA, then the electron might be weakly bound only within the complex

and not by either isolated moiety specifically, i.e., the species might best be considered an anionic cluster[31] or possibly a dipole-supported state.[32]

A plausible explanation for the observed reactivity is that for those alkyl groups with nonpositive electron affinities, the mechanism changes to one involving cleavage to an intermediate for which the binding of the extra electron is insensitive to the nature of the cleaved group R. Under these circumstances, both the energetics and the structure of the intermediate would differ from that in heterolytic cleavage. The relative propensity for alkane elimination would then be determined by the C–R homolytic bond dissociation energy rather than the relative stability of the corresponding alkyl anions. There are at least two structural possibilities for such an intermediate. The simplest one is a change in mechanism to homolytic cleavage where the extra electron resides on the ketone fragment. The reactivity order would obviously reflect the radical stabilities or homolytic bond strengths. The observed reactivity order then makes sense when one realizes that methyl is out of order. The observed order t-Bu $> i$-Pr $>$ Et correlates with relative radical stabilities. Indeed, DePuy's results[23] suggest that the quantitative differences in cleavage energetics for the alkanes (other than CH_4) are about the same size as the differences in radical stabilities, i.e., a few kcal/mol. The only problem with this interpretation lies in whether simple ketones have positive electron affinities.[30b] Another structural possibility for the intermediate is that if neither component of the complex had an appreciable EA, then, as discussed above, the binding of the electron would be weak and perhaps nonspecific. The intermediate would then be best described as an anionic cluster.[32] The reactivity order would again follow the homolytic bond dissociation energies. Since methyl anion is known to be bound,[29] we interpret the position of methyl in the order as evidence that methane elimination proceeds through a heterolytic mechanism. Since the ketone is much more polarizable than the alkyl radical, the ion–molecule interaction energy, ϵ, should be larger for a heterolytic pathway where the ketone "solvates" the anion.[33] Thus, it is reasonable that methane elimination is competitive with isobutane elimination and actually proceeds more readily than ethane or propane elimination. The available data do not allow us to distinguish whether the observed alkane reactivity order is the result of an anomalous alkyl anion stability order[23] or arises from a change in mechanism involving an intermediate for which the binding of the extra electron is insensitive to the nature of the cleaved group (either a radical–ketone radical anion complex or a transient anionic cluster). The simplicity of the homolytic mechanism coupled with the required ad hoc character of the alkyl anion stabilities[34] causes us to prefer the latter possibility.

(30) (a) Negative electron affinities are usually used to describe resonances observed in electron scattering experiments on neutrals (Jordan, K. D. *Acc. Chem. Res.* **1978**, *12*, 36). Along these lines, it is possible that, even though the alkyl anions are not bound, they may be formed in a highly distorted geometry (excited state) which has a finite lifetime (e.g., ref 31). It is unclear whether the negative EA calculated for the alkyl radicals with the above formalism corresponds to such a situation, because very little information is available on electron scattering of these highly reactive species. (b) The electron affinity of acetone and other simple carbonyls is probably very small, ref 30a.

(31) Armbruster, M.; Haberland, H.; Schindler, H. G. *Phys. Rev. Lett.* **1981**, *47*, 323. Klots, C. E. *J. Chem. Phys.* **1979**, *71*, 4172. Quitevis, E. L.; Bowen, K. H.; Liesegang, G. W.; Herschbach, D. R. *J. Phys. Chem.* **1983**, *87*, 2076.

(32) The exact structure of such an intermediate is unclear; however diffuse, bound anion states have been implicated in a number of systems (ref 31). For diffuse, dipole-supported states, see: Jackson, R. L.; Zimmerman, A. H.; Brauman, J. I. *J. Chem. Phys.* **1979**, *71*, 2088. Jackson, R. L.; Hiberty, P. C.; Brauman, J. I. *Ibid.* **1981**, *74*, 3705. Mead, R. D.; Lykke, K. R.; Lineberger, W. C.; Marks, J.; Brauman, J. I. *Ibid.* **1984**, *81*, 4883. Marks, J.; Wetzel, D. M.; Comita, P. B.; Brauman, J. I. *Ibid.* **1986**, *84*, 5284. Marks, J.; Comita, P. B.; Brauman, J. I. *J. Am. Chem. Soc.* **1985**, *107*, 3718. If the electron binding energy of this intermediate were due only to forces within this complex then the binding may be weak and the decomposition threshold would be very close to the threshold for electron detachment. Since we have determined that electron loss is not a significant pathway in these systems, the adiabatic bond cleavage and formation reactions must occur on a shorter time scale than the nonadiabatic electron autodetachment process. We have observed that fragmentation processes can effectively compete with electron detachment even when the fragmentation threshold is ca. 1 eV higher in energy: Foster, R. F.; Tumas, W.; Brauman, J. I. *J. Chem. Phys.* **1983**, *79*, 4625.

(33) Within this mechanistic framework, the ion–molecule stabilization energy, ϵ, must be ca. 8 kcal/mol larger for methane elimination than for isobutane elimination. So, even if this interaction energy were infinitesmal for ethane, propane, and isobutane elimination, the lower limit for this term for methane must be 8 kcal/mol. The position of methyl in the observed reactivity order can be rationalized by a mechanistic change for the other alkyl groups to an intermediate where this stabilization energy is significantly weaker in the transition state (and presumably the intermediate).

Gas-Phase Negative Ion Unimolecular Decompositions

J. Am. Chem. Soc., Vol. 110, No. 9, 1988 2721

Implications for Bimolecular Proton Transfer Reactions. There is an obvious connection between the heterolytic stepwise unimolecular decomposition of gas-phase alkoxide ions and bimolecular proton transfer reactions: the intermediate ion–molecule complex in the IRMP-induced reactions of these alkoxide anions, e.g., $R(CH_3)_2CO^-$, must also be an intermediate in the proton transfer reaction between R^- and acetone. Most of the current understanding of the details of bimolecular ion–molecule reaction dynamics, particularly the general features of the potential energy surfaces and how they are manifested, has come from kinetic studies.[35,36] A model centering on the proposal of an inverted double-minimum potential, which was initially proposed to explain slow proton transfer reactions[37] of several delocalized systems, has found wide acceptance. This model and its application to a wide range of gas-phase ion–molecule reactions have been discussed extensively in the literature.[38] In this model, ion–molecule reactions proceed through long-lived intermediate encounter complexes whose subsequent reactions can be described by statistical theories. The overall rate of the bimolecular reaction depends only on the rate of formation of the intermediate (i.e., the ion–molecule collision rate) and the relative rates of its subsequent unimolecular reactions. A problem in bimolecular reaction dynamics can therefore be reduced to one of understanding the unimolecular reactions of the chemically activated intermediate. The results of this present study on alkoxide anions are particularly informative because they involve a system whose unimolecular decomposition mechanism has been clearly defined and can provide information on the details of the potential energy surfaces for this fundamental class of bimolecular ion–molecule reactions.

The observation of multiple products in the IR photolysis of 2-(trifluoromethyl)-2-propoxide anion (5) provides an independent verification of the dual minimum potential model for proton transfer reactions. Our mechanistic work reveals that the observed photoproducts CF_3^- and acetone enolate ion result from competitive unimolecular reactions of the photochemically generated intermediate (CF_3^-·acetone). Trifluoromethyl anion arises from simple dissociation of the intermediate complex, while acetone enolate anion is the result of a proton transfer reaction within the complex.[39] The branching fraction defined as the ratio of the amount of CF_3^- produced to the total photoproduct yield increases monotonically with laser intensity (and fluence) (Figure 1). At the higher laser intensity (higher fluence) the photochemically generated intermediate has more internal energy which results in the formation of more of the higher energy product (Figure 4). This dependence indicates that the lower energy proton transfer reaction (to form acetone enolate ion) must have a tighter transition state (i.e., lower E but also a lower A factor) than the higher energy dissociation channel leading to CF_3^- and acetone. Such a situation can only occur if there is a barrier to the proton transfer reaction within the intermediate complex (CF_3^-·acetone); thus, these photochemical experiments provide an independent verification of the dual-minimum potential model for proton transfer reactions.[40]

Information on bimolecular ion–molecule reaction dynamics can be obtained from IRMP photochemical studies only in those
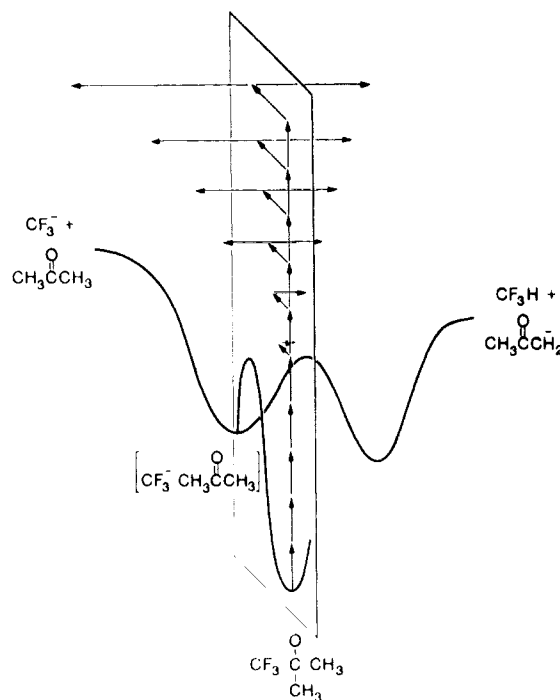

Figure 4. Potential energy surface for $CF_3(CH_3)_2CO^-$. The dual-minimum surface represents the reaction coordinate for the bimolecular proton transfer reaction between CF_3^- and acetone. In this scheme, the alkoxide anion is activated by the sequential absorption of infrared photons (represented by vertical arrows) until it dissociates to generate the intermediate ion–molecule complex (CF_3^-·acetone). The horizontal arrows represent the competing reactions of this photochemically generated intermediate: dissociation to yield separated CF_3^- + acetone and proton transfer to give CF_3H and acetone enolate anion. The lengths of the arrows correspond to the relative magnitudes of the reaction rates.

cases where multiple products are observed. The measurement of intramolecular kinetic hydrogen isotope effects in unimolecular ion decompositions could therefore provide a more general probe into bimolecular proton transfer reactions. The kinetic isotope effect for the proton transfer reaction between R^- and acetone-d_3 within the intermediate can be determined from the ratio of d_3/d_2 acetone enolate anions produced in the IR laser photolysis of the trideuterioalkoxide (eq 21). Kinetic isotope effect studies have provided considerable insight into many of the details of proton transfer reactions in solution;[41] however, only several studies have been carried out on gas-phase ion reactions.[42] The results for three alkoxides (R = CF_3, Ph, and CH_3) are an isotope effect of 6.0 for R = CF_3, a value of 2.5 for R = Ph, and $k^H/k^D = 1.6$ for R = CH_3.

(21)
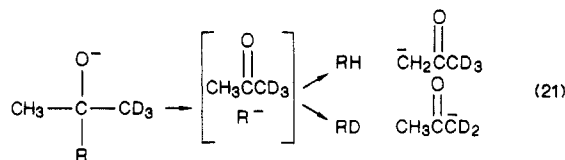
The primary isotope effect (k^H/k^D) decreases substantially as the exothermicity of the proton transfer reaction increases.[43] These

(34) Schleyer does, however, derive the same acidity order and negative electron affinities from theoretical considerations (ref 27).

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(36) Hydrogen exchange studies and related work have also provided insight into particular reactions such as proton transfer. A recent discussion can be found: DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Science* **1982**, *218*, 955.

(37) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891.

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(39) Moylan et al. have reported the formation of multiple products, that are related by a proton transfer reaction, in the IRMP activation of possible intermediates including both hydrogen-bonded complex (ROHF⁻) and covalently bonded moieties (1,1,1-trifluoroacetone enolate): Moylan, C. R.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1985**, *107*, 1934.

(40) This internal energy dependence is analogous to the negative temperature dependence of bimolecular ion–molecule reactions.

(41) Melander, L.; Saunders, W. H. *Reactions of Isotopic Molecules*; Wiley: New York, 1980. More O'Ferrall, R. A. In *Proton Transfer Reactions*; Caldin, E. F., Gold, V., Eds.; Chapman and Hall: London, 1975.

(42) For example: Wellmann, K. M.; Victoriano, M. E.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1979**, *99*, 4198. Jasinski, J. M.; Brauman, J. I. *Ibid.* **1980**, *102*, 2906. Klass, G.; Underwood, D. J.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 507.

(43) The exothermicities (in kcal/mol) of the bimolecular proton transfer reaction from acetone to R^- are estimated to be -7 for R = CF_3, -28 for R = Ph, and -48 for R = CH_3; ref 21. Noest and Nibbering have observed a similar trend in the bimolecular reaction between several alkoxide anions and acetone-d_3. The primary isotope effect was found to decrease from 1.9 to 1.5 as the exothermicity of the proton transfer reaction increased: Noest, A. J.; Nibbering, N. M. M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 383.

results provide a clear demonstration of the variation of primary kinetic isotope effects with reaction free energy (Bell–Westheimer effect) which has been discussed extensively for solution proton transfer reactions.[41] Our observations can be rationalized within the conventional framework; the extent of proton transfer in the transition state (and hence the zero point energy differences of the two isotopically distinct channels) decreases as the reaction becomes more exothermic. These initial results are promising in that they demonstrate the utility of this type of photochemical probe into bimolecular reaction dynamics. Further work involving a systematic investigation of the isotope effects for these and related systems is currently in progress in our laboratory. This work may also provide insight into internal energy effects on ion–molecule reactions through investigations of the laser intensity dependence of the reactivity of photochemically generated intermediates.

Conclusion

Through a systematic investigation of the IRMP photochemically induced decompositions of a number of gas-phase alkoxide anions we have elucidated a general stepwise mechanism involving heterolytic cleavage to an anion–ketone intermediate complex for the formal 1,2-elimination of neutral fragments. Evidence for this mechanism is provided by the observed reactivity patterns as well as measured kinetic isotope effects. One finding of this study is an apparent anomalous order of alkyl group leaving abilities, *t*-Bu > Me > *i*-Pr > Et. Although this reactivity order

may be taken to reflect the relative alkane acidities, we believe that it can be rationalized by invoking a change in mechanism to one involving an intermediate in which the electron is not bound specifically by the alkyl group: either a radical–ketone radical anion complex produced by homolytic cleavage of a transient anionic cluster. In these systems, this mechanism is important only when the electron affinity of the cleaved radical approaches zero. Our results strongly suggest that methane elimination from *tert*-butoxide anion (and other alkoxide anions) proceeds via a heterolytic mechanism. Furthermore, the photochemical generation of ion–molecule complexes that are purported intermediates in bimolecular ion–molecule reactions can be used to probe the dynamics and potential energy surfaces of such reactions.

Ionic Structure and Interactions in 1-Methyl-3-ethylimidazolium Chloride–AlCl₃ Molten Salts

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Abstract: Room temperature chloroaluminate molten salts formed by mixing 1-methyl-3-ethylimidazolium chloride (MEICl) with $AlCl_3$ are of interest as electrolytes and nonaqueous reaction media. Results of NMR studies of MEI^+ in melts of various composition (determined by the mole fraction, N, of $AlCl_3$ used in forming a melt) were originally explained by a stack model of the ionic structure. In this model, the anions are located between stacked "parallel" MEI^+ ring planes. An alternative model has been suggested in which Cl^- forms ion pairs with MEI^+ by a H-bonding interaction through the H on the C-2 in the ring. Our IR studies, particularly on deuteriated MEI^+, now show that Cl^- interacts with the hydrogens at the C-2, C-4, and C-5 members of the MEI^+ ring.

One of the most widely studied room temperature melt systems is the 1-methyl-3-ethylimidazolium chloride–AlCl₃ (MEICl–AlCl₃) melt which is liquid at room temperature for compositions between 33 and 67 mol % AlCl₃.[1,2] This melt exhibits acid–base chemistry which is dictated by the following reactions:

$$MEI^+ Cl^- + AlCl_3 \rightleftharpoons MEI^+ AlCl_4^- \quad K \gg 1 \quad (1)$$

$$MEI^+ AlCl_4^- + AlCl_3 \rightleftharpoons MEI^+ Al_2Cl_7^- \quad K \gg 1 \quad (2)$$

When the mole fraction of AlCl₃ (*N*) used in preparing the melt is less than 0.5, it contains Cl⁻, which acts as a Lewis base, and is basic. For compositions with $N > 0.50$, the melt is considered acidic because it contains $Al_2Cl_7^-$, which acts as a Lewis acid. At $N = 0.50$ the melt is neutral, with $AlCl_4^-$ the only detectable anion. These melts exhibit several attractive features such as large

electrochemical windows and high conductivities. The structure of MEI^+ is shown below:
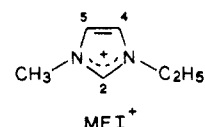
A better understanding of the physical and chemical properties of these melts has been sought through investigation of their ionic interactions. The crystal structure of MEICl's iodide analogue, MEII, has been reported, and based upon the C-2 hydrogen–iodide distance and position, an interaction involving hydrogen bonding through the C-2 hydrogen has been suggested.[3] Previous investigations have also used this model to explain composition dependent features in the IR spectra of basic MEICl–AlCl₃ melts.[4] In the work reported here we studied both normal and deuteriated

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