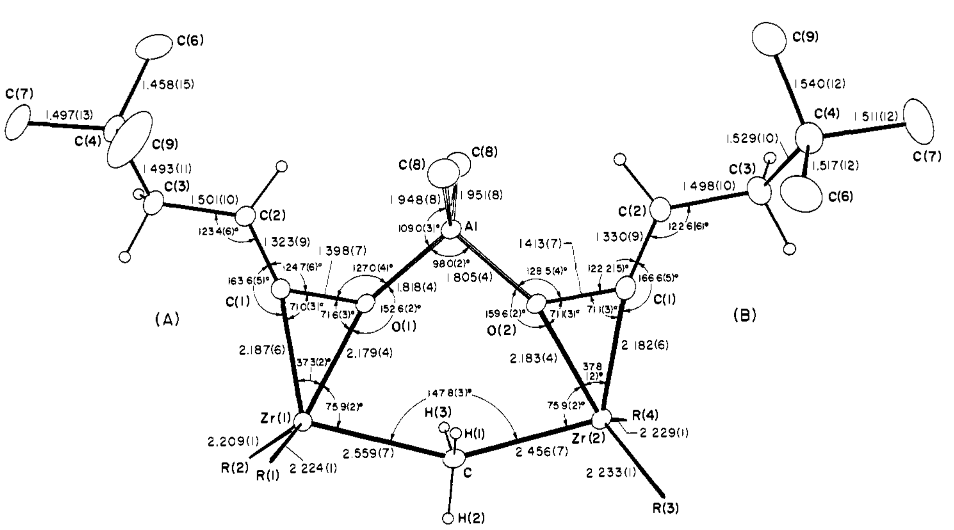

Figure 2. Additional bond lengths and angles: Al–C = 3.739 (8), C–H (1) = 0.94 (5), C–H(2) = 0.98 (5), C–H(3) = 0.86 (5) Å; H(1)–C–H(2) = 119 (4)°, H(1)–C–H(3) = 117 (4)°, H(2)–C–H(3) = 122 (4)°.

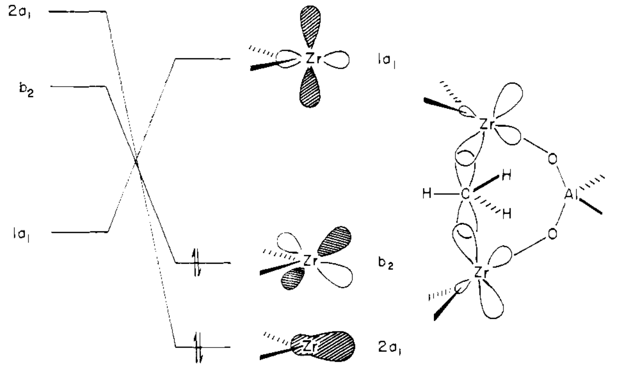

Figure 3.

consistent with the slight distortion of the methyl group from planarity. The bond distance Zr(2)–C of 2.456 (7) Å is comparable to the longest reported terminal Zr–C bond, 2.431 (5) Å, for the methyl group of $Cp_2Zr(\eta^2\text{-}C(NMe)CHPh_2)Me$.[9] The Zr(1)–C bond length of 2.559 (7) Å is not unreasonably long, since bridging metal–alkyl bonds are typically 0.1–0.2 Å longer than the corresponding terminal bond.[10]

The Zr–C–Zr angle is not 180° as might be expected for a trigonal-bipyramidal carbon atom but is 147.8 (3)°. We attribute this to the disposition of the zirconium bonding orbitals. According to Lauher and Hoffmann,[11] the zirconium orbitals available for bonding to the methyl group are derived from orbitals of a_1 symmetry. The orientation of the ketenes in II is such that these orbitals are directed away from the aluminum atom. Maximum overlap is achieved via a bent "banana" bond as illustrated in Figure 3.

The methyl group of II appears to be a pentacoordinate carbanion of approximate $D_{3}h$ symmetry.[3,5b] The C–H coupling constant of 136.18 Hz is consistent with a large amount of sp^2 hybridization. The configuration of the methyl group is strikingly similar to that of Schleyer's $CH_3Li_2^+$, for which calculations indicate that the trigonal-bipyramidal geometry is energetically favored.[3] Our results, and those of Watson[5a] and Schleyer,[3] suggest that the trigonal-bipyramidal geometry is a stable configuration for carbanions in the coordination sphere of Lewis-acidic metals.

Complex II reacts with 1 equiv of pyridine in benzene (12 h, 25 °C) to afford the dimer I and the $Me_3Al\cdot py$ adduct, indicating that methyl transfer between the two metals is reversible.

Acknowledgment. We gratefully acknowledge the generous financial support of the Department of Energy. The many helpful suggestions of D. A. Straus and the assistance of J. D. Meinhart in performing INEPT[12] NMR experiments are greatly appreciated.

Supplementary Material Available: Summary of crystal data and intensity collection information (Table XI), atom coordinates (Tables X2 and X5), anisotropic Gaussian amplitudes (Table X4), bond lengths and angles (Table X3), structure factor amplitudes (Table X6), and labeling scheme (Figure 2) (43 pages). Ordering information is given on any current masthead page.

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(9) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, *462*, ref 10.

(10) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54.

(11) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(12) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

Relative Gas-Phase Acidities of the Alkanes

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Although the gas-phase acidities of a large number of organic molecules have been determined,[1] those of many of the simplest, namely, the alkanes, cycloalkanes, and substituted alkanes, remain to be established. This is so because these compounds are so weakly acidic that no way has yet been devised to generate the carbanions in the gas phase. The only exception is methane whose acidity ($\Delta H°_{\text{acid}}$ = 416.6 kcal/mol) can be calculated from thermochemical data which are unavailable for other alkanes.[2,3]

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(1) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11. Bartmess, J. E., private communication. Boand, G.; Houriet, R.; Gäumann, T. *J. Am. Chem. Soc.* **1983**, *105*, 2203–2206.

(2) $\Delta H°_{\text{acid}}$(RH) is defined as the enthalpy of ionization to R^- and H^+; it can be computed from the bond-dissociation energy of R–H (McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532), the ionization potential of H· (Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables", NSRDS-NBS-37, 2nd ed.; National Bureau of Standards: Washington, D.C., 1971), and the electron affinity (EA) of R·.

0002-7863/84/1506-4051$01.50/0

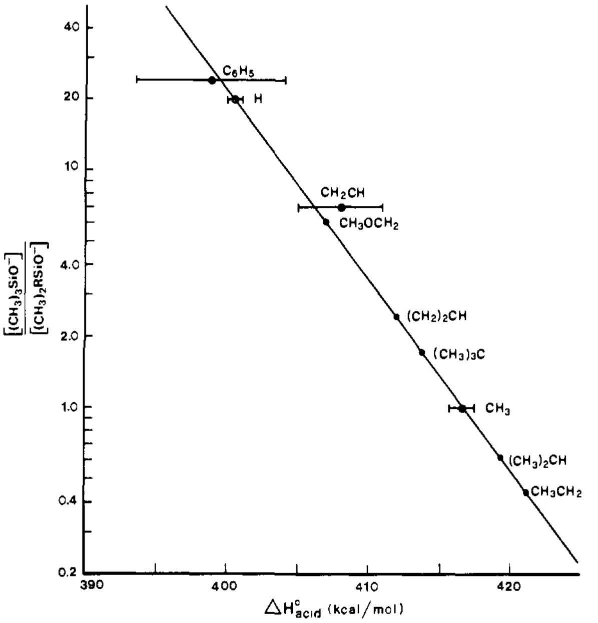

Figure 1. Ratio of product ions from reaction 1 as a function of the acidity of RH. The line is drawn through the best known values, those for CH_4 and H_2. The reproducibility of the experimental ion ratios is ±25%.[13]

It would be particularly interesting to obtain the acidities of substituted methanes in view of recent ab initio calculations which predict ethane to be a *weaker* acid than methane.[4,5] This prediction is unexpected in view of the fact that a methyl group is acid strengthening in the alcohol series [methyl alcohol (379.2) is a much stronger acid than water (390.7)[6]].

We have found that substituted trimethylsilanes undergo a cleavage reaction in the gas phase with hydroxide ion to form a hydrocarbon and a siloxide ion (eq 1).[7] The reaction is rapid,

$$HO^- + (CH_3)_3SiR \rightarrow (CH_3)_3SiO^- + RH \qquad (1a)$$

$$HO^- + (CH_3)_3SiR \rightarrow (CH_3)_2(R)SiO^- + CH_4 \qquad (1b)$$

occurring at every collision, and only two products are formed, arising from loss of RH or of CH_4. For compounds of known acidity, the ratio of RH to CH_4 loss increases as the acidity of RH increases. This correlation leads us to suggest that the relative basicities of the alkyl anions (and hence the relative acidities of the alkanes) can be determined by examining the ratio of products in this cleavage reaction.

The method has its origin in our earlier flowing afterglow[8] studies on the generation of carbanions by reaction of silanes with fluoride ion (eq 2). This reaction cannot be used to generate a

$$F^- + (CH_3)_3SiR \rightarrow R^- + (CH_3)_3SiF \qquad (2)$$

carbanion more basic than $C_6H_5^-$; with tetramethylsilane, for example, the pentacovalent adduct is formed by energy transfer to the helium bath gas.[7] However, when hydroxide ion is used as the base, the reaction is driven to completion by a proton transfer to the carbanion while it is still in the vicinity of the silicon atom (eq 3).[9] The incipient carbanion need not be totally free

$$HO^- + (CH_3)_3SiR \rightarrow [(CH_3)_3SiOH\cdots R^-] \rightarrow (CH_3)_3SiO^- + RH \qquad (3)$$

of covalent bonding to silicon before reaction with the proton and in any event will be stabilized by ion–dipole and ion-induced dipole forces within the complex.[10–12]

Table I. Product Ion Ratios, Predicted Gas-Phase Acidities, and Electron Affinities from the Reaction of Substituted Trimethylsilanes, $(CH_3)_3SiR$, with Hydroxide Ion

R	$\frac{(CH_3)_3SiO^-}{(CH_3)_2RSiO^-}$ [a]	$\Delta H^\circ_{acid}(RH)$,[b] kcal/mol	$EA(R\cdot)$,[c] kcal/mol
CH_3CH_2	0.44	421	−9
$(CH_3)_2CH$	0.61	419	−11
CH_3	1.0	416.6 ± 0.9[d,e]	1.8[d,h]
$(CH_3)_3C$	1.7	414	−7
$(CH_2)_2CH$	2.4	412	8
CH_3OCH_2	6.0	407	0
CH_2CH	7.0	406[f]	17
H	20	400.4 ± 0.6[d,e]	17.4[d,i]
C_6H_5	24	399[g]	25

[a] Statistically corrected. [b] See ref 13. [c] Reference 2. [d] Experimental values. [e] Reference 1. [f] This is in good agreement with an estimate of 408 ± 3 kcal/mol.[15] [g] This is in good agreement with an estimate of 398.8 ± 5.3 kcal/mol.[1] [h] Reference 3. [i] Reference 12.

We have studied the reactions of a series of substituted trimethylsilanes with hydroxide ion using our flowing afterglow apparatus and measured the relative amounts of siloxide ions arising from loss of the substituent as compared to loss of methane. Figure 1 gives the logarithm of this ratio vs. ΔH°_{acid} for compounds of known or approximately known acidity (values with error bars). From this line an approximate ΔH°_{acid} for the other compounds can be calculated.[13] Taking this value together with the bond-dissociation energy one can also predict the electron affinity of the corresponding radical. The derived acidity and electron affinity values are given in Table I.

The order of acidities predicted by this method for cyclopropane, methyl ether,[14] ethylene,[15] hydrogen,[1] and benzene[1] is intuitively reasonable and in accord with experimental data where available. For the alkanes note that ethane and the secondary hydrogens in propane are predicted to be less acidic than methane, in agreement with theory. The tertiary hydrogen in isobutane is predicted to be more acidic than methane, but this result could be due, in part, to relief of strain in the cleavage. In order to test for consistency, we determined the ethane to methane loss ratio (statistically corrected) from dimethyldiethylsilane (0.35) and triethylmethylsilane (0.40). Both of these values are within experimental error of that found from trimethylethylsilane (0.44). As a further check we measured the hydrogen/ethane loss from diethylsilane (40), which, when combined with the hydrogen/methane loss from trimethylsilane (20), leads to a similar ethane/methane ratio (0.50).

In conclusion, we report a simple kinetic method that allows us to estimate the relative acidities of many weakly acidic compounds and the electron affinities of their corresponding radicals. The required compounds are relatively easy to prepare and con-

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(3) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556–2558.

(4) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363–371.

(5) Kollmar, H. *J. Am. Chem. Soc.* **1978**, *100*, 2660–2664.

(6) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986–5992.

(7) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012–5015.

(8) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146–153. DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Science (Washington, D.C.)* **1982**, *218*, 955–960.

(9) The generation of relatively free carbanions within a complex of this type is dramatically illustrated by: Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519–529.

(10) The reaction of HO^- with $(CH_3)_4Si$ to form $(CH_3)_3SiOH$ and CH_3^- separated to infinite distance is approximately thermoneutral in the gas phase.[11,12] The same reaction to form an ion–dipole complex is 10–15 kcal/mol exothermic due to the ion–dipole energy.

(11) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–252.

(12) Janousek, B. K.; Brauman, J. I. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 10.

(13) From the experimental uncertainty in measuring the ion ratios and the graph in Figure 1, the ΔH°_{acid} values are good to ±2 kcal/mol. However, the major uncertainty in the experiment is whether the relative basicity of the anions is the only effect being measured. A solution analogy correlating the acidity of arylalkanes with rates of cleavage of their trimethylsilyl derivatives has been given by Eaborn et al.: Eaborn, C.; Walton, D. R. M.; Seconi, G. *J. Chem. Soc., Chem. Commun.* **1975**, 937–939. For an alternative view see the following paper by Tumas, Foster, and Brauman.

(14) A methoxyl group acidifies the hydrogens in ethylene. DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034–5038.

(15) The acidity of ethylene is estimated to be 408 ± 3 kcal/mol. Grabowski, J. J. Ph.D. Thesis, University of Colorado, Boulder, 1983.

jugative effects are not expected to play an important role in either the pentacoordinate intermediates, the starting materials, or the products. While a thermodynamic method would obviously be preferable, it may prove impossible to find such a method in view of the fact that many of the anions of interest appear to be thermodynamically unstable toward electron detachment.

Acknowledgment. We gratefully acknowledge support of this work by the U. S. Army Research Office [Contract DAAG-29-82-K-0025 (to C.H.D. and V.M.B.)] and by the Research Corporation (to R.D.). We thank Louis Aran for experimental assistance.

Registry No. CH_3CH_3, 74-84-0; $(CH_3)_2CH_2$, 74-98-6; CH_4, 74-82-8; $(CH_3)_3CH$, 75-28-5; $(CH_2)_2CH_2$, 75-19-4; CH_3OCH_3, 115-10-6; CH_2-CH_2, 74-85-1; H_2, 1333-74-0; C_6H_6, 71-43-2; $Me_3SiCH_2CH_3$, 3439-38-1; $Me_3SiCH(CH_3)_2$, 3429-52-5; Me_3SiCH_3, 75-76-3; $Me_3SiC(CH_3)_3$, 5037-65-0; $Me_3SiCH(CH_2)_2$, 930-40-5; $Me_3SiCH_2OCH_3$, 14704-14-4; $Me_3SiCHCH_2$, 754-05-2; Me_3SiH, 993-07-7; $Me_3SiC_6H_5$, 768-32-1; $CH_3CH_2\cdot$, 2025-56-1; $(CH_3)_2CH\cdot$, 2025-55-0; $CH_3\cdot$, 2229-07-4; (C-$H_3)_3C\cdot$, 1605-73-8; $(CH_2)_2CH\cdot$, 2417-82-5; $CH_3OCH_2\cdot$, 16520-04-0; $CH_2CH\cdot$, 2669-89-8; $H\cdot$, 12385-13-6; $C_6H_5\cdot$, 2396-01-2.

Unimolecular Decompositions of Gas-Phase Alkoxide Anions

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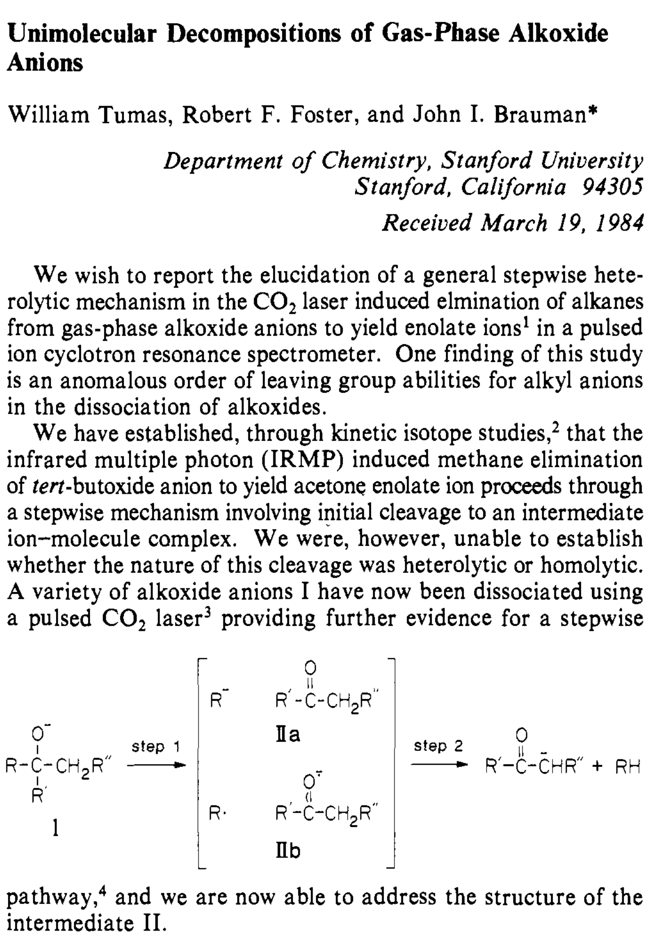
We wish to report the elucidation of a general stepwise heterolytic mechanism in the CO_2 laser induced elmination of alkanes from gas-phase alkoxide anions to yield enolate ions[1] in a pulsed ion cyclotron resonance spectrometer. One finding of this study is an anomalous order of leaving group abilities for alkyl anions in the dissociation of alkoxides.

We have established, through kinetic isotope studies,[2] that the infrared multiple photon (IRMP) induced methane elimination of *tert*-butoxide anion to yield acetone enolate ion proceeds through a stepwise mechanism involving initial cleavage to an intermediate ion–molecule complex. We were, however, unable to establish whether the nature of this cleavage was heterolytic or homolytic. A variety of alkoxide anions I have now been dissociated using a pulsed CO_2 laser[3] providing further evidence for a stepwise pathway,[4] and we are now able to address the structure of the intermediate II.



The structure of intermediate II, which is formally a neutral radical–molecule complex with an additional electron, should depend on the absolute and relative values of the electron affinities (EA's)[5] of the radical R· and ketone as well as ion–molecule interaction forces such as charge–dipole and charge-induced dipole. If the EA of the radical were greater than that of the ketone, then the intermediate should have the structure IIa, whereas structure IIb would result if the opposite were true. If the EA of both species were comparable, then the intermediate might be a hybrid of IIa and IIb or involve an electron-transfer equilibrium. Finally, if neither component has an appreciable EA, binding of the electron would be weak and perhaps nonspecific; the intermediate might be best described as an anionic cluster.[6]

IR photolysis of several 2-substituted 2-propoxides (I, R′ = CH_3; R″ = H; R = CF_3 (Ia), Ph (Ib), H (Ic), vinyl (Id)), in which the C–R bond is weaker than the C–CH_3 bond relative to heterolysis[7] (i.e., $\Delta H_{\mathrm{acid}}°(\mathrm{RH}) < \Delta H_{\mathrm{acid}}°(\mathrm{CH_4})$) but the C–R bond is stronger than the C–CH_3 bond relative to homolysis[8] ($D(\mathrm{C{-}R}) > D(\mathrm{C{-}CH_3})$), resulted in exclusive formation of acetone enolate[9] (elmination of RH). No methane elimination was observed even though this channel is more exothermic overall. This implies a heterolytic stepwise mechanism[10] (through IIa) where the products reflect the relative stability of the intermediate rather than that of the final products.

Further evidence for a heterolytic stepwise pathway is provided by the isotope effects measured in the infrared laser photolysis of three d_3 alkoxides (Ia-d_3, R = CF_3, R′ = CD_3, R″ = H; Ib-d_3, R = Ph, R′ = CD_3, R″ = H; Ie-d_3, R = CH_3, R′ = CD_3, R″ = H). The isotope effects (R:k^H/k^D; CF_3:6.0; Ph:2.5; CH_3:1.6) are consistent with the intermediacy of IIa in that k^H/k^D decreases as the proton transfer in step 2 becomes more exothermic.[11] Moreover, the very different effects observed for Ia-d_3 (R = CF_3) and Ie-d_3 (R = CH_3) are inconsistent with a concerted mechanism where the transition states should be similar in structure for these nearly thermoneutral reactions.

On the basis of observed product enolate ions from laser photolysis of a series of alkoxides,[12] a relative order of leaving group abilities, CF_3 > Ph > H > *t*-Bu > Me > *i*-Pr > Et, can be assigned.[13] The ratio[14] of isobutane to methane loss was 2:1 in If (R = *t*-Ru, R′ = CH_3, R″ = H). If these alkoxides all react via the same heterolytic pathway (via IIa) as above, then the products should reflect the relative stabilities of R^- in IIa and an unusual order of alkane acidities is revealed[13] (*t*-Bu-H > Me-H > *i*-Pr-H > Et-H). This implies an alkyl substituent effect[15] which has no precedent.

There is no reliable evidence that isolated saturated alkyl anions other than methyl[16] are capable of existence as bound species in the gas phase. In fact, if *tert*-butyl radical has even an infinitesimal

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[1] Solution analogy: (a) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; Chapter 4, pp 32, 33. (b) Arnett, E. M; Small, L. E.; McIver, R. T., Jr.; Miller, J. S. *J. Org. Chem.* **1978**, *43*, 815.

[2] Tumas, W.; Foster, R. F.; Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 7464.

[3] For experimental details, see: (a) Jasinski, J. M.; Rosenfeld, R. N.; Meyer, F. K.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 652. (b) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. E. *Ibid.* **1982**, *404*, 658.

[4] Also, see: Morton, T. H. *Tetrahedron* **1982**, *38*, 3195.

[5] Janousek, B. K.; Brauman, J. I. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Wiley: New York, 1979; Vol. 2, Chapter 10.

[6] (a) Armbruster, M.; Haberland, H.; Schindler, H.-G. *Phys. Rev. Lett.* **1981**, *47*, 323. (b) Klots, C. E. Compton, R. N. *J. Chem. Phys.* **1978**, *69*, 1636. (c) Klots, C. E. *Ibid.* **1979**, *71*, 4172. (d) Quitevis, E. L.; Bowen, K. H.; Liesegang, G. W.; Herschbach, D. R. *Ibid.* **1983**, *87*, 2076.

[7] (a) Bartmess, J. E.; McIver, R. T., Jr., ref 5, Vol. 2, Chapter 11. (b) Moylan, C. R.; Brauman, J. I. *Annu. Rev. Phys. Chem.* **1983**, *34*, 187.

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[9] For Ia, dissociation yielding CF_3^- is also observed.

[10] This mechanism may account for some previous observations: (a) Smit, A. L. C.; Field, F. H. *J. Am. Chem. Soc.* **1977**, *99*, 6471. (b) Boand, G.; Houriet, R.; Gaumann, T. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 95. (c) Caldwell, G.; Bartmess, J. E. *Ibid.* **1981**, *40*, 269. (d) Noest, A. J.; Nibbering, N. M. M. *Adv. Mass Spectrom.* **1979**, *8A*, 227.

[11] (a) Melander, L.; Saunders, W. H. "Reactions of Isotopic Molecules"; Wiley: New York, 1980. (b) More O'Ferrall, R. A. "Proton Transfer Reactions"; Academic Press: New York, 1973; Chapter 9.

[12] For most of the alkoxides studied, only one product was observed, so quantitative ratios could not be assessed.

[13] DePuy and co-workers have observed the same reactivity order in gas-phase ion-molecule reactions of alkyltrimethylsilanes: DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.*, in press. Also, see: Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519.

[14] This ratio is independent of laser fluence suggesting that the two channels are very close in energy.

[15] However, see: Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363.

[16] EA($CH_3\cdot$) = 1.8 kcal/mol: Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.