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; $Me_{S}iH$, 993-07-7; $Me_3SiC_6H_5$, 768-32-1; CH_3CH_2·, 2025-56-1; $(CH_3)_2CH$·, 2025-55-0; CH_3·, 2229-07-4; $(CH_3)_3C$·, 1605-73-8; $(CH_2)_2CH$·, 2417-82-5; CH_3OCH_2·, 16520-04-0; CH_2CH·, 2669-89-8; H·, 12385-13-6; C_6H_5·, 2396-01-2.

Unimolecular Decompositions of Gas-Phase Alkoxide Anions

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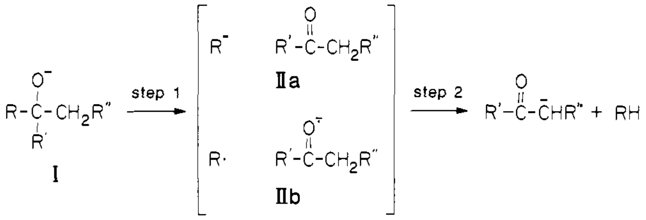
Received March 19, 1984

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., $\Delta H_{\text{acid}}°(\text{RH}) < \Delta H_{\text{acid}}°(\text{CH}_4)$) but the C–R bond is stronger than the C–CH_3 bond relative to homolysis[8] ($D(\text{C–R}) > D(\text{C–CH}_3)$), 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.

(8) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(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·) = 1.8 kcal/mol: Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

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EA, then isobutane would be 10 kcal/mol more acidic than methane;[17] observation of both products from If requires much closer acidities.[14] Coupled with indications that simple aliphatic ketones also have extremely low EA's, this leads to another explanation. If the intermediate for elimination of isobutane, propane, and ethane is actually best described as an anionic cluster where the binding of the electron is weak and dependent on terms other than EA(R·), then the binding of the electron in II will be small and insensitive to the nature of R. The leaving abilities of these alkyl groups would then be determined by the relative homolytic bond dissociation energies (D(C–R)) rather than the relative stabilities of R^-. Since methyl anion is bound, we interpret the position of methyl as evidence that methane elimination proceeds through a heterolytic mechanism (by IIa, $R = CH_3$). The anomalous order of alkyl leaving group abilities can be explained by a mechanism involving an intermediate in which the electron is bound only by the radical–molecule complex and not specifically by either component of this complex. This mechanism is important only when EA(R·) approaches zero.

Acknowledgment. We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also gratefully acknowledge the National Science Foundation for postdoctoral fellowship support for R.F.F. and for graduate fellowship support for W.T. and the Fannie and John Hertz Foundation for fellowship support for W.T. We thank Professor C. H. DePuy for communicating results prior to publication.

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(17) Based on a thermochemical cycle and the relative C–H bond strengths.[7,8]

Hydrogen Abstractions by Triplet Methylene and Silylene

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Received February 17, 1984

While the most common reactions of singlet methylenes are insertions into Y–H or multiple bonds,[1-3] triplet methylenes tend to abstract hydrogens from Y–H bonds.[1,2] Singlet silylenes are also known to insert,[4-6] while little is known about the corresponding triplets. Several theoretical papers have been devoted to analyses of the insertions of singlet CH_2[7-12] and SiH_2[13-15] into a variety of bonds and the abstractions of hydrogen from H_2[16-20] and CH_4[17] by triplet methylene. Ab initio calculations including correlation predict that carbenes insert into Y–H[9,11,12,15] bonds with no barrier, in agreement with the prevailing experimental evidence;[1,2] however, silylene insertions may encounter significant energy barriers.[4,5,13-15]

For the reaction

$$^3\!:\!CH_2 + CH_4 \rightarrow CH_3 + CH_3 \tag{1}$$

bond energy–bond order (BEBO) calculations predict a 25.6 kcal/mol barrier,[21] whereas MINDO/2 predicts a much smaller barrier of 3.8 kcal/mol.[22] Double-ζ (DZ) SCF calculations[17] are in qualitative agreement with the BEBO calculations, predicting a barrier of 33 kcal/mol. On the basis of analogous calculations on the abstraction from H_2,[18] these authors estimate that correlation corrections will drop the barrier for reaction 1 to about 18–23 kcal/mol. This work presents calculations on reaction 1 and the analogous reactions involving silicon:

$$^3\!:\!SiH_2 + CH_4 \rightarrow SiH_3 + CH_3 \tag{2}$$

$$^3\!:\!CH_2 + SiH_4 \rightarrow CH_3 + SiH_3 \tag{3}$$

$$^3\!:\!SiH_2 + SiH_4 \rightarrow SiH_3 + SiH_3 \tag{4}$$

Whereas the singlet methylene insertions are predicted to occur with no barriers, the triplet abstractions from the same substrates have substantial barriers. Likewise, the insertion of singlet silylene into silane occurs with no barrier,[15] while the corresponding triplet abstraction requires a 15.9 kcal/mol barrier. The insertion of singlet silylene into methane has a substantial barrier,[13-15] but even here the corresponding triplet abstraction barrier is larger by about 5 kcal/mol.

All structures were calculated at the UHF/SCF level with the 3-21G basis set[23] using GAUSSIAN80.[24] For the prediction of the energetics of the reactions single-point calculations were carried out with 6-31G**[25] and third-order Møller–Plesset perturbation theory (UMP3[26]). The reliability of the unrestricted wave functions for the species treated here is indicated by the S^2p expectation values. These range from 2.0 to 2.05 for the triplets and from 0.75 to 0.80 for the doublets. The exact values are 2.0 and 0.75, respectively. Force fields at the transition-state structures were calculated by using GAMESS.[27]

The 3-21G geometries for all reactants and products except methylene and silylene have been published previously.[28] For CH_2, we find $R = 1.071$ Å and $\alpha = 131.3°$, in good agreement with experiment.[1,2] The corresponding parameters for silylene (1.482 Å and 118.7°) are very close to those of Schaefer et al.[29]

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(1) Jones, M.; Moss, R. A. "Carbenes"; Academic Press: New York, 1971.

(2) Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1971.

(3) Frey, H. *J. Am. Chem. Soc.* **1957**, *79*, 1259. Frey, H. M.; Kistiakowsky, G. B. *Ibid.* **1957** *79*, 6373. Rabinowitch, B. S.; Tschnikov-Roux, E.; Schlag, E. W. *Ibid.*, **1959**, *81*, 1081.

(4) John, P.; Purnell, J. H. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1455.

(5) Davidson, I. M. T. 17th Organosilicon Symposium, Fargo, ND, June, 1983.

(6) O'Neal, H. E.; Ring, M. A., private communication.

(7) Dobson, R. C.; Hayes, D. M.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6188.

(8) Kollmar, H. *Tetrahedron* **172**, *28*, 5893.

(9) Bauschlicher, C. W.; Haber, K.; Schaefer, H. F., III; Bender, C. F. *J. Am. Chem. Soc.* **1977**, *99*, 3610.

(10) Kollmar, H. *J. Am. Chem. Soc.* **1978**, *100*, 2660.

(11) Kollmar, H.; Staemmler, V. *Theor. Chim. Acta* **1979**, *51*, 207.

(12) Jeziorek, D.; Zurawski, B. *Int. J. Quantum Chem.* **1979**, *16*, 277.

(13) Gordon, M. S. *J. Chem. Soc., Chem. Commun.* **1981**, 890.

(14) Grev, R. S.; Schaefer, H. F., III. *J. Chem. Soc., Chem. Commun.* **1983**, 785.

(15) Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.*, in press.

(16) Baskin, C. P.; Bender, C. F.; Bauschlicher, C. W.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1974**, *96*, 2709.

(17) Bauschlicher, C. W.; Bender, C. F.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 3072.

(18) Bauschlicher, C. W. *Chem. Phys. Lett.* **1978**, *56*, 31.

(19) Cremaschi, P.; Simonetta, M. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1801.

(20) Tan, L. P. *Chem. Phys. Lett. 57*, **1978**, 239.

(21) Carr, R. W. *J. Phys. Chem.* **1972**, *76*, 1581.

(22) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095.

(23) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797.

(24) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

(25) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(26) Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quantum Chem. Symp.* **1979**, *11*, 149.

(27) Dupuis, M.; Spangler, D.; Wendoloski, J. J. *NRCC* Software Cat., University of California, Berkeley, CA, Vol. 1, 1980.

(28) Gordon, M. S.; Gano, D. R.; Boatz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5771.

(29) Colvin, M. E.; Grev, *R.*; Schaefer, H. F., III. *Chem. Phys. Lett.* **1983**, *99*, 399.

0002-7863/84/1506-4054$01.50/0 © 1984 American Chemical Society