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Nucleophilic Substitution in the Gas Phase. The Reactions of Alkoxide–Alkanol Negative Ions with Boron, Carbon, Silicon, and Titanium Alkoxides. An Ion Cyclotron Resonance and ab Initio Study

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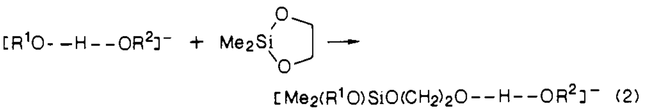
Abstract: When monosolvated alkoxide ions $(R^1O{-}{-}H{-}{-}OR^2)^-$ ($R^1 < R^2$) react with boron, carbon, silicon, or titanium ethers, the major displacement reaction is always that where the smaller alkoxide (R^1O^-) reacts with the central atom, while the larger alcohol (R^2OH) becomes part of the solvated alkoxide product ion, e.g., $(R^1O{-}{-}H{-}{-}OR^2)^- + Me_3SiOR^3 \rightarrow (R^2O{-}{-}H{-}{-}OR^3)^- + Me_3SiOR^1$. Such reactions are exothermic and very fast: the slowest (silicon reactions) occur for one collision in every two. Such rates do not favor either (i) endothermic barriers or (ii) equilibria (i.e., it seems unlikely that the specificity of reaction is due to thermodynamic control). The presence of initial orientation effects controlling the courses of reactions was suggested by ab initio studies (6-31G) for model systems $(F^-{-}{-}HOH)/H_2BOMe$ and $(MeO^-{-}{-}HOH)/H_2BOMe$. In the former case, F^- hydrogen bonds to a methoxy hydrogen thus effecting subsequent attack of HO^- at boron. Internal barriers are small. Ab initio calculations (6-31$^+$G) show for equilibrium $(EtO^-{-}{-}HOMe) \rightleftarrows (EtOH{-}{-}{^-}OMe)$ that the mole ratio of $(EtO^-{-}{-}HOMe)$ is greater than 0.95. Thus in the reaction of $(EtO^-{-}{-}HOMe)$ with say Me_3SiOR, it is proposed that initial approach of the two reactants results in the EtO^- end of the nucleophile H bonding to R, thus directing subsequent attack of MeO^- at silicon.

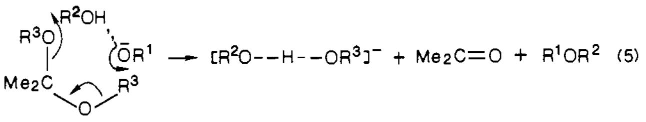
Nucleophilic displacement reactions of silanes and substituted silanes in the gas phase have been studied in depth.[1] A comparison of gas-phase nucleophilic substitution at carbon and silicon shows fundamental differences between the two systems.[2-4] For example, the reactions of various anions with methyl iodide show a gradual reduction in rate as the attacking nucleophile becomes less basic.[2,5] In contrast, trimethylchlorosilane reacts at virtually every collision for exothermic reactions, or not at all for endothermic ones.[2]

$$[R^1O{-}{-}H{-}{-}OR^2]^- + Me_3SiOR^3 \longrightarrow [R^2O{-}{-}H{-}{-}OR^3]^- + Me_3SiOR^1 \quad (1)$$


(2)

$$[R^1O{-}{-}H{-}{-}OR^2]^- + Me_2C(OR^3)_2 \longrightarrow [R^2O{-}{-}H{-}{-}OR^3]^- + Me_2C(OR^3)(OR^1) \quad (3)$$

$$[R^1O{-}{-}H{-}{-}OR^2]^- + Me_2C(OR^3)_2 \longrightarrow [R^1O{-}{-}H{-}{-}OR^3]^- + Me_2C(OR^3)(OR^2) \quad (4)$$


(5)

$$[EtO^-{-}{-}HOMe] + Ti(O\text{-}i\text{-}Pr)_4 \longrightarrow [i\text{-}PrO^-{-}{-}HOEt] + Ti(O\text{-}i\text{-}Pr)_3(OMe) \quad (6)$$

$$[EtO^-{-}{-}HOMe] + Ti(O\text{-}i\text{-}Pr)_4 \longrightarrow [i\text{-}PrO^-{-}{-}HOMe] + Ti(O\text{-}i\text{-}Pr)_3(OEt) \quad (7)$$

When monosolvated alkoxide ions react with silicon and carbon ethers, nucleophilic displacement is observed. When such reactions are carried out at low pressures in either conventional ion cyclotron resonance (ICR) or FT-ICR instruments, surprising specificity is reported for the reactions of $[R^1O{-}{-}H{-}{-}OR^2]^-$ (ref 6) with Me_3SiOR^3 (R^1, R^2, and R^3 = alkyl; $R^1 < R^2$). The smaller alkoxide R^1O^- reacts at silicon, and the larger alkanol R^2OH becomes part of the product alkanol–alkoxide (see eq 1).[7] Cyclotron ejection experiments fail to detect addition of the alkanol–alkoxide in the reverse sense. Reactions of more complex silane substrates show the same specificity (e.g., eq 2).[7] In contrast, carbon ether reactions go *both* ways (see, e.g., eq 3 and 4), with reaction 3 being the predominant one: i.e., the major reaction is again that where the smaller alkoxide reacts at the electrophilic center.[8] In this case, a six-center reaction (eq 5) must also be considered; experimental evidence[8] excludes this possibility and points to the overall four-center reactions shown in eq 3 and 4.

The mechanisms of these reactions are not straightforward, and we suggested initially the possibility of barriers in the reaction pathways.[8] We wondered also whether the specificity of the silicon reaction was due to the intervention of a particular trigonal-bipyramidal intermediate rather than an equilibrating system in which all rotamers were present.[9] In order to check the last proposal we chose to study a system in which all the positions in the reactive intermediate are the same. Thus we investigated the alkoxyborane reaction in which the four-coordinate intermediate is tetrahedral. *The silicon and boron systems reacted in a similar fashion*: reactions directly comparable to reactions 1 and 2 were observed.[10] Thus we believe that a particular arrangement of apical/equatorial substituents in the silicon intermediate is not

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[1] For a recent review see: DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* **1987**, *20*, 127.

[2] Damrauer, R.; DePuy, C. H.; Bierbaum, V. M. *Organometallics* **1982**, *1*, 1553.

[3] Dewar, M. J. S.; Healy, E. *Organometallics* **1982**, *1*, 1705.

[4] Sheldon, J. C.; Hayes, R. N.; Bowie, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 7711.

[5] A density of state (entropy bottleneck) approach has been used to explain the slow rates of some exothermic gas-phase S_N2 reactions; see, e.g.: Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993. Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959.

[6] When $R^1 < R^2$ the ground state is $[R^2O^-{-}{-}HOR^1]$. Structures are drawn in the general case as $[R^1O{-}{-}H{-}{-}OR^2]^-$ to avoid confusion. For specific cases, ground-state structures are indicated: e.g., $[EtO^-{-}{-}HOMe]$.

[7] Hayes, R. N.; Bowie, J. H.; Klass, G. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1167.

[8] Hayes, R. N.; Paltridge, R. L.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* **1985**, 567.

[9] For a discussion of equilibration of rotamers in trigonal-bipyramidal silicon intermediates see: Sheldon, J. C.; Hayes, R. N.; Bowie, J. H.; DePuy, C. H. *J. Chem. Soc., Perkin Trans. 2* **1987**, 275.

[10] Hayes, R. N.; Sheldon, J. C.; Bowie, J. H. *Organometallics* **1986**, *5*, 162.

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an important feature in the mechanistic pathway. Recently,[11] we have studied similar reactions with titanium alkoxides: in a particular case, reactions 6 and 7 both occur, with reaction 6 predominating, as expected.

If the above evidence is considered collectively, three factors, alone or together, may contribute to the specificity of the reactions: viz., (i) there are internal barriers, perhaps also entropy bottlenecks; (ii) the reactions may operate under thermodynamic control, i.e., they are equilibria with the more stable products being isolated; or (iii) there is a specific orientation effect operating in the initial approach (or reaction) of the solvated nucleophile to (with) the substrate. This paper addresses these problems with use of complementary experimental and theoretical approaches.

Experimental Section

Ion cyclotron resonance spectra were measured at 298 K with the University of Amsterdam FT–ICR instrument. The basic hardware,[12a] software,[12b] and general operation procedure[12c,d] of the instrument have been described previously. The partial pressures of the compounds used were kept around 3×10^{-5} Pa. These pressures were measured on an ionization gauge placed in a side arm of the main pumping line. The ionization gauge readings were calibrated against a MKS Baratron (type 170M, head type 94 AH-1) placed in the same side arm over the 10^{-1}–10^{-3}-Pa pressure range. The (i-PrO)$_4$Ti compound was not volatile enough to obtain a pressure in the 10^{-1}–10^{-3}-Pa range.

General Procedure. Primary negative ions were generated by direct electron impact with ~0.1-eV electrons on the appropriate alkyl nitrite. Alkanol–alkoxide negative ions were prepared in the FT–ICR cell by the Riveros reaction,[13] i.e., by the reaction between the appropriate alkoxide ion (from the alkyl nitrite)[14] and the appropriate alkyl formate. In a typical experiment the alkanol–alkoxide negative ions were isolated by the so-called notch ejection technique[15] and the reaction with the substrate was studied as a function of the reaction time.

Rate Constants. Rate constants were measured by monitoring the abundances of the ions present in the cell as a function of the reaction time and calculated by the method of McLachlan.[16] In the kinetic experiments exponential decrease of the abundance of the reactant ion was observed in all cases. Correction for variation of the total ion current expressed as the sum of the ion abundances was achieved by normalizing this sum of the ion abundances. The total ion current varied on an average less than ~30% over the time interval studied. In this way and together with a correction of the ionization gauge pressure to the absolute pressure by using the above mentioned baratron, the rate constant of the reaction $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^+ + CH_3^{\bullet}$ was measured as $13.2 \pm 0.8 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}; similarly, the rate constant of the reaction $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$ was measured as $11.1 \pm 0.6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. These rate constants are the mean values of 5 measurements at different CH$_4$ pressures in the 10^{-5}–10^{-4}-Pa pressure range. They are in good agreement with literature values.[17]

Materials. All compounds used in this study were either commercial products or available from previous studies.[7,8,10]

Ab Initio Calculations. Ab initio calculations were carried out at 6-31G or 6-31$^+$G levels with Gaussian 82.[18] The procedures and strategies used in these calculations have been outlined elsewhere.[4,19]

Results and Discussion

A problem with the systems described above is that the spectra are very complex (see, e,g., Figures 1 and 2 in ref 7), and the presence or absence of a process was determined by cyclotron ejection of one (precursor) ion at a time. It is thus possible that minor reactions could be missed. To overcome this problem we have repeated certain reactions using the FT–ICR instrument at the University of Amsterdam. Cyclotron ejection of all ions except the one under study can be achieved with this instrument by using the notch ejection technique.[15] Thus we can monitor the reactions of a particular precursor ion to the exclusion of all others. Results for the five systems studied are listed in Table I. Moments of inertia are listed in Table II. The results shown in Table I indicate that under the reaction conditions used, there are minor contributions in the silicon and boron systems from the 'reverse' addition. Nevertheless, in all systems, the same situation pertains, i.e. the major process is always that in which the smaller alkoxide adds to the central atom (B, C, Si or Ti),[20]

In the boron and silicon cases, adducts between one of the alkoxide ions of the nucleophile and the substrate are formed in yields varying from 60% of the total initial product distribution in the boron case to ~80% in the silicon cases. With the exception of the [n-PrO$^-$--HOMe]/Me$_3$SiOEt system, the major adduct formation is also that in which the smaller alkoxide is incorporated in the product ion.[21]

Let us consider now the proposition that the alkoxide exchange reactions (e.g., eq 1) shown in Table I are equilibria and that the major products are formed under conditions of thermodynamic control. The ΔH_r values listed in Table I must be used as only a rough guide but the trends are quite clear. In each case the major process has the more negative ΔH_r value and the reaction is either exothermic or close to thermoneutral. In general terms, the relative proportion of the minor process appears to be related to ΔH_r of that reaction: as the ΔH_r value becomes more negative, the relative percentage of the minor process increases. *So far* these data are in accord with the thermodynamic stability proposal.

It should be possible to determine whether (or not) these reactions could be equilibria from a knowledge of the various efficiencies of the reactions. If a reaction is very fast, occurring say for every one, or one in two collisions between nucleophile and substrate, then it is most unlikely that such a reaction will be an equilibrium process. Rates and efficiencies of reactions are listed in Table I. Pratically all rate constants are larger than those predicted by either the ADO (average dipole orientation) theory[26]

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(11) Hayes, R. N.; Bowie, J. H., unpublished observations.

(12) (a) Dawson, J. H. J. *Lect. Notes Chem.* **1982**, *31*, 331. (b) Noest, A. J.; Kort, C. W. F. *Comput. Chem.* **1982**, *6*, 111, 115; **1983**, *7*, 81. (c) Kleingeld, J. C.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1982**, *17*, 136. (d) Ingemann, S.; Nibbering, N. M. M.; Sullivan, S. A.; DePuy, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 6520.

(13) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057. Isolani, P. C.; Riveros, J. M. *Chem. Phys. Lett.* **1975**, *33*, 362. Faigl, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049.

(14) Noyes, W. A. *Org. Synth.* **1936**, *16*, 108.

(15) Kleingeld, J. C.; Nibbering, N. M. M. *Tetrahedron* **1983**, *24*, 4193.

(16) McLachlan, L. A. *J. Magn. Res.* **1977**, *26*, 223.

(17) SIFT measurements were done by Smith and Adams (Smith, D.; Adams, N. G. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 123) while ICR measurements were done by Huntress et al. (Huntress, W. T.; Laudenslager, J. B.; Pinizzotto, R. F. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *13*, 331) for the following reactions:

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

$$k_{SIFT} = 12.0 \pm 2.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; \quad k_{ICR} = 9.0 \pm 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$CH_4^{\bullet+} + CH_4 \rightarrow CH_5^+ + CH_3^{\bullet}$$

$$k_{SIFT} = 15.0 \pm 3.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; \quad k_{ICR} = 11.0 \pm 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

(18) Binkley, J. S.; Frisch, M. T.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Shlegel, H. B.; Fluder, E. M.; Pople, J. A. Gaussian 82, Carnegie Mellon University.

(19) Sheldon, J. C.; Currie, G. J.; Lahnstein, J.; Hayes, R. N.; Bowie, J. H. *Nouv. J. Chim.* **1985**, *9*, 205. Hayes, R. N.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1985**, *38*, 355.

(20) Acceleration of the n-PrO$^-$--HOMe ion with additional RF pulse did not result in a notable change in the product ratio for the studied systems (EtO)$_3$B and Me$_3$SiOEt.

(21) Two tentative explanations may be proposed to explain the specificity of adduct formation, viz., (i) adduct formation and alkoxide displacement (cf. eq 1) proceed through the same intermediate (cf. Figures 1 and 2) (the argument for specificity of adduct formation is then similar to that described (later) to explain the specificity of alkoxide displacement) or (ii) the two reactions proceed through *different* initial intermediates (if this is the case, we suggest that orientation or directing effects during the course of adduct formation may be due to electrostatic interaction between nucleophile and alkoxy groups). With fewer alkoxy groups there appears to be more attack on the central atom (Si or B) and consequently more of an equilibrium state.

(22) Caldwell, G.; Roseboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660.

(23) Bartmess, J. E.; McIver, R. T. In *Gas-Phase Ion Chemistry*; Bowers, M. T. Ed.; Academic: New York, 1979; Vol. 2, Chapter 11.

(24) Benson, S. W. *Thermochemical Kinetics*; 2nd ed.; Wiley-Interscience: New York, 1976.

(25) Baldwin, J. C.; Lappert, M. F.; Pedley, J. B.; Poland, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 1943.

(26) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347. Su, T.; Bowers, M. T. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 1, Chapter 3, p 83.

(27) *Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Cleveland, Ohio, 1979–1980; p E-386.

Table I. Reactions of Alkoxide–Alkanols with Various Substrates. Initial Product Ion Distribution, ΔH_r, Rate, and Efficiency of Reaction

reactants	products	rel abund of product ion	ΔH_r (kcal mol^{-1})[a]	rate constant[b] (cm^3 molecule^{-1} s^{-1})	efficiency of reaction k_{obsd}/k_{ADO}[c]	efficiency of reaction k_{obsd}/k_{AADO}[d]	efficiency of reaction k_{obsd}/k_{SACM}[e]
[*n*-PrO$^-$--HOMe] + Me$_3$SiOEt	[*n*-PrO$^-$--HOEt] + Me$_3$SiOMe	19	−0.3	1.98×10^{-9}	1.34	1.10	1.09
	[EtO$^-$--HOMe] + Me$_3$SiOPr	2	+0.9				
	[Me$_3$Si(OEt)(O-*n*-Pr)]$^-$ + MeOH	41					
	[Me$_3$Si(OEt)(OMe)]$^-$ + *n*-PrOH	26					
	[Me$_3$Si(OMe)(O-*n*-Pr)]$^-$ + EtOH	12					
[*n*-PrO$^-$--HOMe] + Me$_2$Si(OEt)(OC$_2$O$_5$)	[*n*-PrO$^-$--HOEt] + Me$_2$Si(OC$_2$D$_5$)(OMe) (A)	9	−3.2[f]	1.53×10^{-9}	1.00	0.80	0.81
	[*n*-PrO$^-$--HOC$_2$D$_5$] + Me$_2$Si(OEt)(OMe) (B)	9	−3.2				
	[EtO$^-$--HOMe] + Me$_2$Si(OC$_2$D$_5$)(D-*n*-Pr) (C)	2	+0.9				
	[C$_2$D$_5$O$^-$--HOMe] + Me$_2$Si(OEt)(O-*n*-Pr) (D)	2	+0.9				
	[Me$_2$Si(OEt)(OC$_2$D$_5$)(O-*n*-Pr)]$^-$ + MeOH	25					
	[Me$_2$Si(OEt)(OC$_2$D$_5$)(OMe)]$^-$ + *n*-PrOH	45					
	[Me$_2$Si(OEt)(OMe)(O-*n*-Pr)]$^-$ + C$_2$D$_5$OH	4					
	[Me$_2$Si(OC$_2$D$_5$)(OMe)(O-*n*-Pr)]$^-$ + EtOH	4					
[*n*-PrO$^-$--HOMe] + EtC(OEt)$_3$	[*n*-PrO$^-$--HOEt] + EtC(OEt)$_2$(OMe)	88	+0.3				
	[EtO$^-$--HOMe] + EtC(OEt)$_2$(OPr)	12	+0.9				
[*n*-C$_5$H$_{11}$O$^-$--HOMe] + EtC(OEt)$_3$	[*n*-C$_5$H$_{11}$O$^-$--HOEt] + EtC(OEt)$_2$(OMe)	97	+0.2[h]	2.96×10^{-9}	1.83	1.35	1.45
	[EtO$^-$--HOMe] + EtC(OEt)$_2$(O-*n*-C$_5$H$_{11}$)	3	+7.4				
[*n*-PrO$^-$--HOMe] + (EtO)$_3$B	[*n*-PrO$^-$--HOEt] + (EtO)$_2$(MeO)B	35	−25.0	3.85×10^{-9}	2.85	2.45	2.44
	[EtO$^-$--HOMe] + (EtO)$_2$(*n*-PrO)B	7	−14.0				
	[(EtO)$_3$(*n*-PrO)B]$^-$ + MeOH	23					
	[(EtO)$_3$(MeO)B]$^-$ + *n*-PrOH	34					
	[(EtO)$_2$(MeO)(*n*-PrO)B]$^-$ + EtOH	1					
[EtO$^-$--HOMe] + (*i*-PrO$_4$)Ti	[*i*-PrO$^-$--HOEt] + (*i*-PrO)$_3$(MeO)Ti	68	−11.6	5.95×10^{-9}[g]	3.13	2.53	2.64
	[*i*-PrO$^-$--HOMe] + (*i*-PrO)$_3$(EtO)Ti	32	−11.4				

[a] Heats of formation $\Delta H_f°$ of alkanol–alkoxides were calculated as follows: $\Delta H_f° = \Delta H_r(\text{R}^1\text{OH} + \text{R}^2\text{O}^- \rightarrow \text{R}^1\text{OH}\text{--}^-\text{OR}^2) + \Delta H_f°(\text{R}^1\text{OH}) + \Delta H_f°(\text{R}^2\text{O}^-)$. ΔH_r from Bartmess;[22] $\Delta H_f°$(R^{1}OH) and $\Delta H_f°$(R^{2}O$^-$) from Bartmess and McIver.[23] Alkanol–alkoxide [$\Delta H_f°$ (kcal mol^{-1})]: [MeO$^-$--HOMe (−105.8)], [EtO$^-$--HOMe (−115.7)], [EtO$^-$--HOEt (−124.3)], (*n*-PrO$^-$--HOMe (−121.6)], [*n*-PrO$^-$--HOEt (−130.3)], [*i*-PrO$^-$--HOMe (−126.1)],[f] [*i*-PrO$^-$--HOEt (−134.8)],[f] [*i*-PrO$^-$--HOEt (−138.1)],[h] [*n*-C$_5$H$_{11}$O$^-$--HOMe (−146.9)].[h] Other $\Delta H_f°$ values were calculated by use of heats of formation of reactants and products from Bartmess and McIver,[23] and Benson;[24] also, $\Delta H_f°$(Me$_3$SiOEt) = −118.4 kcal mol^{-1};[25] $\Delta H_f°$ values for Me$_3$SiOMe, Me$_3$SiOPr, Me$_2$Si(OMe)(OEt), and Me$_2$Si(OEt)(OPr) are estimated[24] to be −110, −123.4, −193.5, and −204 kcal mol^{-1}. [b] The method for the determination of rate constants is outlined in the Experimental Section: these rate constants refer to the disappearance of the solvated alkoxide ions. [c] k_{ADO} is calculated by the method of Su and Bowers.[26] Polarizabilities were calculated from refractive index data.[27] Dipole moments were taken from McClellan[28] (measured in benzene). Compound [α(10^{-24} cm^3), μ_D(D)]: Me$_3$SiOEt (14.13, 1.18), EtC(OEt)$_3$ (19.32, 1.95), (EtO)$_3$B (15.50, 0.75), (*i*-PrO)$_4$Ti (32.65, 1.20), Me$_2$Si(OEt)(OC$_2$D$_5$) (16.84, 1.36). [d] k_{AADO} (AADO theory: average dipole orientation theory with conservation of angular momentum) is calculated by the method of Su, Su, and Bowers.[29] Moments of inertia (I) were estimated in an additive way with use of known values of related compounds (see Table II), using the following increments in the I values: displacement of group X by Y gives increment Z (× 10^{-40} g cm^2); (X, Y, Z); (F, OCH$_3$, 60); (OCH$_3$, OCH$_2$CH$_3$, 180); (CH$_3$, CH$_2$CH$_3$, 190); (Cl, OCH$_3$, 30), the moments of inertia of Me$_3$SiOEt, EtC(OEt)$_3$, (EtO)$_3$B, (*i*-PrO)$_4$Ti, and Me$_2$Si(OEt)(OC$_2$D$_5$) are estimated to be 590, 1250, 880, 2320, and 850 × 10^{-40} g cm^2. [e] k_{SACM} (SACM: statistical adiabatic channel model) is calculated by the method of Troe.[30] The dipole locking constant C is given by the equation $C \simeq 1\text{–}0,614 \exp[-(B/k_BT)^2]$, where B is the rotational constant, k_B is Boltzmann constant, and T is temperature. In this case, $k_BT \gg B$ (T = 300 K; $B \approx 0.4\text{–}1.7 \times 10^{10}$ Hz; B (Mhz) = $838911/I(10^{-40}\text{ g cm}^2)$); C will be equal to 0.386. [f] ΔH_r for Me$_2$Si(OEt)$_2$ as substrate is given. The $\Delta H_r(\text{R}^1\text{OH} + \text{R}^2\text{O}^- \rightarrow \text{R}^1\text{OH}\text{--}^-\text{OR}^2)$ value of [*n*-PrO$^-$--HOMe/HOEt] is used. [g] Calibration of the ionization gauge pressure (P_{ion}) against the baratron pressure (P_{bar}) was not possible for (*i*-PrO)$_4$Ti. The absolute pressure (P_{abs}) necessary for the determination of the reactant rate constant was derived by the following equation: $P_{abs} = P_{ion}C$, with $C = (0.36\alpha) + 0.3$; α = polarizability (10^{-24} cm^3).[31] [h] The $\Delta H_r(\text{R}^1\text{OH} + \text{R}^2\text{O}^- \rightarrow \text{R}^1\text{OH}\text{--}^-\text{OR}^2)$ value of [*t*-BuCH$_2$O$^-$--HOMe/HOEt] is used.

Table II. Moments of Inertia (I or I_c)[a] for Compounds Related to the Boron, Carbon, Silicon, and Titanium Alkoxides

compd	I, ×10^{-40} g cm^2	I_c, ×10^{-40} g cm^2	ref
^{11}BF$_3$		159.9	32a
CH$_3$F	32.9		32b
CH$_3$OCH$_3$		94.4	33
CH$_3$OCH$_2$CH$_3$		215.6	34
(CH$_2$CH$_2$)$_2$O		399.1	35
CH$_3$CO^{35}Cl		247.2	33
CH$_3$CH$_2$CO^{35}Cl		437.2	36
CH$_3$Si^{35}Cl$_3$	474		32b
H$_3$Si^{35}Cl	125.7		32b
H$_3$SiOCH$_3$		156.7	37
CH$_3$^{35}Cl	63.1		32b
HCO$_2$CH$_3$		158.2	33
HCO$_2$CH$_2$CH$_3$[b]		325.3	38
CH$_3$C(OCH$_3$)$_3$[c]		519.9	39
(CH$_3$)$_3$Si^{35}Cl	381.8		32b
TiCl$_4$	760		40

[a] For asymmetric molecules the principal moment of inertia I_c is given.[32] [b] Trans configuration.[38] [c] Trans–gauche–gauche configuration.[39]

or AADO (average dipole orientation theory with conservation of angular momentum)[29] and SCAM (statistical adiabatic channel model)[30] theories, varying from 0.8 to 3.1 times the theoretical values. The reason for this is not clear, but it may well be due to a higher pressure in the cell than obtained by a linear extrapolation from the baratron readings from 10^{-3}–10^{-5} Pa to lower pressures, especially when compounds with high polarizabilities are used as in this study. Indications for this nonlinear behavior are also found from the FT–ICR rate constant measurements for

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(28) McClellan, A. L. *Table of Experimental Dipole Moments*; Rahara Enterprises: El Carrito, CA, 1974; Vol. 2.

(29) Su, T.; Su, E. C. F.; Bowers, M. T. *J. Chem. Phys.* **1978**, *69*, 2243.

(30) Troe, J. *Chem. Phys. Lett.* **1985**, *122*, 425.

(31) Bartmess, J. E., private communication.

(32) For literature concerning moments of inertia (I) and rotational constants (x) [from which I can be calculated by the equation I(× 10^{-40} g cm^2) = (8.38911 × 10^5)/X(mHz) see: (a) Steinfeld, J. I. *Molecules and Radiation. An Introduction to Modern Molecular Spectroscopy*; M.I.T. Press: Cambridge, Massachusetts, and London, England, 1974; Chapter 7. (b) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; McGraw-Hill Book Co.: New York, Toronto, London, 1955; Chapters 1–4. (c) Gordy, W.; Smith, W. V.; Trambarulo, R. F. *Microwave Spectroscopy*; Dover Publications Inc.: New York, 1966; Chapters 2 and 8.

(33) *Landolt-Börnstein, New Series*: *Molecular Constants from Microwave Spectroscopy*; Hellwege, K. H., Hellwege, A. M., Eds.; Springer-Verlag: Berlin, 1967; Group II, vol. 4.

(34) Hayashi, M.; Kuwada, K. *J. Mol. Struct.* **1975**, *28*, 147.

(35) Hayashi, M.; Kuwada, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3006.

(36) Karlsson, H. *J. Mol. Struct.* **1976**, *33*, 227.

(37) Le Croix, C. D.; Curl, R. F.; McKinney, P. M.; Myers, R. J. *J. Mol. Spectrosc.* **1974**, *53*, 250.

(38) Demaison, J.; Boucher, D.; Burie, J.; Dubrulle, A. *Z. Naturforsch.* **1984**, *39a*, 560.

(39) Kumar, K. *J. Mol. Struct.* **1972**, *12*, 19.

(40) *Landolt-Börnstein*; Eucken, A., Hellwege, K. H., Eds.; Springer-Verlag: Berlin, 1951; Vol. 1, Part II, p 226.

Table III. Reactions of Various Nucleophiles with Me_3SiCl and Me_3SiOEt together with the Rate Constants Measured with the Flowing Afterglow (FA)[2] and the FT-ICR Method (This Study)

		rate constant (10^{-9} cm^3 molecule^{-1} s^{-1})				
reactants	products	k_{FA}	$k_{FT\text{-}ICR}$[a]	k_{ADO}[b]	k_{AADO}[c]	k_{SACM}[d]
$NH_2^- + Me_3SiCl$	$Cl^- + Me_3SiNH_2$ (~50%) $^-CH_2Me_3SiCl + NH_3$ (~50%)	3.4[e]	11.3	3.2	4.2	4.1
$F^- + Me_3SiCl$	$Cl^- + Me_3SiF$	2.1[e]	5.5	3.0	3.9	3.9
$HS^- + Me_3SiCl$	$Cl^- + Me_3SiSH$	2.1[e]	3.0	2.4	3.1	3.1
$N_3^- + Me_3SiCl$	$Cl^- + Me_3Si(N_3)$	1.8[e]	3.2	2.2	2.8	2.8
$NCO^- + Me_3SiCl$	$Cl^- + Me_3Si(OCN)$	2.1[e]	2.6	2.2	2.8	2.8
$MeO^- + Me_3SiOEt$	$[Me_3Si(OEt)(OMe)]^-$	2.0[f]		2.1	2.6	2.6
$MeO^- + Me_3SiOEt$	$EtO^- + Me_3SiOMe$ $Me_3SiO^- + MeOEt$ and/or $MeOH + C_2H_4$		4.2	2.1	2.6	2.6

[a] See footnote *b* of Table I. [b] See footnote *c* of Table I; Me_3SiCl: $\alpha = 11.8 \times 10^{-24}$ cm^3; $\mu_D = 2.09$ D. [c] See footnote *d* of Table I; $Me_3Si^{35}Cl$: $I = 381.8 \times 10^{-40}$ g cm^2 (ref 32b). [d] See footnote *e* of Table I. [e] Reference 2. [f] Reference 41.

the reactions of some nucleophiles with the reference compounds Me_3SiCl and Me_3SiOEt, which have been determined before by the flowing afterglow method (FA).[2,41] The relevant data, which show that the $k_{FT\text{-}ICR}$ values are indeed on the average twice the rate constant values k_{FA}, have been summarized in Table III. Taking this into account, the rate constant values and efficiencies in Table I can be interpreted as being due to very fast ion/molecule reactions, occurring say for every one, or one in two collisions between nucleophile and substrate.

Thus the overall rates of reactions are fast: the boron and titanium reactions are the fastest, occurring virtually at every collision; then carbon (reaction occurs for four in every five collisions), and finally the silicon system in which reaction proceeds for one in two collisions between reactants. *Not only is it unlikely from these figures that the alkoxide displacement reactions are equilibria, it is also clear that internal endothermic barriers are not involved.* If there are barriers in these reactions, transition states must be more negative in energy than reactants.[5,42]

Further information pertaining to equilibria and barriers may be obtained from data for the reactions between $[PrO^- \cdot\cdot HOMe]$ and $Me_2Si(OEt)(OC_2D_5)$ (see Table I). Deuterium isotope effects could occur if there is either an endothermic barrier or the reactions involve equilibria.[43] Within experimental error, no isotope effects are noted.[44]

Since the evidence so far does not favor either equilibria or the existence of pronounced internal barriers, we must turn to a third possibility, viz., an orientation effect occurring during the first stages of the reaction. Since we know of no way to prove this experimentally, we must turn to theory, i.e., to ab initio calculations. The systems we have studied experimentally are too large to calculate, and we have thus chosen to investigate the model systems $[F^- \cdot\cdot HOH]/H_2BOMe$ and $[MeO^- \cdot\cdot HOH]/H_2BOMe$. Calculations have been carried out at the 6-31G level,[45] and the results are summarized in Figures 1 and 2.

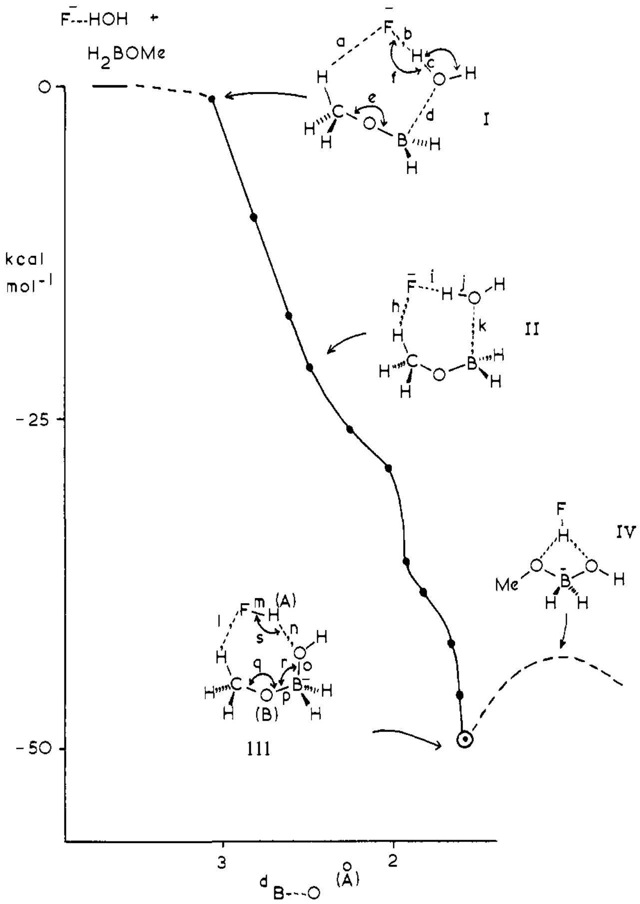
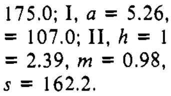


Figure 1. Ab initio calculations (6-31G level) for the reaction of $[F^- \cdot\cdot HOH]$ with H_2BOMe. Structures for $[F^- \cdot\cdot HOH]$, H_2BOMe, and III are full optimized. Other points (•) are the result of relaxation runs. Absolute energies (au) and geometries (Å, deg) as follows:



, −175.45244, F–H_1 = 1.32, H_1–O = 1.00; O–H_2 = 0.95, F–H–O = 171.0, H_1–O–H_2 = 109.2; H_2BOMe, −140.26887, H–B = 1.25, B–O = 1.46, O–C = 1.40, H–B–O = 120.0, B–O–C = 175.0; I, *a* = 5.26, *b* = 1.38, *c* = 1.05, *d* = 3.09, *e* = 177, *f* = 190.5, *g* = 107.0; II, *h* = 1.82, *i* = 1.38, *j* = 1.04, *k* = 2.50; III, −315.77071, *l* = 2.39, *m* = 0.98, *n* = 1.47, *o* = 1.57, *p* = 1.48, *q* = 129.2, *r* = 110.5, *s* = 162.2.

We chose to study the $[F^- \cdot\cdot HOH]/H_2BOMe$ model system first since (i) $[F^- \cdot\cdot HOH]$ is the simplest relevant nucleophile to calculate and (ii) it is strongly polarized, and if it shows *no* initial orientation effect we can safely assume that alkanol–alkoxides will similarly show no such effect. That there is indeed an initial orientation effect was apparent in the very early stages of the ab initio investigation. If $[F^- \cdot\cdot HOH]$[46] and H_2BOMe[47] are placed 5 Å apart and allowed to approach from any direction, the nu-

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(41) Hayes, R. N. Ph.D. Thesis, University of Adelaide, 1985, p 81.

(42) For a recent discussion of varying rates in exothermic ion-molecule reactions see: Sheldon, J. C.; Bowie, J. H.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 6794.

(43) Since the electron affinity of EtO• and C_2D_5O• is 1.726 and 1.702 eV, respectively (Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Phys. Chem.* **1982**, *86*, 4873), reaction A (Table I) should be more exothermic than B, and C more exothermic than D.

(44) The experiment is really excluding the possibility of a pronounced equilibrium or primary deuterium isotope effect. A secondary deuterium isotope effect of say 1.05 ± 0.05 could not be detected under the experimental conditions used.

(45) We are aware that accurate representation of this model system requires diffuse functions, particularly since it involves a complex hydrogen movement. (Chandraseker, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609). However, the model systems are most complex, and we judge that the results are so clear-cut that the additional computing time required for 6-31$^+$G or 6-31^{++}G calculations is unjustified.

(46) (i) Newton, M. D.; Ehrenson, S. *J. Am. Chem. Soc.* **1971**, *93*, 4971. Kraemer, W. P.; Diercksen, G. H. F. *Theor. Chim. Acta* **1972**, *23*, 398. Jorgensen, W. L.; Ibrahim, M. *J. Comput. Chem.* **1981**, *2*, 7. Klass, G; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1982**, *35*, 2471. (ii) See also ref 22 for experimental and thermochemical data.

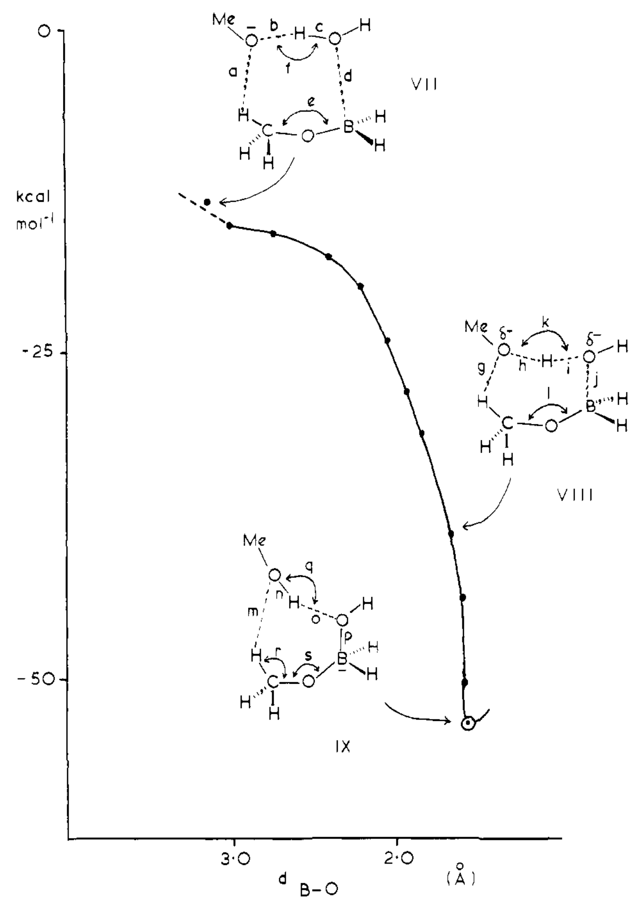
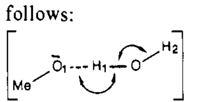
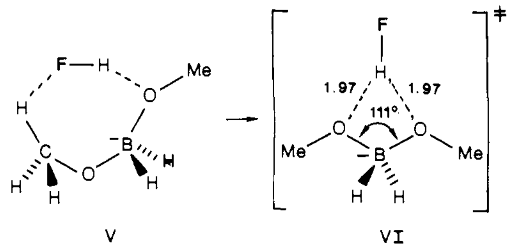


Figure 2. Ab initio calculations (6-31G level) for the reaction of [MeO^---HOH] with H_2BOMe. Structures for [MeO^---HOH], H_2BOMe, and IX are fully optimized. Other points (•) are the results of relaxation runs. Absolute energies (au) and geometries (Å, deg) as follows:



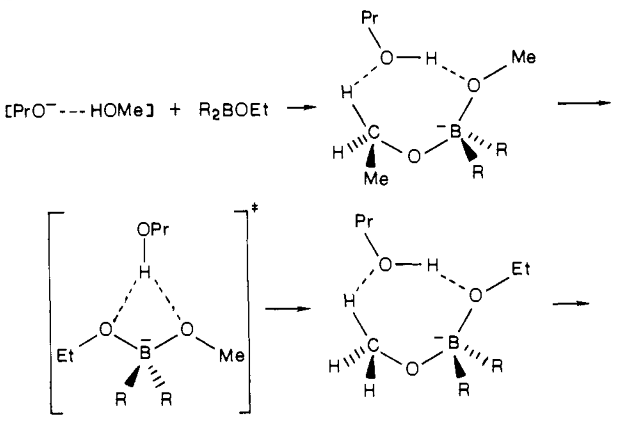
, −190.37216, O_2–H_1 = 1.53, H_1–O = 1.02, O–H_2 = 0.95, O_1–H_1–O = 189.2, H_1–O–H_2 = 107.9. VII, a = 2.08, b = 1.51, c = 1.02, d = 3.12, e = 156, f = 176; VIII, g = 2.31, h = 1.18, i = 1.11, j = 1.63, k = 173, l = 120; IX, −330.72072, m = 2.69, n = 0.98, o = 1.71, p = 1.55, q = 164, r = 127, s = 110.

cleophile always swings around so that the fluoride end of the anion is pointing toward a methyl hydrogen with the water molecule situated above boron. The final stages of the reaction were studied commencing through structure I (Figure 1), in which the H–F and O–B distances are 5.2 and 3.1 Å, respectively. There is then a steeply descending channel involving a sequence of atom movements to reactive intermediate III. The process has specifically directed attack of "HO^-" at boron, with III being essentially the tetrahedral boron anion $H_2B^-(OMe)(OH)$ solvated with HF.



V VI

Scheme I



The next stage of the reaction must involve movement of H_A toward O_B (see III, Figure 1) as a prelude to the formation of products [F^---HOMe] and H_2BOH. Such a reaction must proceed through an unsymmetrical transition state (IV). Because of its complexity we have chosen not to calculate IV. Instead, we have used as a model the analogous and simpler process V (cf. III, Figure 1) to the symmetrical transition state VI. The barrier for this conversion is 6.5 kcal mol^{-1} (6-31G) as we use this figure as an estimate for the position of the barrier crest shown in Figure 1.[48] Formation of products from III will follow a course analogous to the reverse of the pathway to III. *The model reaction therefore shows specificity and high efficiency, with an internal barrier which is very small compared with the high negative energy of formation of the system at that point.*[50]

The results of calculations on the second and more realistic model [MeO^---HOH]/H_2BOMe are summarized in Figure 2. We did not study the orientation effects of [MeO^---HOH].[51] Instead, a plane of symmetry was imposed upon the system and [MeO^---HOH] was allowed to approach H_2BOMe *in order to adopt structure VII* (Figure 2). Our purpose was to show that VII will proceed to intermediate IX in the same way that I goes to III (cf. Figure 1). This is confirmed by the data shown in Figure 2.

We now propose that the major reaction between, for example, [PrO^---HOMe] and R_2BOEt proceeds as shown in Scheme I and that the reactions with C, Si, and Ti substrates occur similarly except that there will be differences in geometries of reactive intermediates and transition structures in these cases.

If we return now to Table I we see that reactions calculated to be exothermic or close to thermoneutral occur, but that the less exothermic reaction is unfavorable. This is the expected trend. We have proposed that initial orientation effects are controlling the courses of reactions, thus we need to know the relative mole fractions of ions in the possible equilibria [R^1OH--$^-OR^2$] $\rightleftarrows$ [R^1O^---HOR^2] in order to predict the major pathway. Early ab initio studies have been carried out on solvated ions;[46] these are not accurate enough for our present needs,

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(47) A reviewer has suggested that H_2BOMe is a poor model for silicon and carbon ethers. Trigonal boron is the least sterically hindered (of the systems under consideration) toward nucleophilic attack at the central atom, and it is thus a good model to demonstrate initial orientation unmasked by other effects.

(48) The barrier crest is likely to be over estimated: electron correlation[49] (which we are unable to use with our facilities because of the complexity of the system) will reduce the barrier, indicating little inhibition to the forward reaction.

(49) Shavitt, I. In *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*; Dykstra, C. E., Ed.; D. Reidel: Dordricht, 1984; p 185.

(50) A reviewer has suggested that an alternative (and more likely) explanation may be that there is a long-lived intermediate from which the more stable products would be produced. We have searched without success for such an intermediate. The potential surface is simple, there are no long-lived intermediates, and there appears to be no impediment to either the forward or reverse reactions.

(51) The problem was simply availability of computing facilities. The calculations shown in Figure 2 required a continuous 8.5 CPU days on a Vax II 780.

$$[\mathrm{MeO^- \cdot\cdot HOMe}] \rightleftarrows [\mathrm{MeO \cdot\cdot H \cdot\cdot OMe}]^{-\ddagger} \rightleftarrows [\mathrm{MeOH \cdot\cdot {}^-OMe}] \quad (8)$$

$$[\mathrm{EtO^- \cdot\cdot HOMe}] \rightleftarrows [\mathrm{EtOH \cdot\cdot {}^-OMe}] \quad (9)$$

The following calculations on alkoxide–alkanols have been carried out at the 6-31$^+$G level.[52] First, the interconversion of methanol–methoxide ions (eq 8) proceeds through a symmetrical transition state with a barrier of 1.9 kcal mol^{-1}; this can be used as a guide for the interconversion of unsymmetrical alkanol–alkoxides. Second, [EtO$^-$- -HOMe] (eq 9) is a true energy minimum with formation energy −25.8 kcal mol^{-1} (relative to EtO$^-$ plus HOMe). In contrast, [EtOH- -$^-$OMe] is a very shallow minimum (formation energy −23.2 kcal mol^{-1}). If reaction 9 is an equilibrium, and given thermal energies, [EtO$^-$- -HOMe] will have a mole ratio >0.95. Even if this ion is vibrationally excited it will be the larger contributor in any reaction. This is in accord with the data listed in Table I and with the mechanisitic proposals summarized in Figure 1 and Scheme I.

In conclusion, we propose that exothermic (or thermoneutral) alkoxide displacement reactions of alkanol–alkoxides with boron, carbon, silicon, and titanium ethers are mainly controlled by specific orientation effects as the two reagents approach and not solely by internal barriers as suggested earlier.[8] Reports of such orientation effects are rare in gas-phase ion chemistry,[53] and the present study demonstrates the importance of the application of experiment and theory in concert.

Acknowledgment. Part of this work was carried out while J.H.B. was on leave at the University of Amsterdam during the tenure of a visitors grant from the Netherlands Organization for the Advancement of Pure Research (ZWO). J.H.B. and N.M.M.N. acknowledge financial support from the Australian Research Grants Scheme and the Netherlands Organization for Pure Research, respectively.

Registry No. Me_3SiOEt, 1825-62-3; $Me_2Si(OEt)(OC_2D_5)$, 109929-93-3; $CH_3CH_2C(OEt)_3$, 115-80-0; $(EtO)_3B$, 150-46-9; $(i\text{-}PrO)_4Ti$, 546-68-9; Me_3SiCl, 75-77-4; NH_2^-, 17655-31-1; F^-, 16984-48-8; HS^-, 15035-72-0; N_3^-, 14343-69-2; NCO^-, 71000-82-3; MeO^-, 3315-60-4; H_2BOMe, 54098-92-9.

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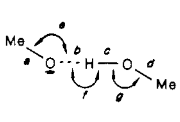
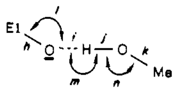
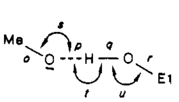
[52] Absolute energies (au) and geometries (Å, deg) for solvated ions as follows:



−229.40171, $a = 1.39$, $b = 1.54$, $c = 1.01$, $d = 1.41$, $e = 128.0$, $f = 185.2$, $g = 111.3$.



−268.42849, $h = 1.39$, $i = 1.55$, $c = 1.01$, $d = 1.41$, $l = 129.1$, $m = 190.5$, $n = 111.4$.



−268.40054, $o = 1.43$, $p = 1.54$, $q = 1.01$, $r = 1.44$, $s = 111.4$, $t = 190.5$, $u = 128.3$.

[53] de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.*, accepted for publication.

A Theoretical Study of Some Cobalt Carbonyl Complexes Present in the Catalytic Cycle of Hydroformylation

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Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received January 8, 1987*

Abstract: The molecular geometry and electronic structure of formylcobalt tricarbonyl, (η-ethylene)hydridocobalt tricarbonyl, and ethylcobalt tricarbonyl were investigated by means of ab initio Hartree–Fock and configuration-interaction calculations in a Gaussian basis set. Several stable conformations of each of the complexes were found, and the geometry, frontier orbitals, and the character of chemical bonds of these conformations were examined. Two intramolecular hydrogen migration reactions were investigated, and their energy barriers were found to depend considerably on the choice of the initial and terminal sites of the migrating hydrogen. The effect of electron correlation upon the molecular geometry was examined in some detail in the case of the η-ethylene complex.

The hydroformylation reaction, occurring in the presence of hydridocobalt tetracarbonyl catalyst, has been extensively studied, and a mechanism proposed by Orchin[1] and by Heck and Breslow[2] has been widely accepted. This mechanism involves a cycle of tetra- and pentacoordinated complexes of cobalt, the hydroformylation being carried out as a sequence of complexations and metal-to-ligand migrations. Of the postulated steps of the mechanism, the initial few are of particular interest here: at the beginning of the cycle, the reactive species $HCo(CO)_3$ forms a π complex with the alkene. The adjacent hydrogen ligand migrates toward the alkene and is inserted into the carbon–carbon double bond. Thus saturated, the carbon chain migrates toward one of the carbonyls. This last step results in the incorporation of the carbonyl ligand into the original hydrocarbon chain, in the form of an aldehyde group. The entire cycle is discussed in detail in the studies quoted above.

Few experimental facts are known about the postulated intermediate species, of which the tetracoordinated ones can be expected to be particularly unstable. In an earlier article[3] (referred to as paper 1), we described the results of an SCF ab initio theoretical study of the hydridocobalt tetracarbonyl and of the simplest tetracoordinated intermediate, hydridocobalt tricarbonyl. Within a more elaborate theoretical framework, we describe here three further species occurring in the postulated mechanism. We

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[1] Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259.

[2] Heck, R. F. *Adv. Organomet. Chem.* **1966**, *4*, 243. Schrauser, G. N., Ed. *Transition Metals in Homogeneous Catalysis*; Marcel Dekker: New York, 1971.

[3] Antolovic, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 977.