A New Four-centre Reaction of Alkanol–Alkoxide Negative Ions. The Reaction of $[RO^- \cdots HOR]$ with Alkoxysilanes. An Ion Cyclotron Resonance Study

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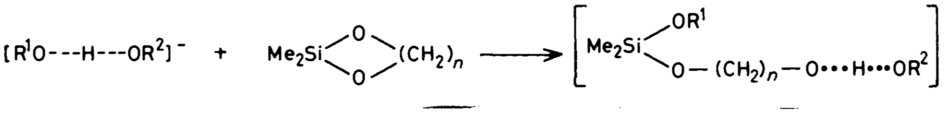
Alkanol–alkoxide negative ions $[R^1O \cdots H \cdots OR^2]^-$ react with alkoxysilanes Me_3SiOR^3 to produce both $[M + R^1O^-]$ and $[M + R^2O^-]$ ions of trigonal bipyramidal geometry. When $R^1 < R^2$ and either R^1 or $R^2 \geqslant$ Pr, the four-centre reaction $[R^1O \cdots H \cdots OR^2]^- + Me_3SiOR^3 \longrightarrow [R^2O \cdots H \cdots OR^3]^- + Me_3SiOR^1$ is observed. Addition of $[R^1O \cdots H \cdots OR^2]^-$ in the reverse direction is not detected. Analogous reactions do not occur between Me_3SiX and $[R^1O \cdots H \cdots OR^2]^-$ when X = F, NHR, NR_2, $SiMe_3$, alkyl, allyl, propargyl, benzyl, or aryl, but $[R^1O \cdots H \cdots X]^-$ ions of small abundance are formed when X = HO, OCOMe, OCN, and SR. Cyclic ethers react with alkanol–alkoxide negative ions by reaction (i; n = 2—4).


(i)

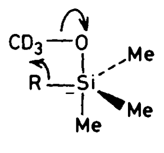
In this paper we are concerned with the difference in reactivity of the negative ions RO^- (R = H or alkyl) and $[RO^- \cdots HOR]$ towards alkoxysilanes. There are many examples of the difference in reactivity of these ions towards carbon-containing systems.[1–4] For example, the rate of the S_N2 reaction (1) is dependent upon the extent of solvation of the HO^- species;[5] the methoxide negative ion undergoes the Riveros reaction[6–8] with alkyl formates [reaction (2)], methanol–methoxide does not; MeO^- deprotonates acrolein [reaction (3)[9,10] whereas $[MeO^- \cdots HOMe]$ reacts with acrolein to give the species $[M + MeO^-]$, the structure of which has not yet been defined.[10]

$$[HO^-(H_2O)_n] + MeBr \longrightarrow [Br^-(H_2O)_n] + MeOH \quad (1)$$

$$MeO^- + HCO_2R \longrightarrow [MeO^- \cdots HOR] + CO \quad (2)$$

$$MeO^- + CH_2{=}CH{-}CHO \longrightarrow CH_2{=}C{=}CO^- + MeOH \quad (3)$$

In contrast, gas-phase silicon chemistry has been little explored. Fluoride[11–16] and alkoxide[17] negative ions undergo a number of characteristic reactions with silanes. For example, CD_3O^- and F^- react with the majority of silanes to produce both *stable* and *decomposing* adducts $[(M + CD_3O^-)$ and $(M + F^-)]$ of trigonal bipyramidal geometry. The decomposing adducts may eliminate a neutral molecule to produce a stable tetrahedral negative ion. For example, the reaction between CD_3O^- and Me_3SiR (R = H or alkyl) produces an intermediate which decomposes by the four-centred reactions shown in (4) and (5) to produce respectively Me_3SiO^- and $Me(CD_3O)(R)SiCH_2^-$. Although apical–equatorial elimination is shown in (4) and (5), equatorial–equatorial elimination is also possible. Other reactions of these systems include nucleophilic displacement [see (6), R = Oalkyl, Oacyl, Oaryl, Salkyl, Saryl, allyl, propargyl, benzyl, *etc.*], and for alkoxysilanes, the S_N2 reaction at carbon [see (7)].[17]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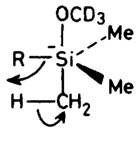
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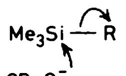
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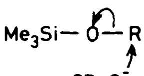
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Results and Discussion

The structures of a number of $[RO^- \cdots HOR]$ species have been investigated by *ab initio* methods. Both $[HO^- \cdots HOH]$[18,19] and $[MeO^- \cdots HOMe]$[19,20] are unsymmetrical in the ground state.† The barrier for the interconversion $[MeO^- \cdots HOMe] \longrightarrow [MeOH \cdots {}^-OMe]$ is computed to be < 2 kJ mol⁻¹; this result is consistent with the experimental observation that this species reacts as a symmetrical reagent.[20] Alkanol–alkoxides used as primary reactant ions in this study were formed by the Riveros reaction [see reaction (2)[6–8]]. The mechanism of the Riveros reaction has been studied using *ab initio* calculations; a three-centred transition state is predicted.[21]

Both RO^- and $[RO^- \cdots HOR]$ negative ions react with tri- (and tetra-)alkylsilanes to produce stable trigonal bipyramidal $(M + RO^-)$ species. Decomposing forms of the $(M + RO^-)$ ions fragment by the characteristic reactions shown in (4) and (5). Alkoxide ions also react with silanes by processes (6) and (7); these reactions do not occur with $[RO^- \cdots HOR]$ ions.

The first indication of a new reaction of alkanol–alkoxide negative ions was observed for the systems $[RO^- \cdots HOR]$–hexamethyldisiloxane (R = Me and Et) (see Table 1). In addition to $[M + RO^-]$ species, $[RO^- \cdots HOR]$ ions form

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† Since alkanol–alkoxides are unsymmetrical in the ground state, they are represented as $[RO^- \cdots HOR]$ or, for example, $[R^1O^- \cdots HOR^2]$. In cases where $R^1 \neq R^2$ and where *ab initio* calculations have not been performed to confirm the correct structure, the alkanol–alkoxide is represented as $[R^1O \cdots H \cdots OR^2]^-$.

Table 1. Reactions of [RO$^-$ ••• HOR] with $(Me_3Si)_2O$[a] (the figures listed refer to the relative power absorptions of the appropriate peaks)

R	[RO$^-$]	[RO ••• HOR]	[Me_3SiO^-]	[Me_3SiO^- ••• HOR][b]	[*M* + RO$^-$]
Me	36	32	100	19	5
Et	13	24	100	26	7

[a] [RO$^-$ ••• HOR] produced from RONO–HCO_2R. Cell pressures, RONO (5×10^{-6} Torr), HCO_2R (5×10^{-6} Torr), and $(Me_3Si)_2O$ (1×10^{-5} Torr). For other experimental conditions see Experimental section. [b] Ions formed primarily by the four-centred reaction between [RO$^-$ ••• HOR] and $(Me_3Si)_2O$. A minor contribution is produced by the Riveros reaction between Me_3SiO^- and HCO_2R.

Table 2. Reactions of [MeO$^-$ ••• HOMe] with Me_3SiOR[a]

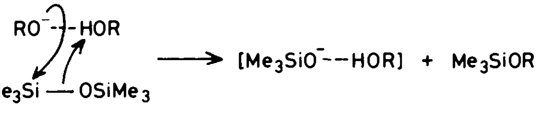
R	[MeO$^-$]	[RO$^-$]	[MeO$^-$ ••• HOMe]	[RO ••• H ••• OMe]$^-$[b]	[RO$^-$ •••• HOR][c]	[*M* + MeO$^-$]	[*M* + RO$^-$]
CD_3	75	5	100	11		50	
Et	100	80	78	80	10	82	30
Pr	80	100	80	45	51	81	38
Pr^i	43	98	84	52	58	100	
Bu	80	55	84	28	5	9	
Hexyl	75	95	90	51	10	73	

[a] [MeO$^-$ ••• HOMe] produced from MeONO–HCO_2Me. Cell pressures, MeONO (5×10^{-6} Torr), HCO_2Me (5×10^{-6} Torr), and Me_3SiOR (1×10^{-5} Torr). [b] [RO ••• H ••• OMe]$^-$ is produced solely by the Riveros reaction between RO$^-$ and HCO_2Me (RO$^-$ formed by the reaction between MeO$^-$ and Me_3SiOR) [MeO$^-$ ••• HOMe] does not react with Me_3SiOR to yield [RO ••• H ••• OMe]$^-$. [c] Produced solely by the four-centre reaction between [RO ••• H ••• OMe]$^-$ and Me_3SiOR.

Table 3. Reaction of [RO$^-$ ••• HOR] with Me_3SiOMe[a]

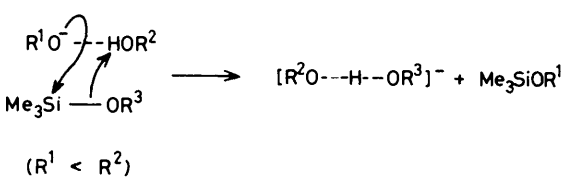
R	[RO$^-$]	[MeO$^-$]	[RO$^-$ ••• HOR]	[RO ••• H ••• OMe]$^-$	[*M* + RO$^-$]	[*M* + MeO$^-$]
Et	100	23	58	24[b]	47	
Pr	82	5	100	4[c]	43	10
Pr^i	100	7	63	8[c]	5	
Bu^t	100	2	44			

[a] [RO$^-$ ••• HOR] produced from RONO–HCO_2R. Cell pressures, RONO (5×10^{-6} Torr), HCO_2R (5×10^{-6} Torr), and Me_3SiOMe (1×10^{-5} Torr). [b] Produced solely by the Riveros reaction between MeO$^-$ and HCO_2Et. [c] Produced by two processes, *viz*. the Riveros reaction MeO$^-$–HCO_2Pr and the four-centre reaction [RO$^-$ ••• HOR]–Me_3SiOMe.



(8)

$$Me_3SiO^- + HCO_2R \longrightarrow [Me_3SiO^- \text{---} HOR] + CO \qquad (9)$$



Scheme.

products which correspond to [Me_3SiO^- ••• HOR].* This product ion disappears on ejection of [RO$^-$ ••• HOR]; thus we propose that the four-centre process (8) is the major pathway. The product ions [Me_3SiO^- ••• HOR] are also coupled to Me_3SiO^- but in a reverse direction (as shown by cyclotron double resonance experiments), *i.e.* increasing the energy of Me_3SiO^- causes an increase in the size of the peak corresponding to [Me_3SiO^- ••• HOR]. The latter process is thus likely to be an endothermic Riveros reaction corresponding to sequence (9). We now report on an extensive survey of the reactions between alkoxysilanes and [RO$^-$ ••• HOR] negative ions. The results are shown in Tables 2—5. It is ironic that although we first observed this reaction with [MeO$^-$ ••• HOMe] and [EtO$^-$ ••• HOEt], no other monoalkoxysilane undergoes the four-centre reaction with either of these reagents.

The data listed in Table 2 may be summarised as follows. The ion [MeO$^-$ ••• HOMe] is the major precursor of all [*M* + MeO$^-$] species listed in Table 1; on the other hand it does not undergo a four-centre reaction [*cf.* equation (8)] with alkoxysilanes. However, the methoxide negative ion liberates RO$^-$ from Me_3SiOR and this ion undergoes a Riveros reaction [*cf.* equation (2)] to yield the solvated species [RO ••• H ••• OMe]$^-$. This ion undergoes a four-centre reaction with Me_3SiOR (to yield [RO$^-$ ••• HOR]) when R $\geqslant$ Pr. The data in Tables 3 and 4 demonstrate that for an unsymmetrical alkoxide–alkanol [R^1O ••• H ••• OR^2]$^-$, where $R^1 < R^2$ and where either R^1 or $R^2 \geqslant$ Pr, it is always the *smaller* alkoxide group R^1O^- which reacts at silicon; the *larger* alkanol residue becomes part of the new alkanol-alkoxide (see Scheme). Addition in the opposite direction is not detected. The specificity of this reaction is surprising, since *ab initio* calculations (at the STO-3G level) suggest that both the reaction shown in the Scheme, and addition in the reverse sense (to form [R^1O ••• H ••• OR^3]$^-$), are very close to thermoneutral. Both reactions have barriers (in the range 30—50 kJ mol^{-1} [22]), perhaps that involving addition of the smaller alkoxide to silicon has the smaller barrier thus favouring the reaction shown in the Scheme.

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* The structures of these ions are supported by *ab initio* calculations (at STO-3G level) on the model system $[H_3Si\text{–}O \overset{a}{\cdots} H \overset{b}{\cdots} OMe]^-$; ΔE (from H_3SiO^- and MeOH) -125 kJ mol^{-1}, a 1.43 Å, b 1.05 Å.[22]

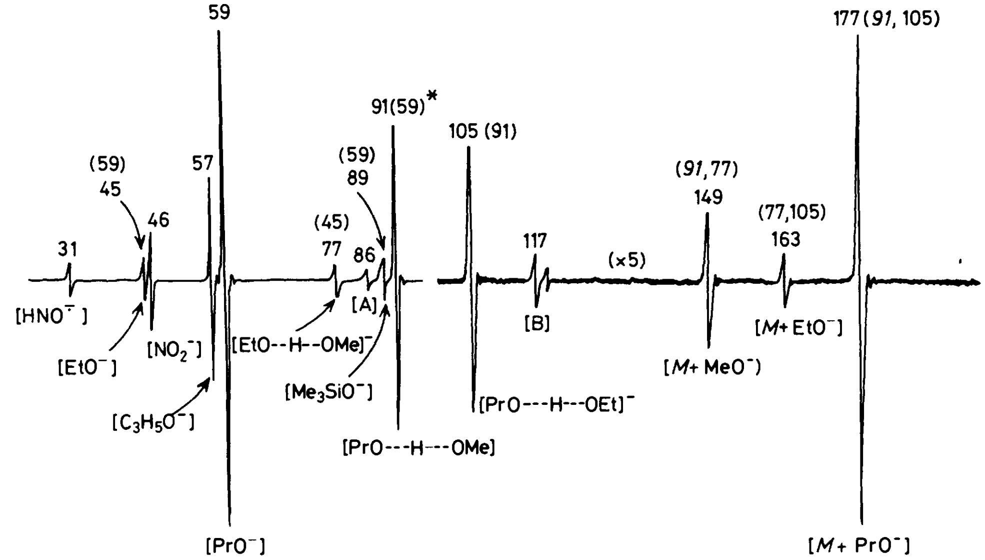

Figure 1. I.c.r. spectrum of the PrONO–HCO_2Me–Me_3SiOEt system. Dynaspec ICR 9 spectrometer. Sample pressures, PrONO (5×10^{-6} Torr), HCO_2Me (5×10^{-6} Torr), and Me_3SiOEt (1×10^{-5} Torr). For other experimental conditions see Experimental section. Numbers in parentheses refer to precursor ions, as determined by the cyclotron ejection technique. Where there are two (or more) precursor ions, the major precursor (as defined by cyclotron ejection) is italicised. [A] is produced by the reaction $CH_3CH{=}CHO^- + PrONO \longrightarrow \bar{O}CH{=}C(Me)NO + PrOH$ (*m*/*z* 57). [B] is formed by the reaction $PrO^- + Me_3SiOEt \longrightarrow Me_2(EtO)SiCH_2^- + PrOH$. The i.c.r. spectrum of the system PrONO–HCO_2CD_3–Me_3SiOEt shows a peak at *m*/*z* 94 corresponding to $[PrO \cdots H \cdots OCD_3]^-$. There is no peak in this spectrum due to $[EtO^- \cdots HOEt]$ (*m*/*z* 91)

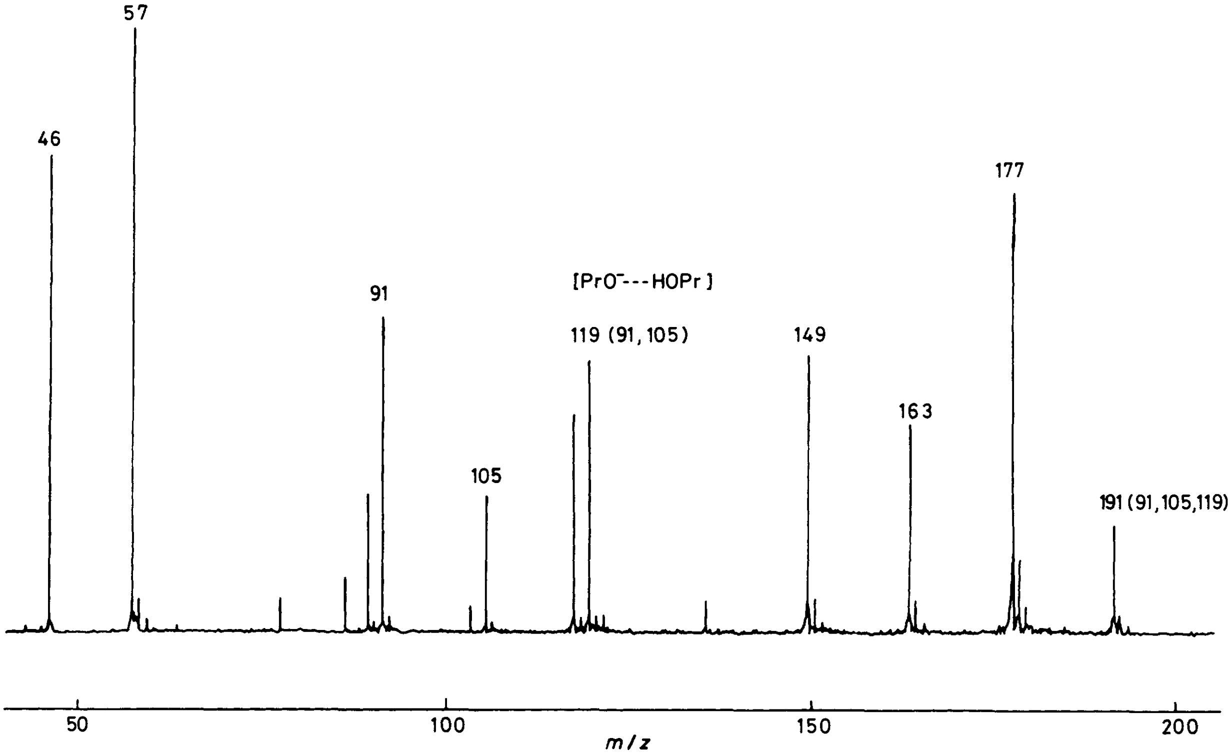

Figure 2. I.c.r. spectrum of the PrONO–HCO_2Me–Me_3SiOEt system. Spectrospin CMS 47 spectrometer,[23] operating in the 'fast correlation' mode[24] with a trapped ion cell. The spectrum was obtained at 70 eV. The pulse sequence contained a 5 s delay between ionisation and detection. Sample pressures, PrONO (3×10^{-8} Torr), HCO_2Me (3×10^{-8} Torr), and Me_3SiOEt (3×10^{-8} Torr).

We chose to study one system, $[PrO\cdots H\cdots OMe]^-$–$Me_3SiOEt$, in detail by (*i*) investigating the analogous reactions occurring for the labelled systems $[PrO\cdots D\cdots OMe]^-$–$Me_3SiOEt$ and $[PrO\cdots H\cdots OCD_3]^-$–$Me_3SiOEt$ (Table 4), and (*ii*) by monitoring any changes in reaction sequences as the maximum reaction time is varied from 10^{-3} to 25 s. The normal spectrum (using transit time 10^{-3} s) is shown in Figure 1. A spectrum of the same system after a 5 s reaction period, measured with a Spectrospin Fourier transform CMS 47 i.c.r. spectrometer, is shown in Figure 2.

The spectra shown in Figures 1 and 2 are complex. The propoxide negative ion undergoes a number of reactions with Me_3SiOEt (*M*) to yield the following product ions: the trigonal bipyramidal species $[M + PrO^-]$ (*m/z* 177), $[Me_3SiO^-]$ (*m/z* 89) formed by an S_N2 reaction [*cf.* (6)], $[Me_2(EtO)SiCH_2^-]$ (*m/z* 117, see legend to Figure 1), and EtO^- by nucleophilic displacement [*cf.* (6)]. The EtO^- ion reacts with methyl formate to yield $[EtO\cdots H\cdots OMe]^-$ which in turn reacts with Me_3SiOEt to give both $[M + MeO^-]$ and $[M + EtO^-]$ species.

The reactions of $[PrO\cdots H\cdots OMe]^-$ are different from those of PrO^-. The alkanol–alkoxide ion is the major precursor of $[M + MeO^-]$ (*m/z* 149) and $[M + PrO^-]$ (*m/z* 177). The only other reaction that it undergoes is the four-centre reaction (Scheme) to produce $[PrO\cdots H\cdots OEt]^-$ (*m/z* 105).*

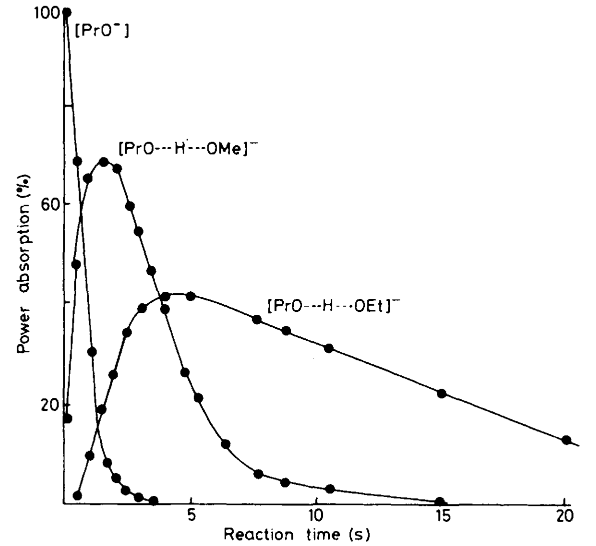

Figure 3. Relative power absorptions of the ions PrO^-, $[PrO\cdots H\cdots OEt]^-$, and $[PrO\cdots H\cdots OMe]^-$ in the i.c.r. spectrum of the system $PrONO$–HCO_2Me–Me_2SiOEt as a function of reaction time. Spectrospin CMS 47 instrument, experimental conditions as shown in the legend to Figure 2, except that experiments were carried out for a variety of different reaction times. The three ions are formed by the following processes:

$$PrONO + e \longrightarrow PrO^- + NO^{\bullet}$$

$$PrO^- + HCO_2Me \longrightarrow [PrO\cdots H\cdots OMe]^- + CO$$

$$[PrO\cdots H\cdots OMe]^- + Me_3SiOEt \longrightarrow [PrO\cdots H\cdots OEt]^- + Me_3SiOMe$$

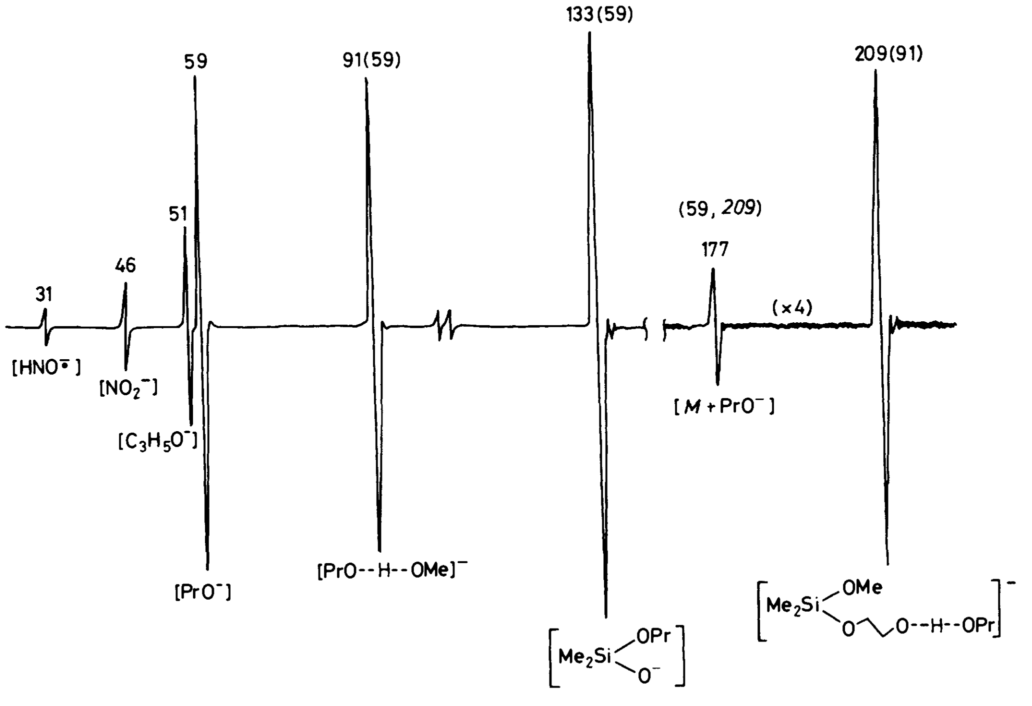

Figure 4. I.c.r. spectrum of the $PrONO$–HCO_2Me–$\mathrm{Me_2Si}\genfrac{<}{>}{0pt}{}{\mathrm{O}}{\mathrm{O}}\mathrm{(CH_2)_2}$ system. Dynaspec ICR 9 spectrometer. Sample pressures, PrONO, (5×10^{-6} Torr), HCO_2Me (5×10^{-6} Torr), and $\mathrm{Me_2Si}\genfrac{<}{>}{0pt}{}{\mathrm{O}}{\mathrm{O}}\mathrm{(CH_2)_2}$ (1×10^{-5} Torr). For other experimental conditions see Experimental section. (It is reported[25] that this compound exists as the dimer $\mathrm{Me_2Si}\genfrac{<}{>}{0pt}{}{\mathrm{O{-}(CH_2)_2{-}O}}{\mathrm{O{-}(CH_2)_2{-}O}}\mathrm{SiMe_2}$. The i.c.r. spectrum shown is clearly that of the monomer)

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* The reactions between $[PrO\cdots D\cdots OMe]^-$ and Me_3SiOEt produce $[M + MeO^-]$, $[M + PrO^-]$, and $[PrO\cdots D\cdots OEt]^-$; no H–D equilibration occurs. This should be contrasted with the H–D equilibration which precedes product ion formation in reactions of $[RO\cdots DOR]$ with carbonyl systems $>CH$–CO–.[20]

Table 4. Reaction of $[R^1O\cdots H\cdots OR^2]^-$ with Me_3SiOR^3 [a]

R^1	R^2	R^3	$[R^1O^-]$	$[R^2O^-]$	$[R^3O^-]$	$[R^1O\cdots H\cdots OR^2]^-$	$[R^2O\cdots H\cdots OR^3]^{-c}$	$[R^1O\cdots H\cdots OR^3]^{-d}$	$[M + R^1O^-]$	$[M + R^2O^-]$	$[M + R^3O^-]$
Pr	CD_3	Me	69	1	8	100	2	12	5	8	1
Pr	Me	CD_3	74	3	2	100	13	7	19	10	4
Pr	Et	Me	100	5	1	59	20	33	5	12	1
Bu	Et	Me	88		17	100		8	4		
Pr	Me	Et	100	20	37	60	3	11	17	7	3
Pr	CD_3	Et	90	1	8	100	30	10	19	10	9
Pr	Me	Bu	100	2	30	60	55	58	70	35	
Bu	Pr	Hexyl	100	86	30	49	18	2	15	12	4
Pr	Me	Allyl	100	1	35	83	78	9	11	11	7
Pr	Me	C_6H_5	100	1	70	49	7	4			

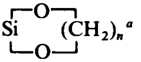
[a] $[R^1O\cdots H\cdots OR^2]^-$ produced from R^1ONO–HCO_2R^2. Cell pressures, R^2ONO (5×10^{-6} Torr), HCO_2R^2 (5×10^{-6} Torr), and Me_3SiOR^3 (1×10^{-5} Torr). [b] Primary Riveros ion from R^1O^-–HCO_2R^2. [c] Riveros ion from R^3O^-–HCO_2R^2 (R^3O^- produced by the reaction between R^1O^- and Me_3SiOR^3). [d] Produced solely by the four-centre reaction between $[R^1O\cdots H\cdots OR^2]^-$ and Me_3SiOR^3.

Table 5. Reactions of $[PrO\cdots H\cdots OMe]^-$ with $R_nSi(OEt)_{4-n}$ [a]

R	*n*	$[PrO^-]$	$[EtO^-]$	$[MeO^-]$	$[PrO\cdots H\cdots OMe]^b$	$[EtO\cdots H\cdots OMe]^c$	$[EtO\cdots H\cdots OR]^d$	$[M + PrO^-]$	$[M + EtO^-]$	$[M + MeO^-]$
Me	2	80	5	4	100	9	6	12	2	7
H	1	100	4	5	56	5	19	7	1	2
Me	1	100	13	7	78	9	2			
	0	100	3	7	87	5	1	13	2	4

[a] $[PrO\cdots H\cdots OMe]^-$ produced from PrONO–HCO_2Me. Cell pressures, PrONO (5×10^{-6} Torr), HCO_2Me (5×10^{-6} Torr), and $R_nSi(OEt)_{4-n}$ (1×10^{-5} Torr). [b] Primary Riveros ion, produced specifically as indicated in footnote *a*. [c] Riveros ion from EtO^-–HCO_2Me (EtO^- produced by the reaction between PrO^- and $R_nSi(OEt)_{4-n}$). [d] Produced solely by the four-centre reaction between $[PrO\cdots H\cdots OMe]^-$ and $R_nSi(OEt)_{4-n}$.

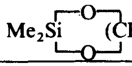
Table 6. Reactions of $[R^1O\cdots H\cdots OR^2]^-$ with



$Me_2Si(O)_2(CH_2)_n$ [a]

n	R^1	R^2	$[R^1O^-]$	$[R^2O^-]$	$[R^1O\cdots H\cdots OR^2]^-$	$[Me_2(R^1O)SiO^-]$	$[Me_2(R^2O)SiO^-]$	$[M + R^1O^-]$	$[M + R^2O^-]$	$[M + (R^1O\cdots H\cdots OR^2)^-]$
2	Me	Me	100	100	78	67	67			10
2	CD_3	Me	74	20	69	100	37			17
3	Pr	Me	100	2	87	33	4	12	3	2
4	Pr	Me	100	3	90	80	1	90	15	3.5

[a] $[R^1O\cdots H\cdots OR^2]$ produced from R^1ONO–HCO_2R^2. Cell pressures, R^1ONO (5×10^{-6} Torr), HCO_2R^2 (5×10^{-6} Torr),



$Me_2Si(O)_2(CH_2)_n$ (1×10^{-5} Torr).

Addition in the reverse direction to produce $[EtO \cdots H \cdots OMe]^-$ (*m*/*z* 77) is not observed. Although *m*/*z* 77 is present in the spectrum, the ion is produced exclusively by the Riveros reaction between EtO^- and methyl formate. Ejection of all ions of *m*/*z* values less than 91 (using the CMS 47 instrument) does not affect the power absorption of *m*/*z* 105; ejection of *m*/*z* 91 achieves complete collapse of the peak at *m*/*z* 105. In Figure 3, the relative power absorptions of PrO^-, $[PrO \cdots H \cdots OMe]^-$, and $[PrO \cdots H \cdots OEt]^-$ are plotted as a function of maximum reaction time in the CMS 47 cell. The PrO^- negative ion has completely reacted within 4 s of formation, $[PrO \cdots H \cdots OMe]^-$ has virtually disappeared by 15 s, while there is still an appreciable concentration of $[PrO \cdots H \cdots OEt]^-$ after 20 s.

It appears, from Figure 2, that a neutral product formed in a reaction sequence may, after a suitable reaction period, build up to a concentration sufficient for ion-molecule reactions of that neutral to be observed. When we first observed this phenomenon we very carefully purified the Me_3SiOEt by preparative g.c., so that there was no possibility of a trace impurity being present. Repeating the experiment gave the same results. The peaks in question in Figure 2 are *m*/*z* 119 and 191. The neutral, Me_3SiOPr, is formed by the displacement reaction (10). The adduct at *m*/*z* 191 is first observed at a reaction time of 2 s and builds up steadily as the reaction period is increased. Its major mode of formation is shown in equation (11); the ions PrO^- and $[PrO \cdots H \cdots OEt]^-$ are minor contributors. The peak at *m*/*z* 119 is produced by the four-centre reaction (Scheme) shown in equation (12).

$$PrO^- + Me_3SiOEt \longrightarrow EtO^- + Me_3SiOPr \qquad (10)$$

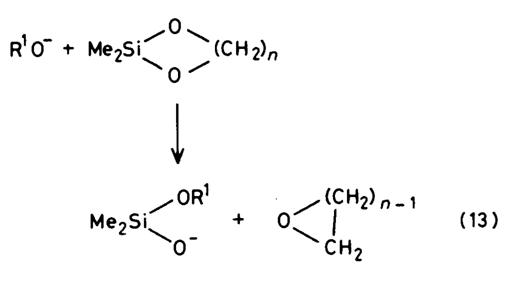
$$[PrO \cdots H \cdots OMe]^- + Me_3SiOPr \longrightarrow Me_3\bar{Si}(OPr)_2 + MeOH \qquad (11)$$

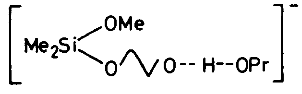
$$[PrO \cdots H \cdots OMe]^- + Me_3SiOPr \longrightarrow [PrO^- \cdots HOPr] + Me_3SiOMe \qquad (12)$$

It seemed possible that if the number of alkoxy-groups attached to silicon was increased, the abundance of the four-centre product ion might also increase. The data shown in Table 5 indicate this not to be the case; an *increase* in the number of alkoxy-groups causes a *decrease* in the abundance of the production.

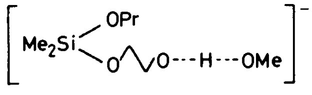
One of the features of the gas-phase chemistry of $[RO^- \cdots HOR]$ ions is that although $[M + (RO^- \cdots HOR)]$ species are reactive intermediates in reaction pathways, *stable* ions corresponding to these adducts have not, to our knowledge, been observed in i.c.r. experiments. The mechanism shown in the Scheme suggests an intriguing possibility. If the alkoxide residue (OR^3) is doubly bound to silicon as part of a cyclic system, the product ion should correspond formally to $[M + (R^1O \cdots H \cdots OR^2)^-]$, where R^1O^- has attached to silicon, and R^2OH has solvated the resulting O^- moiety. The results of experiments designed to test this suggestion are shown in Table 6 and Figure 4.

The reactions of R^1O^- with the cyclic ethers in some cases (Table 6) give $[M + R^1O^-]$ ions; the major reaction produces $Me_2(R^1O)SiO^-$ as shown in equation (13). As in previous instances R^1O^- and $[R^1O \cdots H \cdots OR^2]^-$ ions react differently. The characteristic reaction of $[R^1O \cdots H \cdots OR^2]^-$ (in these cases both R^1 and R^2 may be Me) is the formation of $[M + (R^1O \cdots H \cdots OR^2)^-]$ adducts. The reaction is illustrated in Figure 4. The product ion (*m*/*z* 209) could in principle correspond to (14) or (15), but structure (14) would be predicted from the data accumulated concerning the mechanism shown in the Scheme. Structure (14) is correct, since the *m*/*z* 209 ion is the major precursor of $[M + PrO^-]$ (*m*/*z* 177). No peak corresponding to $[M + MeO^-]$ is observed, thus there is no evidence to support the formation of (15).





(14)



(15)

Finally, solvated nucleophiles are generally made by the Riveros reaction,[6–8] directly[5] or by solvent-exchange reactions.[26,27] Solvated nucleophiles are often difficult to produce in high yield, and it was thus of interest to determine whether reactions similar to that shown in the Scheme could be used for the preparation of other solvated nucleophiles. Unfortunately, the four-centre reaction either did not work or produced a product ion in very small yield from the various substrates studied. The ion $[PrO \cdots H \cdots OMe]^-$ did not produce $[PrO \cdots H \cdots X]^-$ from Me_3SiX (X = alkyl, $-CH_2-CH{=}CH_2$, $-CH_2-C{\equiv}CH$, cyclo-C_5H_5, benzyl, aryl, F, NMe_2, $NHSiMe_3$, and $SiMe_3$), but yielded a product of small abundance when X = HO, OCOMe, OCN, and Salkyl.

Experimental

I.c.r. spectra (except those shown in Figures 2 and 3) were measured with a Dynaspec ICR 9 spectrometer equipped with a three-section cell. Spectra were obtained at 70 eV (primary negative ions formed by dissociative secondary electron capture). Other reaction conditions: $\omega_c/2\pi = 125.0$ kHz, total pressure of reactants in cell 2×10^{-5} Torr, ion current in 10^{-10} A range, emission current 0.2 μA, and ion transit time 1×10^{-3} s. Precursor ions in reaction sequences were determined by the cyclotron ejection technique.

The spectrum shown in Figure 2 was measured using a Spectrospin CMS 47 spectrometer. Experimental conditions are described in the legend to Figure 2.

Alkyl nitrites were prepared from the appropriate alcohol and sodium nitrite by a reported method.[28] Formates, including methyl [^{2}H]formate, were prepared by the method of Stevens and Van Es.[29] All alkoxysilanes are known and were prepared by reported procedures: *viz*. Me_3SiOR (R = Me,[30] Et,[30] Pr,[31] Pr^i,[32] Bu,[30] Bu^t,[33] hexyl,[31] and phenyl[34]), $Me_2Si(OEt)_2$,[35] $HSi(OEt)_3$,[36] $MeSi(OEt)_3$,[36] $Si(OEt)_4$,[36] and dimethylpolymethylenedioxysilanes.[25] Other silanes were available from a previous study.[17] Formates and alkoxysilanes were purified by preparative g.c. (15% FFAP).

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