The Relative Gas-phase Proton Affinities and Polarisabilities of Alkyl and Silyl Ethers

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The relative gas-phase proton affinities of a number of alkyl and silyl ethers have been determined by ion cyclotron resonance spectroscopy and compared with the relative basicities toward weaker protic and Lewis acids. The basicities of the silyl ethers are enhanced by the stronger acid, but are still weaker than the isostructural carbon ethers. The CNDO/2 method has been used to estimate the extent of electron redistribution in charged silyl and alkyl derivatives.

BASICITY measurements [1,2] using weak protic acids (*e.g.* $CDCl_3$ or PhOH) and Lewis acids (*e.g.* B_2H_6 or BF_3), and in one case a pK_b determination,[3] have shown that silicon ethers and amines are generally much weaker bases than their carbon analogues. This result is commonly attributed to conjugative stabilization of the lone pair electrons by the formally vacant silicon 3*d* orbitals, *i.e.* $(p \longrightarrow d)\pi$ bonding, which more than compensates for the base-strengthening inductive effect of the electropositive silicon atom.[2]

However, basicity is a relative property, dependent on the type and strength of the reference acid. As the strength (demand) of the reference acid increases, the polarisability of the base can become a significant factor.[4,5] This factor is believed responsible for reversals in the relative proton affinities (PA) of aliphatic and aromatic amines in the gas phase,[6,7] where enthalpies are typically

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>800 kJ mol^{-1}, compared with <60 kJ mol^{-1} in solution.[8] While molecular refractivity measurements [9,10] indicate that bonds to silicon compounds are more polarisable than those of their carbon analogues, the relevance of this to basicity and other chemical properties which reflect charge development is unknown. With this in mind, we have measured the relative gas-phase PAs of a series of alkyl and silyl ethers and compared the results with the basicity order obtained using weaker reference acids.

RESULTS AND DISCUSSION

Gas-phase Proton Affinities.—The gas-phase PAs of the silyl and alkyl ethers were determined by ion cyclotron resonance spectroscopy. The recently developed equilibrium method [11] of measuring absolute PAs could not be applied because of interference from fast competing processes involving fragment ions. Therefore, the relative PAs were determined by establishing the preferred direction of proton transfer in reaction (1) for a series of different base pairs, using the standard ion cyclotron double resonance technique.[12,13]

$$B^1 + B^2H^+ \rightleftharpoons B^1H^+ + B^2 \qquad (1)$$

The basis of this technique has been discussed previously.[14-16] The observation of a decrease in product ion abundance on increasing the kinetic energy of the reactant ion is usually evidence of an exothermic or thermoneutral reaction. The observation of an increase in product ion abundance is usually evidence of an endothermic process. No change in product ion intensity is generally considered to mean that the reaction is too slow to be significant, even when the kinetic energy of the reactant is increased. Provided process (1) is studied in both the forward and reverse directions with consistent results, and a very low field strength is used, this technique produces rankings of proton affinities identical to those obtained by the equilibrium method.[17]

TABLE 1

Pulsed double resonance results for the reaction $B^1H^+ + B^2 \rightleftharpoons B^1 + B^2H^+$

Reactants		Sign of double resonance signal [a]		IP of B^1 (eV) [b]
B^1	B^2	Forward	Reverse	
$(Me_3C)_2O$	$Me_3COCHMe_2$	—	0	8.93 [c]
	$(Me_2HC)_2O$	—	0	
	$(Me_3Si)_2O$	—	0	
	Me_3SiOH	—	0	
	Et_2O	—	0	
$Me_3COCHMe_2$	Me_3COMe	—	0	
	$(Me_3Si)_2O$	—	0	
	Et_2O	—	0	
$(Me_2HC)_2O$	Me_3COMe	—	0	9.18 [e]
	$(Me_3Si)_2O$	—	0	
	$(Me_2HSi)_2O$	—	+	
Me_3COMe	$(Me_2Si)_2O$	—	0	9.42 [d]
	Et_2O	—	0	
	$Me_2C{=}CH_2$	—	0	
$(Me_3Si)_2O$	$(Me_2HSi)_2O$	—	0	9.43 [e]
	Me_3SiOMe	—	0	
	Me_3SiOH	—	0	
	Et_2O	—	0	
$(Me_2HSi)_2O$	Me_3SiOMe	—	0	
Me_3SiCH_2OMe	Me_3SiOMe	—	0	8.68 [e]
	Et_2O	—	+	
Me_3SiOMe	Me_3SiOH	—	+	9.54 [e]
	Et_2O	—	0	
Me_3SiOH	NH_3 [f]	0	—	9.73 [e]
	$Me_2C{=}CH_2$ [g]	—	0	
PhOMe	Et_2O [h]	—	0	8.20 [d]
	$Me_2C{=}CH_2$	—	0	

[a] Negative, positive, and zero signs indicate decrease, increase, and zero change, respectively, in product ion concentration on irradiation of reactant ion. [b] Adiabatic ionization potential. [c] B. J. Cocksey, J. H. D. Eland, and C. J. Danby, *J. Chem. Soc.* (*B*), 1971, 790. [d] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, ' Molecular Photoelectron Spectroscopy,' Wiley–Interscience, London, 1970. [e] T. Baer, personal communication. [f] Reported PA, 866 kJ mol^{-1} (M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, 1969, **50**, 2029). [g] Reported [12,16] PA, 816 kJ mol^{-1}. [h] Reported (note *c*) IP, 9.50 eV.

On the basis of the results of the double resonance experiments summarized in Table 1, the following order of PAs was established: $(Me_3C)_2O \gg Me_3COCHMe_2 \gg (Me_2CH)_2O \gg Me_3COMe \gg (Me_3Si)_2O \gg (Me_2HSi)_2O$; Me_3SiCH_2OMe, $(Me_2HSi)_2O \gg Me_3SiOMe \gg Me_3SiOH$, Et_2O; $PhOMe \gg Et_2O$.

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This series may be expanded by using the reported [12,18] PAs of Et_2O (833, 858 ± 12 kJ mol^{-1}) > Me_2O (778, 782 ± 4, 795 ± 20 kJ mol^{-1}) ≈ EtOH (778, 782 ± 8, 807 kJ mol^{-1}) > MeOH (761 ± 12, 753 ± 12 kJ mol^{-1}) > H_2O (686 ± 12, 703 ± 12 kJ mol^{-1}). It is then apparent that the silyl ethers are substantially stronger bases than Me_2O, EtOH, MeOH, and H_2O, and that the substituent effect is $Me_3C \geqslant Me_2CH \geqslant Me_3Si \geqslant Me_2HSi \geqslant Et > Me > H$. Anisole, the single aryl ether studied, is also a strong base, but insufficient comparisons could be made to place the phenyl group in the above substituent order.

The substituent order of the alkyl groups is that observed for primary, secondary, and tertiary amines.[19] It is also the order of decreasing ionization potentials (IPs) of these ethers (Table 1). PAs may be analysed in terms of the thermodynamic cycle (2), where $HA(B^{+\cdot})$ is the hydrogen affinity of the radical cation of the base B, and $EA(H\cdot)$ is the electron affinity of the hydrogen atom. Using the standard sign convention,[19,20] this leads to relationship (3).[12,16] Since previous studies [19,20] of alkyl amines have shown that $HA(B^{+\cdot})$ is relatively constant for a homologous series, a correlation between the PA and IP orders of the alkyl ethers is not unexpected.

$$\begin{tikzcd}
BH^+ \arrow[r, "PA(B)"] \arrow[d, "HA(B^{+\cdot})"] & B + H^+ \arrow[d, "IP(B)"] \\
B^{+\cdot} + H\cdot \arrow[r, "EA(H\cdot)"] & B^{+\cdot} + H^+
\end{tikzcd} \qquad (2)$$

$$PA(B) = -IP(B) + HA(B^{+\cdot}) + EA(H^+) \qquad (3)$$

The fact that the relative PAs of $(Me_3Si)_2O$ and Me_3SiOMe also correlate with the IP order indicates that the $HA(B^{+\cdot})$ term is not greatly affected by the Me_3Si group.

Comparison with Weaker Reference Acids.—The reactivity of silyl ethers has restricted basicity measurements with Lewis acids, although it is reported [21] that the complex of $(Me_3Si)_2O$ and BF_3 is completely dissociated at −78°. In contrast, Me_2O and Et_2O form stable, distillable 1 : 1 complexes with BF_3, $-\Delta H_f$ 57.11 and 49.92 kJ mol^{-1}, respectively.[22,23] On the PA scale the disiloxane is the stronger base.

While this reversal might be attibuted to steric effects, which are known to influence the stability of boron halide complexes,[22] silyl ethers show a similar relative lack of affinity for weak protic acids. The most complete comparison is available from studies using phenol as the reference acid, the basicity being determined by the shift ($\Delta\nu$) in the hydroxy stretching frequency in CCl_4 induced by the base.[24-27] Here $\Delta\nu$ has been taken as the measure of basicity, or used to calculate the enthalpy of the acid–base interaction from the empirical relationship (4).[26] The enthalpies of interaction of

$$\Delta H(\text{kJ mol}^{-1}) = 0.0431\Delta\nu\ (\text{cm}^{-1}) + 12.9 \qquad (4)$$

alkyl and silyl ethers and alcohols with phenol determined by this method are: $(MeC)_2O$, 27.1 > $Me_3COCHMe_2$, 26.7 > Me_3COMe, 26.0 > $(Me_2CH)_2O$, 25.8 > Me_3SiCH_2OMe, 25.3 > Me_3SiOMe, Et_2O, 24.9 > Me_2O, 23.8 > EtOH, 22.8 > MeOH, 22.5 > $MeOSiH_3$, 20.7 > $(Me_3Si)_2O$, 20.2 > PhOMe, 19.7 > $(Me_2HSi)_2O$, 19.6 kJ mol^{-1}. While the accuracy of the Badger–Bauer relationship embodied in the use of $\Delta\nu$ and equation (4) has been criticised,[27] enthalpies of interaction with phenol derived from reliable equilibrium measurements [28] confirm the qualitative correctness of the i.r. method: $(Me_3C)_2O$, 30.6 > Me_3COEt, 27.3 > Me_3SiOEt, 24.1 > $(Me_3Si)_2O$, 16.0 kJ mol^{-1}. The generality of these results is indicated by studies with other weak protic acids, and the already cited low basicity of silylamines.[1-3]

The order of basicities of the alkyl ethers and alcohols are essentially the same on both the phenol and PA scales. It is only the basicities of the silyl ethers and anisole which change significantly with the strength of the reference acid. For example, $(Me_3Si)_2O$, $(Me_2HSi)_2O$, and anisole are weaker bases than alkyl ethers, and even weaker than methanol, when the reference acid is phenol; on the PA scale these ethers are stronger bases than Et_2O. The fact that the siloxanes and anisole show the same behaviour suggests that the basicities of these compounds are determined by the same electronic effects. That is, conjugative delocalisation of the lone pair electron density is largely responsible for the low basicity toward weak acids, but becomes less important as the stronger acid polarises the *total* electron distribution of the base.

It is significant that even on the PA scale the silyl ethers are still slightly weaker bases than their isostructural carbon analogues. It is difficult to see how this can be rationalised without invoking $p \longrightarrow d(\text{Si})$ bonding or some equivalent delocalisation mechanism.[29]

MO Calculations.—The polarisability of alkyl substituents and its effect on gas-phase basicities has been attributed to both dipole stabilisation and charge delocalisation. To compare the importance of the charge delocalisation mechanism for alkyl and silyl ethers, we have carried out some model CNDO/2 calculations [30] of

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the electron redistribution associated with protonation of ROH (R = H, CH_3, and SiH_3) (Table 2).* The calculations indicate that the electron transfer to the proton (q_{H^+}), which increases in the same order as the enthalpy (ΔH), is primarily at the expense of the oxygen substituents. The percentage of q_{H^+} donated by the oxygen atom is relatively constant ($25 \pm 2\%$), while the percentage donated by R increases in the order H < CH_3 < SiH_3 (*sp*) ≈ SiH_3 (*spd*).

ΔH May be separated into its one- and two-centre components, ΔH_A and ΔH_{AB},[30,45] or into the energy gained by the proton (E_{H^+}) and the energy lost by ROH (ΔE_{ROH}) in accommodating the new bond to oxygen (Table 2). This provides some insight into the protonation process, although it is not possible to separate ΔH into terms uniquely associated with the polarisation of R and the inductive effect.

TABLE 2

Energies (eV) and electron redistribution for protonation of ROH

R	q_O	q_{H^+}	$\%\delta q_R$	$\%\delta q_H$	$\%\delta q_O$	ΔH	ΔH_A	ΔH_{AB}	E_H	ΔE_{ROH}
H	6.263	0.628	38	38	23	−10.95	0.55	−11.50	−25.62	14.67
CH_3	6.231	0.665	42	31	27	−11.60	0.18	−11.78	−26.57	14.97
SiH_3(*spd*)	6.347	0.683	51	24	24	−12.21	−3.57	−8.64	−27.10	14.90
SiH_3(*sp*)	6.407	0.721	50	25	25	−13.22	−2.86	−10.36	−27.77	14.55

q_O Is electronic charge on oxygen in ROH; q_{H^+} is electronic charge on proton in ROH_2^+; $\%\delta q_{R,H,O}$ are percentages of q_{H^+} donated by R, H, and O atoms of ROH.

Acidities. The contribution which the polarisation of the silyl group makes to the calculated PAs cannot be evaluated because the calculated order $SiH_3 > CH_3 > H$ is the same as the generally accepted inductive order of these groups. However, since the inductive effect of a group is unidirectional, a clear distinction between the inductive effect and the polarisability can be made if stabilisation of both positive and negative charge can be established.[46] If substituent polarisation is an important factor, enhancement of acidity as well as basicity is expected. This criterion has already been used to demonstrate the polarisability of alkyl groups.[4,46] While the gas-phase acidities of silanols have not been determined, solution studies [47-50] have shown that silanols are stronger acids than alcohols and water. This implies greater stabilisation of the oxyanion by the silyl group despite its inductive effect. Here, however, it is not possible to distinguish experimentally between stabilisation by polarisation of the σ-bonds *versus* $(p \longrightarrow d)\pi$ conjugative stabilisation. CNDO/2 Calculations implicate both mechanisms.

The calculated charge redistribution and enthalpy (ΔH) associated with proton dissociation from ROH are shown in Table 3. The delocalisation of the anionic charge increases in the order H < Me < SiH_3 (*spd*) < SiH_3 (*sp*), while the acidity increases in the order H < Me < SiH_3 (*sp*) < SiH_3 (*spd*). If ΔH is partitioned into the energy required to separate the proton (E_{OH}), and the energy acquired on addition of its original electronic charge to RO (ΔE_{RO}) it is apparent that E_{OH} is essentially constant, and that ΔE_{RO} is responsible for the relative acidity. The order of this term is $SiH_3 > CH_3$, regardless of the silicon basis set.

TABLE 3

Energy (eV) and electron redistribution for
$ROH \longrightarrow RO^- + H^+$

R	δq	$\%\delta q_R$	ΔH	ΔE_H	ΔE_{RO}
H	0.869	41	26.30	31.38	−5.08
CH_3	0.870	48	24.86	31.31	−6.45
SiH_3(*spd*)	0.849	75	23.09	31.16	−8.07
SiH_3(*sp*)	0.903	78	24.10	31.45	−7.35

δq is electronic charge acquired by RO on loss of proton; $\%\delta q_R$ is percentage of δq which resides on R group.

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* CNDO/2 [31-34] and *ab initio* [35-39] calculations of the gas-phase basicities and acidities of homologous alkylamines and alcohols have been reported previously. It is well known that heats of reactions calculated by the CNDO/2 method are too large, partly because of the use of theoretical repulsion integrals.[40-42] The greatest success of the CNDO/2 method appears to be in the calculation of charge distribution.[43] Because of the uncertainty in some of the parameters for second row elements,[44] the calculations for silyl compounds might better be considered to reflect changes resulting from an increase in the principal quantum number of the valance electrons and the inclusion of *d*-orbitals.

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EXPERIMENTAL

Relative gas-phase PAs were determined using a Varian V-5900 ion cyclotron resonance spectrometer equipped with a standard three-section flat cell, grid modulation, split drift voltages, and a 20 l s^{-1} noble ion pump. Pairs of bases were introduced into the spectrometer after degassing at least three times by freeze–pump–thaw cycles. Pressures were typically 5×10^{-3} N m^{-2} and the ionising voltage was 15 V. The emission current was initially set at 100 nA and the double resonance oscillator at 100 mV cm^{-1}. Double resonance was verified by observing the signal to the sensitivity limit of the instrument, or to a field strength of 40 mV cm^{-1} and less than half the original emission current. The adiabatic ionisation potentials of the silyl ethers were determined using a custom built photoelectron–photoion coincidence spectrometer equipped with a quadrupole mass analyser. Values of $\Delta\nu$ (phenol, base, CCl_4) were determined or checked by the method of West *et al.*[24]

Silyl ethers were prepared by literature methods. Alkyl ethers were obtained from commercial sources. All compounds were purified by distillation, their purity being verified by g.l.c.

CNDO/2 Calculations.—The standard program by P. A. Dobosh, QCPE 141, available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, was modified to permit optimization of molecular geometry and partition of energy terms.[45] Silicon 3*d* overlap integrals were reduced by 30%. Standard C–H (1.09), Si–H (1.48), C–O (1.43), Si–O (1.64), and C–C (1.54 Å) bond lengths,[2] tetrahedral angles, and staggered conformations, were assumed. Optimized O–H bond lengths were found to be 1.04 ± 0.01 Å; therefore, a value of 1.04 Å was assumed throughout. ROH bond angles were optimized.

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