International Journal of Mass Spectrometry 206 (2001) 53–61

Lewis acid–base interactions of SiF_4 with molecular anions formed by electron capture reactions

D.H. Williamson, W.B. Knighton, E.P. Grimsrud

Department of Chemistry, Montana State University, Bozeman, Montana 59717, USA

Received 9 August 2000; accepted 29 September 2000

Abstract

Lewis acid–base interactions between SiF_4 and a wide range of molecular negative ions are reported here for the first time. The molecular anions include those formed by simple electron attachment to *p*-benzoquinone, benzophenone, nitrobenzene, and 21 substituted nitrobenzenes and also include the *o*- and *p*-nitrophenoxy anions. From measurements performed by pulsed electron-beam high pressure mass spectrometry, equilibrium constants and free energies for the association reactions, $M^- + SiF_4 \rightleftharpoons M^-(SiF_4)$, at 150 °C are reported for each of the molecular anions, M^-. It is shown that the strengths of these Lewis acid–base interactions of SiF_4 are much greater than ion–dipole interactions previously reported between these molecular anions and several common solvent molecules of relatively high dipole moment, including methanol, acetonitrile, dimethylformamide, and dimethlysulfoxide. The strengths of the Lewis acid–base interactions of SiF_4 with molecular anions show a strong inverse dependence on the electron affinity of the parent molecule and on the availability of a specific Lewis base site on the molecular anion that can be closely approached by the central Si atom of SiF_4. It is also shown that strong interactions between SiF_4 and the molecular anions derived from compounds of very low electron affinity can be gainfully used for the trace detection of such compounds by electron capture mass spectrometry. (Int J Mass Spectrom 206 (2001) 53–61) © 2001 Elsevier Science B.V.

Keywords: Electron capture mass spectrometry; Ion clustering; Thermal electron detachment; Silicon tetrafluoride; Substituted nitrobenzenes

1. Introduction

In the environmental, biomedical, and forensic sciences an ever-increasing need exists for the trace detection and analysis of specific target substances in complex samples. In meeting these needs, some of the most promising methods that have been developed are based on the gas phase negative ionization of compounds having positive electron affinities (EA) by the simple attachment of thermal-energy electrons as symbolized by

$$e + M \rightleftharpoons M^- \qquad (1)$$

Resonance electron capture (REC) reactions of this type have been shown to often occur with exceedingly large rate constants, k_{REC}, if the buffer gas pressure within the ion source is sufficiently high so that the excited molecular anion initially formed by electron attachment is rapidly stabilized by collisions with the buffer gas molecules [1]. This accounts for the extraordinarily high sensitivity that can be obtained by methods based on REC. The most common instrumental forms of such methods have been the electron capture detector (ECD) [2,3] for gas chromatography,

---

* Corresponding author. E-mail: grimsrud@montana.edu

PII S1387-3806(00)00388-2

the ion mobility spectrometer (IMS) [4], and the negative chemical ionization mass spectrometer [1,5–7]. In the use of these REC-based methods for chemical analysis, however, a number of associated problems have been encountered. Perhaps the most important of these is related to the fact that REC reactions inherently include an elementary step called thermal electron detachment (TED) that is the reverse of reaction 1 [1,8,9]. This reaction is undesirable since it can either partially or completely destroy the molecular anions of interest, M^-, and the associated response to the compound, M. The rates of TED reactions increase strongly with increased temperature and decreased EA of M so that, at commonly used ion source temperatures of about 150 °C or greater, TED typically becomes unacceptably fast for compounds having EA values of less than about 18 kcal mol^{-1} [1].

A means of overcoming the detrimental effects of TED reactions on the response of an ECD to REC-active compounds of low EA has been demonstrated by the intentional addition of ethyl chloride to the ECD make-up gas [3,10]. Although ethyl chloride does not attach thermal energy electrons, it will react rapidly and irreversibly with many molecular anions by a dissociative electron transfer reaction, $M^- + C_2H_5Cl \rightarrow Cl^- +$ neutrals. With sufficient ethyl chloride present, this reaction can be made to compete favorably with the reverse of reaction 1, thereby preventing the liberation of a free electron by M^- and the loss of ECD response to M. This ethyl chloride-sensitized mode of the ECD has been shown to provide about two orders of magnitude increase in the ECD's response to several low-EA compounds, including phenanthrene, anthracene, pyrene, benz(a) pyrene, and benzophenone [3,10]. Unfortunately, this method of response enhancement for REC-active compounds is not as useful for mass spectrometry- and IMS-based methods where it is generally essential that the negative ion detected includes the molecular entity of interest, M.

In order to improve the REC responses of mass spectrometry- and IMS-based methods to low EA compounds, a strong ion–molecule association reaction of the general type shown in the following reaction would be much more useful:

$$M^- + L \rightleftharpoons ML^- \qquad (2)$$

By a reaction of this type, a suitable binding agent, L, would hold the M^- species in an associated form, ML^-, that would be stable against TED and the negative ion thereby observed by a mass spectrometry or IMS-based method would then include the molecular species of interest, M. In addition, some other beneficial effects of a strong reaction 2 can also be envisioned. One is that the stabilizing effect of this reaction might also inhibit other undesirable reactions that are sometimes observed between molecular anions, M^-, and common buffer gas impurities, such as O_2 [11] and H_2O [12]. Another is that an association reaction of the type shown in reaction 2 might also provide additional mass spectral information concerning the identity of M [13]. This would be possible if the rates of reaction 2 were fast in both the forward and reverse directions and the position of the equilibrium condition thereby established was sensitive to the detailed chemical composition of M^- and even to the relatively subtle structural differences that might exist within isomeric sets of compounds, M. In that case, a mass spectral measurement of the intensity ratios of the ML^- and M^- ions could provide an additional means for the identification of M.

In order to achieve these envisioned benefits of a reaction 2 under typical ion source conditions involving temperatures of about 150 °C or greater, the strength of the clustering reaction would have to be relatively great. For example, in order to hold at least one-half of the molecular anions, M^-, in the complex form, ML^-, the standard free energy change at 150 °C, $\Delta G°_2$ (150 °C), has to be at least 10 kcal mol^{-1} if the total buffer gas pressure was set to 1.0 Torr and if 1% (mole ratio) of the buffer gas was the complexing agent, L. In addition, it is essential that the complexing agent, L, not undergo an electron capture reaction, itself, since this would deplete the population of thermal electrons within the ion source and interfere with the initial negative ionization of M. With these criteria for L in mind, it is instructive to consider the results obtained in previous studies by Chowdhury et al. [14] of equilibrium clustering reactions between the molecular anions of various substituted nitrobenzenes with the common solvent molecules, methanol, acetonitrile, dimethylformamide, and dimethlysulfoxide, at 70 °C. For the molecular anion of nitrobenzene (NB^-), $\Delta G°_2$ (70 °C) values for these four clustering agents were found to be 6.3, 6.6, 6.2, and 8.6 kcal mol^{-1}, respectively. Using an estimate of -25 cal mol^{-1} K^{-1} for the entropy change of these reactions [14], their standard free energy changes at the higher temperature of 150 °C are expected to be only about $\Delta G°_2$ (150 °C) = 4.3, 4.6, 4.2, and 6.6 kcal mol^{-1}, respectively. For the other substituted nitrobenzenes included in the study of Chowdhurry et al., which had greater electron affinity than NB, weaker interactions were observed for all four clustering agents. Therefore, it appears that none of these classic solvent molecules of relatively high dipole moment cluster sufficiently strongly to the molecular anions of substituted nitrobenzenes as to offer the level of assistance needed in addressing the analysis problems associated with REC reactions described previously.

In attempting to envision other types of negative ion–neutral interactions which might be stronger than those of the conventional solvent molecules, the interaction of strong Lewis acids, such as BCl_3, BF_3, $SiCl_4$, and SiF_4 [15], with negative ions has also been considered. These compounds have been shown to associate very strongly with the monoatomic halide ions, F^- and Cl^- [15], and moderately strongly with Br^- [16]. In our initial tests of these Lewis acids, BCl_3, BF_3, and $SiCl_4$, were quickly eliminated from consideration because none of these compounds could be introduced in moderately high concentration into high pressure ion sources without almost complete depletion of the electron population by their electron capture reactions. On the other hand, when moderate amounts of SiF_4 were added to the ion source buffer gas, no significant depletion of the electron population and relatively little production of negative ions was observed. Therefore, the present study of the Lewis acid–base interactions of SiF_4 with molecular anions was undertaken in the hopes that SiF_4 would undergo clustering reaction 2 in a manner which might provide some of the advantages for chemical analyses sought here. The anions included in this study are primarily those formed by electron attachment to numerous substituted nitrobenzenes. A few other types of molecular anions are also included, however, to provide insight into the general classes of molecular anions for which strong interactions with SiF_4 might be expected.

2. Experimental

A pulsed high pressure mass spectrometer (PHPMS) was used for all experiments. The PHPMS was constructed in our laboratory and has been described in detail previously [12,17]. For the present experiments, a mixture of gas consisting of small quantities of the compound, M, and SiF_4 in the major diluent gas, methane, is first prepared in an associated gas handling plant. This mixture then flows slowly through the thermostated ion source of the PHPMS. A brief pulse (20 μs) of 3000 eV electrons produces positive ions and electrons within the ion source. In methane buffer gas at a pressure of 4 Torr, the secondary electrons are rapidly thermalized and then captured by the compound M (reaction 1) to form molecular anions, M^-, which are also rapidly brought to thermal energy by collisions with the buffer gas. The M^- ions then engage in an association reaction with the added SiF_4 to form cluster ions of the type, $M^-(SiF_4)$, if such a reaction is favorable. The number density of ions within the source is sufficiently low so that the dominant loss of charge is by their diffusion to the ion source walls. Relative ion abundances within the ion source are determined as a function of time after the electron-beam pulse by measuring the relative ion wall currents, that is, by bleeding the gas mixture through a narrow slit into an evacuated region where the ions are mass analyzed (quadrupole mass filter), detected (ion-counting channeltron) and time analyzed (multichannel scaler).

3. Results and discussion

An example of the results obtained in the present experiments is shown in Fig. 1. The mass spectrum

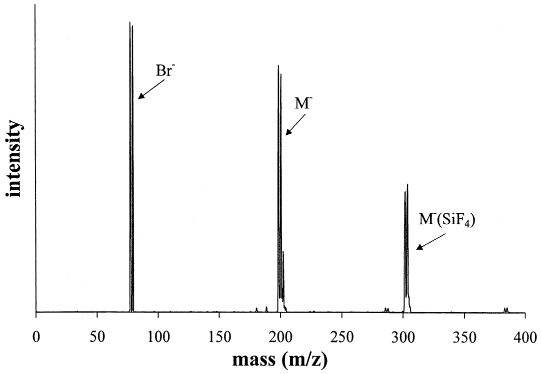

Fig. 1. Electron capture mass spectrum produced in the PHPMS ion source when 0.1 mTorr *p*-bromonitrobenzene (M) and 0.025 mTorr SiF_4 are added the methane buffer gas at a total ion source pressure of 5.0 Torr and temperature 150 °C.

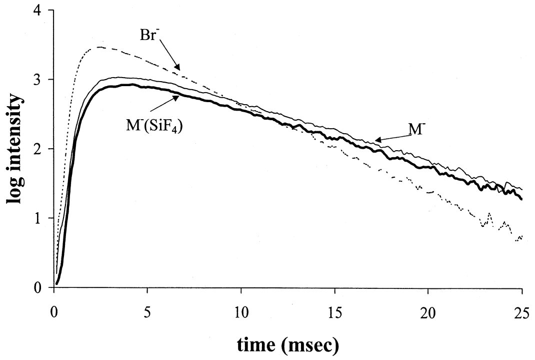

Fig. 2. Temporal measurements of ion intensities displayed in Fig. 1. The ratio of the intensities of the M^- and $M^-(SiF_4)$ ions becomes and remains constant a few milliseconds after the electron-beam pulse, indicating that a state of chemical equilibrium has been reached for the association reaction between SiF_4 and the molecular anion of *p*-bromonitrobenzene.

shown indicates that three negative ions of major intensity were produced when small amounts of *p*-bromonitrobenzene (*p*-BrNB) and SiF_4 are introduced to the ion source along with methane buffer gas at a pressure of 5 Torr and a temperature of 150 °C. For *p*-BrNB, a molecular anion is formed by REC along with an approximately equal amount of bromide ion that is simultaneously formed by a competitive dissociative EC pathway. The electron capture chemistry of this compound is slightly more complex than that of the others studied here in that the molecular anion is usually the dominant ion produced by the EC reaction of M. In Fig. 1, a SiF_4 cluster of the molecular anion of *p*-BrNB is also observed. It is significant to note in this figure that the relative intensity of the $Br^-(SiF_4)$ cluster ion, which would appear as a doublet peak at *m/z* values of 183 and 185 if a more sensitive recorder attenuation had been used, is exceedingly small relative to that of *p*-$BrNB^-(SiF_4)$, indicating that SiF_4 binds much more strongly to the molecular anion of *p*-BrNB than it does to the monoatomic Br^- ion. Note also that no additional ions due to an EC reaction by SiF_4 are observed under these conditions.

In Fig. 2, the time dependence of the three major ions in Fig. 1 is shown. For a short period immediately after the e-beam pulse, all negative ion signals are weak due to a positive ion space-charge field, which inhibits the diffusion of negative ions to the ion source walls [18]. As the electrons are converted to negative ions by the EC reaction of *p*-BrNB, this space-charge field dissipates and negative ions begin to diffuse to the walls and are detected by the mass spectrometer. After about 5 ms, the intensity of all ions decreases with time due to their losses by diffusion to the ion source walls. Although the initial EC reaction of *p*-BrNB has resulted in the initial formation of Br^- and *p*-$BrNB^-$ ions, a state of chemical equilibrium for the clustering reaction,

$$M^- + SiF_4 \rightleftharpoons M^-(SiF_4) \qquad (3)$$

is also very quickly established so that the ratio of the intensities of the *p*-$BrNB^-(SiF_4)$ and *p*-$BrNB^-$ ions is maintained constant by reaction 3 over the entire time interval from about 4 to 25 ms after the electron-beam pulse. The additional Br^- ion produced by the initial EC reaction has no effect on the clustering reaction 3 of interest and is lost by simple diffusion to the walls. The rate of its diffusional loss is somewhat greater than that of the equilibrium-coupled *p*-$BrNB^-$ and *p*-$BrNB^-(SiF_4)$ ions, as expected [18], due primarily to the lower mass of the Br^- ion.

From measurements such as the one described above, equilibrium constants, K_3, were obtained for all molecular anions from the relationship[18],

Table 1
Thermochemical values for association reactions, $M^- + SiF_4 \rightleftharpoons M^-(SiF_4)$

M	EA of M[a]	$-\Delta G_3^0$ (150 °C)[b]	$-\Delta H_3^0$ [c]	$-\Delta S_3^0$ [d]
1 F (atom)	78.5	>45[f]		
2 Cl (atom)	83.4	14.1[f,g]	22[f]	23[f]
3 Br (atom)	77.5	6.4[g]		
4 *p*-dinitrobenzene	46.2	4.2	21 ± 1	40 ± 2
5 *p*-benzoquinone	44.1	13.2	24 ± 2	26 ± 5
6 *o*-dinitrobenzene	38.1	7.2		
7 3,5-bis(trifluoromethyl) nitrobenzene	41.3	7.3		
8 *m*-dinitrobenzene	38.1	8.2		
9 *o*-cyanonitronbenzene	35.1	9.2		
10 *m*-cyanonitrobenzene	36.0	9.5		
11 *p*-trifluoromethylnitrobenzene	34.0	9.6		
12 1-nitronaphthalene	28.4	10.2		
13 *o*-trifluoromethylnitrobenzene	30.7	10.6		
14 *m*-trifluoromethylnitrobenzene	32.6	10.9		
15 *m*-bromonitrobenzene	30.5	11.3		
16 *m*-chloronitrobenzene	29.6	11.7		
17 *p*-bromonitrobenzene	29.8	11.7		
18 *p*-chloronitrobenzene	29.1	12.0	32 ± 2	48 ± 4
19 *o*-fluoronitrobenzene	24.7	12.5		
20 *m*-fluoronitrobenzene	28.4	12.5		
21 *o*-chloronitrobenzene	26.3	13.6		
22 *o*-nitrophenoxy radical		13.7		
23 *p*-nitrophenoxy radical		13.8		
24 *p*-fluoronitrobenzene	25.9	13.9	33 ± 2	47 ± 5
25 *m*-methylnitrobenzene	22.9	15.2		
26 nitrobenzene	23.3	15.5	35 ± 2	47 ± 6
27 *o*-methylnitrobenzene	21.9	15.6		
28 *p*-methylnitrobenzene	21.9	15.7	35 ± 3	49 ± 6
29 2,6-dimethylnitrobenzene	18.7	19.8		
30 benzophenone	14.3	22.0		

[a] Electron affinities (kcal mol^{-1}) of molecules were obtained from [19] and those of the halide atoms from [21].

[b] Free energies (kcal mol^{-1}) for association reactions of all polyatomic negative ions were determined here by measurements made at 150 °C. The estimated uncertainty of each of these measurements is ±0.6 kcal mol^{-1}.

[c] Standard enthalpies (kcal mol^{-1}) for association reactions determined from van't Hoff plots reported here unless otherwise indicated. The uncertainties indicated are the standard deviations determined by linear regression analysis.

[d] Standard entropies (cal mol^{-1} K^{-1}) for association reactions determined from van't Hoff plots reported here unless otherwise indicated. The uncertainties indicated are the standard deviations determined by linear regression analysis.

[f] Obtained from [15].

[g] Obtained from [16].

$$K_3 = \frac{I_{M^-(SiF_4)}}{I_{M^-} P_{SiF_4}} \tag{4}$$

where I_i are the measured intensities of the ions, i, and P_{SiF_4} is the partial pressure of SiF_4 in the ion source in units of atmospheres. The free energies for all clustering reactions at a given temperature, T, were then obtained from the relationship, $\Delta G°_3(T) = -RT \ln K_3$. Determinations of this kind were made for all molecular anions at a temperature of 150 °C and the $\Delta G°_3$(150 °C) values thereby obtained are indicated in Table 1 along with EA values previously determined [19] for each compound, atom, or radical species listed in Table 1. The anions included in the present study include molecular anions formed by simple electron attachment to nitrobenzene (NB), 21 substituted nitrobenzenes, *p*-benzoquinone, and benzophenone. Also included are the two phenoxy anions that were formed by the reactions of the M^- ions of *o*-chloronitrobenzene and *p*-chloronitrobenzene with

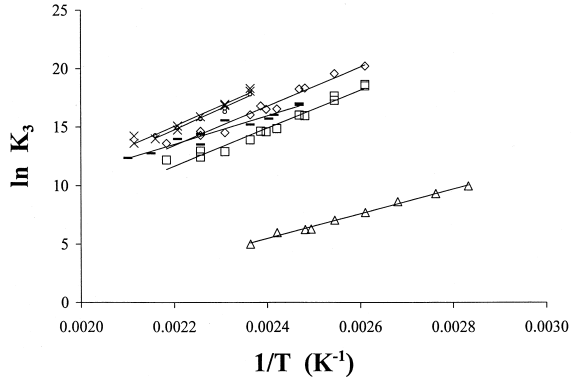

Fig. 3. Van't Hoff plots for the association reactions of SiF_4 with six different molecular anions over the temperature range, 80–200 °C. The molecular anions were formed from *p*-methylnitrobenzene (circle), nitrobenzene (cross), *p*-fluoronitrobenzene (diamond), *p*-benzoquinone (solid line), *p*-chloronitrobenzene (square), and *p*-dinitrobenzene (triangle).

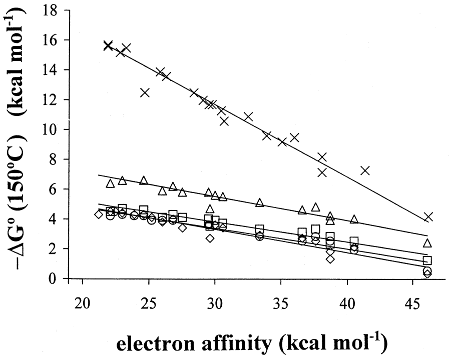

Fig. 4. ΔG°_3(150 °C) values for the interactions of the molecular anions formed from a wide range of monosubstituted nitrobenzenes with SiF_4 (cross) plotted as a function of the electron affinity of the substituted nitrobenzene. For comparison with the present measurements, previous determinations of ΔG°_2(150 °C) values for the interactions of these molecular anions with the common solvent molecules, dimethylsulfoxide (triangle), acetonitrile (square), dimethylformamide (circle), and methanol (diamond) are also shown. Electron affinity values were taken from [19]. The ΔG°_2(150 °C) values of the solvent molecules were taken from [14].

small amounts of oxygen intentionally added to the buffer gas [11].

The temperature dependencies of the equilibrium constants K_3 for some of the equilibria were determined also and standard enthalpy, ΔH°_3, and entropy, ΔS°_3, changes for reaction 3 ($\Delta G^\circ_3(T) = \Delta H^\circ_3 - \Delta S^\circ_3$) were obtained from the van't Hoff plots [18] shown in Fig. 3. These values are also summarized in Table 1. We would expect that, for different M^-, as $\Delta G^\circ_3(T)$ decreases so would $-\Delta H^\circ_3$ with ΔS°_3 changing little and this expectation is at least roughly reflected in these data. However, considering that the equilibrium constants, K_3, could be measured only over a relatively narrow temperature range, the separation of ΔG°_3(T) into ΔH°_3 and ΔS°_3 terms might not be entirely reliable. For this reason and also because the ΔG°_3(150 °C) values listed in Table 1 are much more comprehensive, we will discuss the results below only on the basis of the ΔG°_3(150 °C) data.

In Fig. 4 the ΔG°_3(150 °C) values observed for molecular anions of all of the singly substituted nitrobenzenes have been plotted as a function of the EA of M. Also, included in this plot are ΔG°_2(150 °C) values previously determined by Chowdhury et al. [14] for the clustering reactions of these molecular anions with the common solvent molecules, methanol, acetonitrile, dimethyl formamide, and dimethyl sulfoxide. It is noted that the $-\Delta G^\circ_3$(150 °C) values for SiF_4 are uniformly and significantly greater than those of the common solvent molecules and exceed the desired level of $-\Delta G^\circ_3(150\ °C) = 10\ \mathrm{kcal\ mol^{-1}}$ for all compounds in this class that have EA values less than about 30 $\mathrm{kcal\ mol^{-1}}$. As was observed for the solvent molecules, the $-\Delta G^\circ_3$(150 °C) values for SiF_4 decrease continuously and smoothly with increases in the EA of M. For the solvent molecules, this relationship was explained as follows [14]. The addition of an electron withdrawing substituent to the conjugated ring system of nitrobenzene is thought to increase the EA of M by causing a delocalization of negative charge within M^- which, in turn, decreases electron density in the region of the nitro group. This delocalization of charge is then expected to weaken the coulombic attractive force between M^- and the dipole moment of the solvent molecule by increasing the distance of closest approach between the solvent dipole and the center of negative charge within M^- [14]. Although the ΔG°_3(150 °C) values shown for SiF_4 in Fig. 4 also show a smooth and continuous inverse dependence on the EA of M, it is noted that the magnitude of this dependence on EA is much

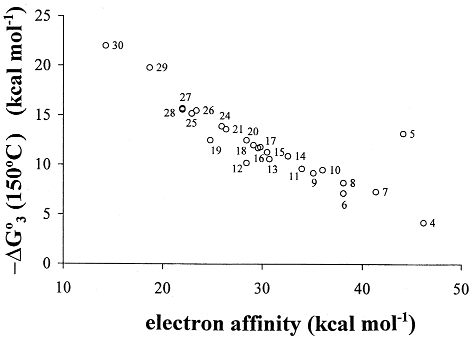

Fig. 5. $\Delta G°_3$(150 °C) values for all of the molecular anions as a function of the electron affinity of the molecule. The identity of each compound is indicated by the assigned number in Table 1. The electron affinity value for each molecule was taken from [19].

greater than that for the solvent molecules. A reasonable explanation for this difference might be the following. The interactions between the M^- ions and SiF_4 are expected to differ significantly from the ion–dipole interactions of the solvent molecules discussed above in that the interactions with SiF_4 are expected to be very short range Lewis acid–base interactions between one of the oxygen atoms of the nitro group and the electron deficient Si atom of SiF_4. As the $M^-(SiF_4)$ complex is formed, the tetrahedral coordination of SiF_4 is expected to change towards a trigonal bipyramidal coordination. The strength of the Lewis acid–base interaction will depend more on the magnitude of negative charge remaining at the oxygen atom involved in the Lewis interaction than on the location of the center of charge within M^-. Due to these fundamental differences in the ion–dipole and Lewis acid–base mechanisms of interaction, it is reasonable that the binding strengths of SiF_4 to the molecular anions observed here are more sensitive to changes in the delocalization of charge within M^- than was the binding strengths of the common solvent molecules.

In Fig. 5, a plot of $\Delta G°_3$(150 °C) versus EA of M is shown for all compounds studied here with identification of each compound by its number assigned in Table 1. Several of these results are worthy of individual consideration. It is interesting to note that $\Delta G°_3$(150 °C) for 2,6-dimethylnitrobenzene (compound #29) is in good agreement with expectations based on the EAs of the monosubstituted nitrobenzenes. This result would be surprising if a large steric hindrance to the interaction of this negative ion with SiF_4 was introduced by the two methyl groups adjacent to the nitro group of M^-. The observed strong interaction can be explained, however, by considering the reason previously suggested for the unusually low EA value of 2,6-dimethylnitrobenzene [20]. In the molecular anion of this compound, the two ortho methyl groups discourage delocalization of negative charge into the benzyl ring by steric hindrance of the resonance structures in which the C-N bond assumes double bond character and the nitro group becomes coplanar with the benzyl ring. This steric effect promotes the localization of negative charge on the oxygen atoms of the nitro group and an out-of-plane orientation of the nitro group. We would then expect this out-of-plane orientation of the nitro group to minimize any steric hindrance of the two otho methyl groups on the ensuing strong interaction between SiF_4 and an oxygen atom of the nitro group. Inspection of the other ortho-substituted nitrobenzenes shown in Fig. 5 also provides evidence of only small ortho steric effects. The interactions of the molecular anions of *o*-fluoronitrobenzene, *o*-trifluoronitrobenzene, and *o*-dinitrobenzene with SiF_4 appear to be only slightly weaker than those expected based on their respective EA values.

In Fig. 5, the somewhat lower than expected $\Delta G°_3$(150 °C) for 1-nitronapthalene (compound #12) suggests that the interactions of SiF_4 with the molecular anions of nitro-substituted aromatic hydrocarbons will be reduced with increased size of an extended aromatic ring system by an amount which is greater than that expected based solely on the EA of such compounds. This point is additionally reinforced by our observation that the molecular anion of azulene, $C_{10}H_8^-$, does not interact with SiF_4 to any detectable extent ($-\Delta G°_3$(150 °C) for this compound is thereby estimated to be no greater than 3.5 kcal mol^{-1}). Considering that the EA of azulene is only about 16 kcal mol^{-1} [19], this very weak interaction with SiF_4 must be attributed to the lack of a specific Lewis base site on the $C_{10}H_8^-$ ion which can be closely approached by SiF_4.

In Fig. 5, the strength of the interaction between SiF_4 and the molecular anion of *p*-benzoquinone (compound #5) is shown to be much greater than that of the substituted nitrobenzenes of similar EA. This strong interaction might be due to a greater degree of negative charge localization on the oxygen atoms and/or less steric hindrance in the Lewis acid interaction of SiF_4 with one of the oxygen atoms in *p*-benzoquinone as compared to the substituted nitrobenzenes. A strong argument for the principal importance of low steric hindrance in this case is provided by the $\Delta S°_3$ value listed in Table 1 for *p*-benzoquinone which is significantly lower than all of those determined for the substituted nitrobenzenes. It is also noted in Table 1 that relatively high $-\Delta G°_3$(150 °C) values of about 14 kcal mol^{-1} were measured for both the *o*-nitrophenoxy and *p*-nitrophenoxy anions (compounds #22 and #23). Considering that the EAs of the *o*-nitrophenoxy and *p*-nitrophenoxy radicals are likely to be extremely high (about 60 kcal mol^{-1} [21]), the very strong interactions of their molecular anions with SiF_4 are somewhat unexpected and are best explained if the Si atom of SiF_4 is envisioned to bind to the oxygen atom of the phenoxy rather than the nitro group in these cases. In a complex of this type, greater negative charge on the Lewis base site and low steric hindrance to complex formation would lead to a very stable complex ion.

The interactions of SiF_4 with the molecular anions that are readily formed by electron capture to perfluorinated and perchlorinated aromatic compounds, such as C_6F_6 [22] and C_6Cl_6 [6], were also studied. For these molecular anions, however, a halide ion transfer reaction of the type, $M{-}X^- + SiF_4 \rightarrow SiF_4X^- + M^\cdot$, occurs instead of the association reaction 3. Therefore, it was not possible to determine $\Delta G°_3$(150 °C) values for these types of molecular anions. The molecular anions of nonaromatic perfluorinated compounds, such as SF_6 and perfluoromethylcyclohexane, were also found to undergo fluoride transfer rather than association upon reaction with SiF_4, as expected [23].

In view of the information provided, one might expect that the Lewis acid, SiF_4, will interact particularly strongly with very low EA compounds that have a specific Lewis base site which can be closely approached by SiF_4. Further, by this interaction it should be possible to prevent the troublesome TED reaction commonly associated with low EA compounds. This expectation is verified in Fig. 6 where the EC mass spectrum of benzophenone is shown before (A) and after (B) adding only 5 ppm SiF_4 to the methane buffer gas in an ion source of temperature, 110 °C. The EA of benzophenone is known to be quite low, about 15 kcal mol^{-1}. Therefore, at this ion source temperature, the EC mass spectral response to this compound at $m/z = 182$ is greatly reduced by the fast TED reaction of its molecular anion. As indicated in Table 1 and Fig. 5, however, we know that the molecular anion of benzophenone will bind very strongly to SiF_4 ($-\Delta G°_3$(150 °C) = 22.0 kcal mol^{-1}). Therefore, by the addition of a small amount of SiF_4 to the buffer gas, a new ion of much greater intensity appears at m/z = 286 in Fig. 6(B) along with the expected Si and C isotopic ions at m/z = 287–289. The greatly improved ECMS response to benzophenone demonstrated in Fig. 6(B) is clearly due to a strong Lewis acid–base interaction by which a large fraction of the M^- ions is held in the clustered form, $M^-(SiF_4)$, which is stable against destruction by TED. It is reasonable to expect that similarly strong interactions between SiF_4 and the molecular anions of numerous other compounds having relatively low electron affinities and unobstructed Lewis base sites

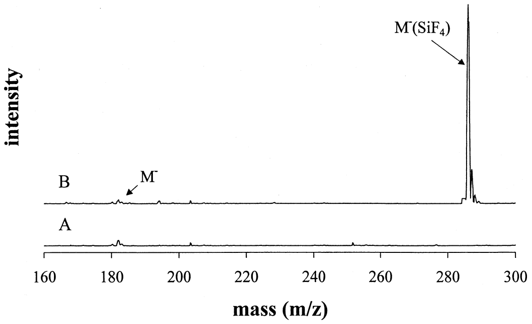

Fig. 6. Electron capture mass spectra of benzophenone produced by the PHPMS ion source under conditions of 1.0 Torr methane buffer gas pressure and 125 °C without (A) and with (B) 5×10^{-6} Torr added SiF_4.

will enable such compounds to be detected readily by methods based on electron capture reactions.

Acknowledgement

The work was supported by grant no. CHE-9816643 from the Chemistry Division of the National Science Foundation.

References

[1] W.B. Knighton, L.J. Sears, E.P. Grimsrud, Mass Spectrom. Rev. 14 (1996) 327.
[2] A. Zlatkis, C.F. Poole, Electron Capture, Theory and Practice in Chromatography, Elsevier, New York, 1981.
[3] E.P. Grimsrud, in Detectors for Capillary Chromatography, H. Hill, D. McMinn (Eds.), Wiley, New York, 1992, p. 83.
[4] G.A. Eiceman, Z. Karpas, Ion Mobility Spectrometry, CRC Press, Boca Raton, FL, 1994.
[5] R.C. Dougherty, J. Dalton, F.J. Biros, J. Org. Mass Spectrom. 6 (1972) 1171.
[6] E.A. Stemmler, R.A. Hites, Electron Capture Negative Ion Mass Spectra of Environmental Contaminants and Related Compounds, VCH, New York, 1988.
[7] L.J. Sears, J.A. Campbell, E.P. Grimsrud, Biomed. Environ. Mass Spectrom. 14 (1987) 401.
[8] E.P. Grimsrud, S. Chowdhury, P. Kebarle, J. Chem. Phys. 83 (1985) 3983.
[9] A.A. Viggiano, R.A. Morris, J.F. Paulson, J. Phys. Chem. 94 (1990) 3286.
[10] C.A. Valkenburg, W.B. Knighton, E.P. Grimsrud, J. High Res. Chromatogr. Chromatogr. Commun. 9 (1987) 320.
[11] W.B. Knighton, J.A. Bognar, E.P. Grimsrud, J. Mass Spectrom. 30 (1995) 557.
[12] W.B. Knighton, D.R. Zook, E.P. Grimsrud, J. Am. Soc. Mass. Spectrom. 1 (1990) 372.
[13] L.A. Krieger, E.P. Grimsrud, Int. J. Mass Spectrom. Ion Processes 83 (1988) 189.
[14] S. Chowdhury, E.P. Grimsrud, P. Kebarle, J. Phys. Chem. 91 (1987) 2551.
[15] J.W. Larson, T.B. McMahon, J. Am. Chem. Soc. 107 (1985) 766.
[16] J.A. Bognar, W.B. Knighton, E.P. Grimsrud, Anal. Chem. 64 (1992) 2451.
[17] W.B. Knighton, E.P. Grimsrud, J. Am. Chem. Soc. 114 (1992) 2336.
[18] P. Kebarle, in Techniques for the Study of Ion Molecule Reactions, J.M. Farrar, W. Saunders (Eds.), Wiley, New York, 1988, p. 221.
[19] P. Kebarle, S. Chowdhury, Chem. Rev. 87 (1987) 513.
[20] M. Mishima, C.H. Kang, C. Huh, M. Fujio, Y. Tsuno, Chem. Lett. (1993) 889.
[21] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) 710.
[22] W.B. Knighton, J. Bognar, E.P. Grimsrud, Chem. Phys. Lett. 192 (1992) 522.
[23] L.G. Huey, E.R. Lovejoy, Int. J. Mass Spectrom. Ion Processes 155 (1996) 133.