Communication

Observation of the Nucleophilic Displacement (S_N2) Reaction $F^- + CH_3Br \rightarrow CH_3F + Br^-$ Induced by Dissociative Electron Capture in Binary van der Waals Clusters

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We report on the S_N2 reaction $F^- + CH_3Br \rightarrow FCH_3 + Br^-$ in binary clusters composed of CH_3Br and C_2F_6 in a crossed electron/molecular beam experiment. The reaction is induced by resonance dissociative electron attachment to the C_2F_6 component where the nucleophile F^- is generated at an energy (around 3.8 eV) where CH_3Br does not capture electrons to form Br^-. The results indicate that the cross section for the S_N2 reaction is independent of the total excess energy which can be varied between 1.7 and 5 eV in the present system.

Introduction

Reactions occurring between nucleophiles and electrophiles are probably the most common and important molecular processes. The prototype bimolecular nucleophilic displacement (S_N2) reaction is

$$X^- + CH_3Y \rightarrow XCH_3 + Y^- \quad (1)$$

with X, Y representing halogen atoms. For an S_N2 reaction in solution it is well known that the reaction rate generally depends on the nature of the solvent [1] which controls the thermodynamics and activation energy of the process, i.e., the relative energy of reagents and products with respect to the energy of the transition state. In the absence of solvation, the S_N2 reaction (1) has a much lower activation energy (if at all) and thus a much higher reaction rate. In the case of X = Cl and Y = Br a gas phase rate constant of $k = 2.1 \times 10^{-11}\ cm^3\ s^{-1}$ was deduced [2] which is about 15 orders of magnitude (!) larger than the rate constant for the corresponding reaction in water [2, 3].

Techniques to study gas phase S_N2 reactions include ion cyclotron resonance (ICR) mass spectrometry [4–6], the flowing afterglow (FA) method [7, 8] and high pressure mass spectrometry [9, 10].

In this contribution we present the observation of the S_N2 reaction

$$F^- + CH_3Br \rightarrow CH_3F + Br^- \quad (2)$$

induced by dissociative electron attachment (DA) in binary van der Waals clusters composed of CH_3Br and a second, fluorine containing compound. The idea is to generate the nucleophile F^- via DA from the second component (M) of the mixed cluster.

$$e^- + M \rightarrow M^{-(*)} \rightarrow R + F^- \quad (3)$$

The *necessary* requirement for an unambiguous identification of the S_N2 reaction (2) is that the DA process (3) is operative in an electron energy range where the first component (CH_3Br) does not generate Br^-. If then from a binary cluster the product Br^- is observed in the energy range where the nucleophile F^- is formed (reaction (3)), we have strong evidence that Br^- is the product of the S_N2 reaction (2) in the binary clusters. As will be shown the molecule $M = C_2F_6$ fulfills these necessary requirements.

Due to its resonant character, dissociative electron attachment (DA) usually occurs within a more or less narrow energy region [11, 12]. Since the energy of the reacting system is solely given by the energy of the attaching electron, the excess energy of the S_N2 reaction is thus varied within the width of the resonance where the nucleophile is generated.

To the best of our knowledge, we report the first observation of an S_N2 reaction of the type (1) in a mixed cluster system. We mention here related studies in clusters, namely S_N2 reactions in cationic systems like $(NH_3/C_6H_5Cl)^+$ generated by resonantly enhanced multiphoton ionization (REMPI) [13] and a study of the reaction dynamics upon excitation of the $I^- . CH_3I$ ion-molecule complex to the first optically allowed state [14, 15] which represents the $[ICH_3I]^-$ intermediate for S_N2 identity reaction.

Experimental

The experiments were carried out in a crossed electron beam/molecular beam apparatus elsewhere described in detail [12, 16–18]. In brief, a supersonic molecular beam containing the binary clusters is crossed at right angles with an energy selected electron beam (Fig. 1). Negative ions resulting from this interaction are extracted and identified

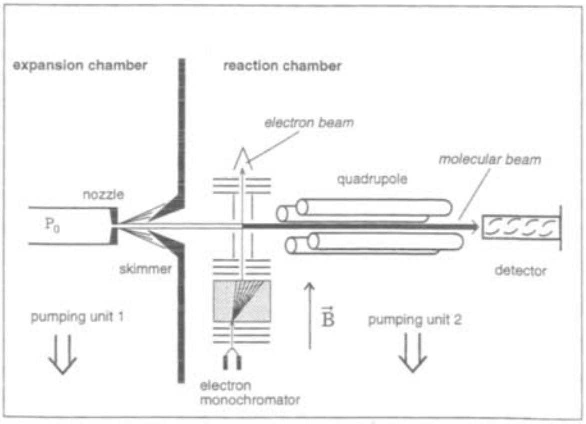

Fig. 1
Schematic of the experimental setup for the study of reactions following electron attachment to clusters

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by means of a quadrupole mass filter. The cluster beam is generated by adiabatic expansion of a mixture of C_2F_6 and CH_3Br seeded in Ar through an 80 µm nozzle. The beam contains a distribution of clusters the average size and composition of which can be varied by the expansion conditions (composition of the gas mixture, stagnation pressure and temperature of the nozzle).

The electron beam is produced by a "trochoidal electron monochromator" (TEM) [19] which is particularly suited to study electron-molecule interactions at low energies.

The electron energy scale is calibrated by the well known resonance in SF_6 yielding SF_6^{-*} near 0 eV [12, 20]. The TEM was operated at an energy resolution of ≈ 140 meV (FWHM) at a current of ≈ 15 nA.

Results and Discussion

Before discussing the S_N2 reaction (2) induced in the binary van der Waals cluster system CH_3Br/C_2F_6 it is worth to briefly characterize results from a pure C_2F_6 expansion and a pure CH_3Br expansion. In the gas phase these compounds are reasonably well investigated.

Electron attachment to single perfluoroethane (C_2F_6) yields a broad resonance feature (between 2 and 6 eV) peaking at 3.8 eV [21–23] associated with F^- formation via DA. Fig. 2a and b present the energy profiles of two product ions obtained from a pure C_2F_6 expansion seeded in Ar (1 : 10) at a stagnation pressure of 2.5 bar. In addition to F^- formed from isolated molecules, we observe stabilized molecular cluster anions M_n^- and also solvated ions of the form $F^- \cdot M_n$ (not shown here).

Electron attachment to gas phase CH_3Br yields Br^- from a resonance near 0 eV and from a further, comparatively weaker resonance near 6.5 eV [24]. A similar result is observed from a pure CH_3Br expansion (also seeded in Ar) (Fig. 2c). In that case, solvated ions of the form $Br^- \cdot (CH_3Br)_n$ are also formed near 0 eV, their intensity increasing with n up to n = 5, the largest component which can be observed with the present mass spectrometer.

While F^- formation from C_2F_6 is endothermic by 2.1 ± 0.1 eV [23], Br^- formation from CH_3Br is exothermic by 0.36 eV [25]. The cross section for the latter process, however, is comparatively small. This is due to an appreciable activation barrier (0.3 eV) for the reaction.

$$e^- + CH_3Br \rightarrow Br^- + CH_3$$

which is obtained from the temperature dependence of the attachment rate in a flowing afterglow Langmuir probe (FALP) experiment [25]. In terms of potential energy curves, the activation barrier represents the energy at which the dissociative anionic potential energy curve crosses the neutral curve. At room temperature an attachment rate of $k = 6 \times 10^{-12}\,cm^3\,s^{-1}$ was derived corresponding to a cross section of $\sigma \approx 6 \times 10^{-19}\,cm^2$. For C_2F_6 an electron attachment cross section of $\sigma = 1.3 \times 10^{-17}\,cm^{-2}$ at an energy near 4 eV is reported [26]. These gas phase numbers also approximately reflect the intensity ratio $F^-/C_2F_6 : Br^-/CH_3Br$ in the cluster experiment (Figs. 2).

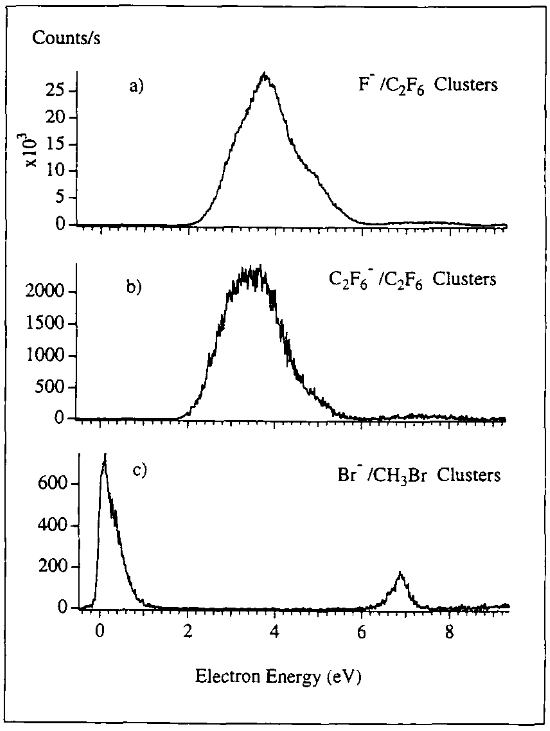

Fig. 2
F^- and $C_2F_6^-$ signal from a pure C_2F_6 expansion (a) and (b); Br^- signal from a pure CH_3Br expansion (c). Both gases were seeded in Ar (10 : 1) and the spectra were recorded at a stagnation pressure of 2.5 bar

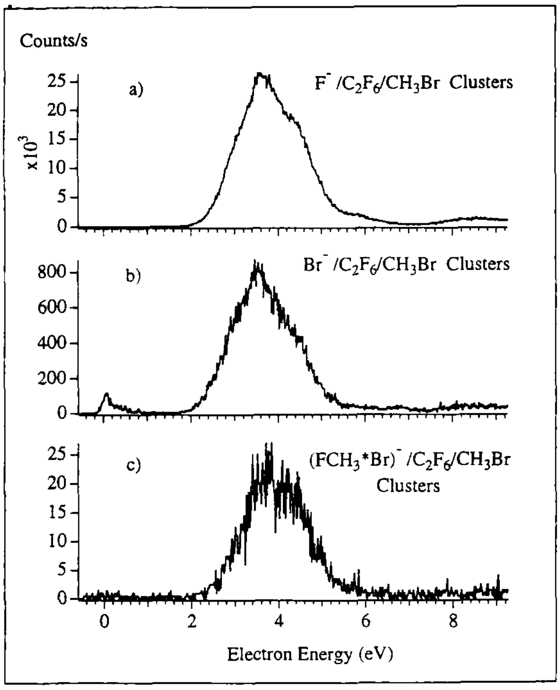

Fig. 3
F^-, Br^-, and $(FCH_3 \cdot Br)^-$ signal from a C_2F_6/CH_3Br expansion seeded in Ar (10 : 1 : 100), stagnation pressure 2.5 bar. The Br^- signal around 3.8 eV is due to the S_N2 reaction $F^- + CH_3Br \rightarrow FCH_3 + Br^-$

We now proceed to the results obtained from a mixed expansion of C_2F_6 and CH_3Br (10:1) seeded in Ar (Fig. 3). While the F^- profile is virtually indentical to that from a pure C_2F_6 expansion (Fig. 2), the Br^- yield shows an additional strong signal within the energy range of the F^-/C_2F_6 resonance. We ascribe this signal to the occurrence of the S_N2 reaction (2) in a mixed cluster.

It should be noted that during the expansion the background pressure is sufficiently low (10^{-5} mbar) to definitely exclude the corresponding S_N2 reaction between uncorrelated gas phase molecules.

A further possible source of Br^- formation at higher electron energies is inelastic scattering from either C_2F_6 or CH_3Br and dissociative capture of the slowed down electron by CH_3Br in the same cluster thus generating Br^-. These intracluster scavenging features can in fact be seen when a strong scavenger component is present in the cluster. In such cases the scavenging features carry the signature of the electronically excited states of the neutral scatterer [18]. Since CH_3Br is a very weak scavenger (in particular in the vibrationally cold cluster, *supra vide*) and since the Br^- signal closely resembles the F^-/C_2F_6 resonance profile, we must conclude that it is a product of the S_N2 reaction (2).

Gas phase ion-molecule reactions reflect the intrinsic properties of the corresponding ions and molecules; a collinear S_N2 reaction (1) hence proceeds along a double minimum potential (Fig. 4) where the isomeric reagents ($F^- \cdot CH_3Br$) and products ($FCH_3 \cdot Br^-$), bound by the long-range ion-induced dipole interaction, are separated by an activation barrier [14, 27, 28]. According to a model introduced by Shaik and Pross [29–31] the barrier arises from an avoided crossing between the two electronic curves containing reactant-like (F^-CH_3Br) and product-like (FCH_3Br^-) Heitler-London VB forms. These diabatic potential energy curves describe methyl transfer without simultaneous electron transfer (Fig. 4). The relevant S_N2 potential curve is then obtained by introducing an electron transfer matrix element, which splits the diabatic curves. The two low lying electronic configurations are then asymptotically identified as $F^- + CH_3Br$ and $FCH_3 + Br^-$.

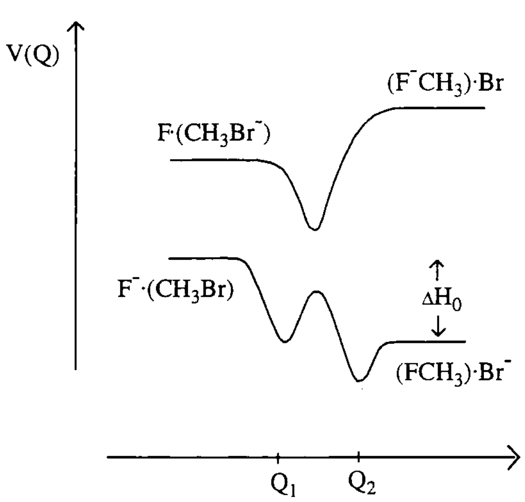

Fig. 4
Schematic representation of the potential energy surface along the reaction coordinate of the collinear S_N2 reaction $F^- + CH_3Br \rightarrow FCH_3 + Br^-$. Also shown are the mixed diabatic states corresponding to methyl transfer without simultaneous electron transfer (see text)

For the present S_N2 reaction we calculate a gas phase exothermicity of $\Delta H_0 = -1.7$ eV (taking D(CH_3-Br) = 3.08 eV, D(CH_3-F) = 4.77 eV [32] and EA(F) = 3.399 eV, EA(Br) = 3.365 eV [33]).

In the present cluster experiment we do not know the structure of the neutral target cluster nor do we know its exact size or composition. It is also a question as to which extent the ion-molecule reaction proceeds along the colinear reaction coordinate depicted in Fig. 4. In any case, the reactant system $F^- \cdot CH_3Br$ will initially be created via DA most likely at some configuration away from the minimum of the ion-molecule complex ($Q < Q_1$), but eventually with some translational energy. In single gas phase C_2F_6 molecules F^- is formed with comparatively low translational energy ranging from 40 meV (at 2 eV electron energy) to 300 meV (at 6 eV) [21]. This points towards a unimolecular decomposition of $C_2F_6^{-*}$ according to the "statistical" picture. If an ion-molecule reaction is solely controlled by the long-range ion-induced dipole potential

$$V(R) = -\frac{e^2\alpha}{2R^4} \tag{4}$$

(α: polarizability of the molecule) the cross section can be expressed by the well known Langevin equation [34, 35]

$$\sigma = (E_T)^{-1/2} \cdot \pi (2e^2\alpha)^{1/2} \tag{5}$$

which decreases with collision energy E_T.

The S_N2 reaction under consideration is certainly much more complex as it, e.g., proceeds over an activation barrier. Since the Br^- yield closely resembles the F^- yield, however, we can conclude that the cross section for the S_N2 reaction is *insensitive* to the translational energy of the nucleophile F^- and also *insensitive* to the vibrational energy deposited in the target cluster (amounting up to more than 3 eV).

Returning to Fig. 3, it can be seen that in the energy range 2–6 eV the F^-/Br^- intensity ratio is $\approx 25/0.8$. Superficially this would indicate that about 3% of F^- ions generated via DA in a mixed cluster undergo the S_N2 reaction (2).

The F^- signal obtained in Fig. 3, on the other hand, is the result of DA reactions from (i) C_2F_6 containing clusters traveling in the molecular beam, (ii) C_2F_6 monomers in the molecular beam and (iii) C_2F_6 monomers of the scattered background gas. We have applied a TOF technique which allows to separate products resulting from reactions in the molecular beam from those in the scattered background gas [18, 36]. From this procedure it can be shown [37] that under the present expansion conditions only $\approx 30\%$ of the F^- signal arise from targets traveling in the molecular beam. Apart from aggregated C_2F_6 molecules the beam may also contain C_2F_6 monomers. This same procedure, on the other hand, shows that the small Br^- feature near 0 eV solely arises from scattered CH_3Br monomers. It thus appears that most of the C_2F_6 molecules present in the interaction region exist as monomers (scattered and in the beam), while the CH_3Br component in the molecular beam only exists in an aggregated form.

It can hence be concluded that the efficiency of the S_N2 reaction (2) under the present expansion conditions is considerably larger than 10%.

Due to the much lower condensation temperature of C_2F_6 (195 K) as opposed to CH_3Br (276.6 K) one in fact expects a strong enrichment of the CH_3Br component in the mixed clusters, with the last component probably in excess.

Apart from the atomic ions F^- and Br^- (representing the isolated entering and leaving group of the reaction) we observe additional negatively charged ions or complexes at an energy near 4 eV. Among them molecular cluster ions $(C_2F_6)_n^-$, solvated fragment ions of the form $F^- \cdot (C_6F_6)_n$, but also the pair of complexes of the form $F^- \cdot (CH_3Br)_n / Br^- \cdot (CH_3Br)_{n-1}$ which is observed with decreasing intensity up to $n = 2$. This ion pair can be interpreted as members of the S_N2 reaction

$$F^- \cdot (CH_3Br)_n \rightarrow FCH_3 + Br^- \cdot (CH_3Br)_{n-1} \tag{2a}$$

In that sense Figs. 3a (Br^-) and 3c ($F^- \cdot CH_3Br$) show this ion pair for $n = 1$. We can, however, not decide whether the compound on the left hand side of Eq. (2a) is the ion-molecule complex before or after electron transfer, i.e., $F^- \cdot CH_3Br$ or $FCH_3 \cdot Br^-$. We find that in every case the intensity of the product ($Br^- \cdot (CH_3Br)_{n-1}$) is much higher than that of the precursor complex $F^- \cdot (CH_3Br)_n$. This must be related to the appreciable excess energy of reaction (2a) which is -1.7 eV in the case of $n = 1$ (see Fig. 4).

We are currently studying the S_N2 reaction [38]

$$Cl^- \cdot (C_2H_5Br)_n \rightarrow C_2H_5Cl + Br^- \cdot (C_2H_5Br)_{n-1} \tag{2b}$$

which is only exothermic by -0.26 eV (taking the bond dissociation energies from Ref. [32]) for $n = 1$. In this case the intensity of the undissociated complex is much larger than that of the product ion $Br^- \cdot (C_2H_5Br)_{n-1}$.

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