vicinity of the positive charge and this solvent exclusion reduces the nonspecific solvation. The same should be true for Nb^+ (relative to t-Bu^+ or c-Pe^+).

The above observations have some bearing on the Nb^+ controversy (see preceding section). The ΔH_2(sol) changes based on Arnett's data[39] for reactions 15–20 were given in the preceding section. Clearly the solution data appear to present a less dramatic case for the special stability of Nb^+. Thus Nb^+ is less stable than t-Bu^+ in solution reaction 15, while the opposite is true in the gas phase. For the change i-Pr^+, c-Pe^+, Nb^+, reactions 16 and 17, one observes also a reduced trend in solution. Thus the change c-Pe^+ to Nb^+ is only ~4 kcal/mol more exothermic than the change i-Pr^+ to c-Pe^+ while in the gas phase the value is ~6 kcal/mol. Also the changes in the methyl substituent series reactions 18–20 are less pronounced in solution.

When one considers the above ΔH changes in solution one must remind oneself that they are used as models to the stability of Nb^+ in connection with the exo–endo solvolysis rate differences.[30] The experimental solvolysis rates establish a difference of about 6 kcal/mol between the exo and endo transition states $(R^+–X^-)^*$ in solution.[30] In the nonclassical view only the exo transition state is significantly stabilized by σ bridging. Since the exo state is electronically more stabilized one expects that the nucleophilic solvent stabilization will be somewhat less for that state than for the endo state. As was pointed out above some differential nucleophilic stabilization is probably affecting the Arnett solution data. Thus, in this respect these data may be suitable models for the exo–endo norbornyl transition states. However, it was seen that Arnett's data are much more strongly affected by differential nonspecific solvation, i.e., solvent exclusion by bulky hydrocarbon structures that lead to poorer solvation. This change of general solvation present in the Arnett results makes the energy changes in eq 16–20 in solution not suitable for modeling of the exo–endo transition-states energies. No gross changes of the size of ion occur for the exo relative to the endo transition state, and thus no significant changes of nonspecific solvation for these transition states can be expected. Thus Arnett's solution data, if they are to be applied for modeling energy changes of exo–endo transition states, should be corrected for the presence of nonspecific solvation. The corrections, which cannot be quantitatively assessed, will be in the direction of greater agreement with the gas-phase results and increased support of reactions 16–20 energy change models for the unusual stability of Nb^+ and by implication also of the *exo*-Nb^+–X^- transition state in solution.

Registry No. Cl^-, 16887-00-6; H^-, 12184-88-2; $PhCH_2^+$, 6711-19-9; t-Bu^+, 14804-25-2; p-$FPhCH_2^+$, 29180-23-2; o-$MePhCH_2^+$, 63246-55-9; p-$MePhCH_2^+$, 57669-14-4; $PhCHCl^+$, 56683-65-9; o-$MePhCH_2Cl$, 552-45-4; p-$MePhCH_2Cl$, 104-82-5; $PhCCl_3$, 98-07-7; p-$MeOPhCH_2Cl$, 824-94-2; $PhCHCH_3^+$, 25414-93-1; $(CH_3)_2CH^+$, 19252-53-0; m-$FPhCH_2^+$, 65108-06-7; o-$FPhCH_2^+$, 65108-14-7; p-$ClPhCH_2^+$, 29180-24-3; m-$MePhCH_2^+$, 60154-94-1; $PhCCl_2^+$, 24154-22-1; AdCl, 935-56-8; 2-NbCl, 29342-53-8; Ad^+, 19740-18-2; Nb^+, 24321-81-1; 1-Cl-*c*-Pe, 930-28-9; 2-Me-NbCl, 96246-73-0; 1-Me-*c*-Pe^+, 17106-22-8; *c*-Pe^+, 25076-72-6.

Stabilities of Halonium Ions from a Study of Gas-Phase Equilibria $R^+ + XR' = (RXR')^+$

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Abstract: The gas-phase ion equilibria $R^+ + B = RB^+$, where $R^+ = Et^+$, i-Pr^+, c-Pe^+, t-Bu^+, 2-Me-2-Bu^+, and 2-Nb^+ and $B = CH_3Cl$, CH_2Cl_2, $CHCl_2$, $CHCl_3$, SO_2F_2, CF_3H, and CF_4 were determined in a pulsed electron beam high pressure mass spectrometer. van't Hoff plots provide $\Delta G^\circ{}_{300}$, ΔH°, and ΔS°. For the chloronium ions the following trends were observed. The bond energy $D(R^+–ClR_o)$, where R^+ changes and R_o is constant, decreases with increasing electronic stabilization of R^+, i.e., in the order Me^+, Et^+, i-Pr^+, c-Pe^+, t-Bu^+, Nb^+. The same order was observed earlier in this laboratory for $D(R^+–Cl^-)$, i.e., the chloride affinity of R^+. However, the changes of $D(R^+–ClR_o)$ for R^+ = 2-Me-2-Bu^+, Nb^+, and t-Bu^+ are very small. This means that little differential, specific nucleophilic solvation of these ions in solution is to be expected when solvents of low nucleophilicity like CH_2Cl_2 and SO_2ClF are used. The bond energies $D(Me^+–ClR)$ increase in the order R = Me, Et, i-Pr, t-Bu. The bond energies $D(t\text{-}Bu^+–B)$ decrease in the order $B = C_2H_5Cl$, $CH_2Cl_2 \approx CH_3Cl$, CCl_3H, SO_2F_2, CF_3H, CF_4. The significance of these trends is discussed.

Measurements of ion equilibria in the gas phase[1] include acceptor–donor (Lewis acid-base) equilibria of the type in eq 1,

$$R^+ + B = RB^+ \qquad (1)$$

$$R^+ + XR' = (RXR')^+$$

where R^+ is a carbocation and B a σ, π, or n donor base. Determination of the equilibrium constant K_1 with a pulsed electron beam high pressure mass spectrometer leads via van't Hoff plots to the corresponding $\Delta G^\circ{}_1$, $\Delta H^\circ{}_1$, and $\Delta S^\circ{}_1$.

The present work describes results for systems where R = ethyl (Et), isopropyl (i-Pr), *tert*-butyl (t-Bu), 2-methyl-2-butyl (t-Pe), cyclopentyl (c-Pe), and 2-norbornyl (Nb), while $B = XR' = CH_3Cl$, CH_2Cl_2, $CHCl_3$, C_2H_5Cl, CHF_3, CF_4, and SO_2F_2. The work is an extension of measurements described in an earlier publication[2] in which reactions involving Et^+, i-Pr^+, and MeCl were studied. The present results allow one to observe the change of bonding in R^+–B with increasing stabilization of the carbocation R^+. They also give the bonding changes for a given R^+ with changing donor character (nucleophilicty) of B. Chloronium ions are important alkylating agents in solution.[3] Their usefulness as alkylating agents in the gas phase was pointed out recently.[4] Thus, the dimethylchloronium ion can be used[4] for the clean gas-phase preparation of tertiary oxonium and quaternary ammonium ions as shown in reaction 2. The product ions can then

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$$CH_3ClCH_3^+ + (CH_3)_2O = CH_3Cl + (CH_3)_3O^+ \quad (2)$$

be used in other measurements. Thus Meot-Ner[5] has studied the gas-phase hydration of Me_4N^+ prepared in the above manner. More recently many Me^+ transfer equilibria between two bases B were determined and a Me^+ affinity ladder established in this laboratory.[6] The reagents most often used for the preparation of Me^+B were the dimethylchloronium and the dimethylfluoronium ions.

Alkylation reactions like (2) also can be useful in analytical chemical ionization work, but this potential has not been realized yet. Alkyl cation transfer reactions involving halonium ions and bases B are S_N2 reactions. The gas-phase kinetics of these reactions have been studied[4] and have proven of considerable interest to the development of the theory of gas-phase S_N2 ion–molecule reactions.[7] Knowledge of the energetics provided by equilibria 1 is of significant utility in all the above cases.

Arnett and co-workers[8,9] have measured enthalpy changes ΔH_3 for the ionization processes 3 in SO_2ClF and CH_2Cl_2 solutions.

$$RCl + SbCl_5 = R^+ + SbCl_6^+ \quad (3)$$

The ΔH_3 were then used to evaluate enthalpy changes for the chloride-transfer reactions 4 and relative heats of formation

$$R_o^+ + RCl = R_oCl + R^+ \quad (4)$$

$$\Delta H_4 = \Delta H_3(R^+) - \Delta H_3(R_o^+) \quad (5)$$

$\Delta H_f(R^+)$ of the ions in solution.[8,9] On the basis of comparisons with available corresponding data in the gas phase, Arnett et al. concluded that there is little differential solvation of the carbenium ions R^+ in solution. More recently, relative chloride affinities in the gas phase were determined in this laboratory.[10] These provided a somewhat better basis for comparison with the solution data[8,9] and indicated that significant differential solvation can be present in some cases. To be able to separate the (differential) solvent effect into the components of specific nucleophilic solvation of R^+ by one solvent molecule and the nonspecific solvation by the solvent dielectric, information on the energetics of ion solvent molecule complexes like R^+ClCH_2Cl is required. The energetics provided by measurement of equilibria 1 also prove useful for this purpose.

Experimental Section

The measurements of the equilibrium constant K_1 for equilibria 1—$R^+ + B = RB^+$ (where R^+ were carbocations like c-Pe$^+$, t-Bu$^+$, etc., and B various halo compounds like CH_3Cl, CH_2Cl_2, CHF_3, etc.)—were executed with a pulsed electron beam high ion source pressure mass spectrometer which has been described previously.[1,11] Briefly, the principle of the method is as follows. A short pulse of 2000 V electrons produces the primary ionization in the temperature-controlled ion-source-reaction chamber maintained at some 2–8 torr of total pressure. The ions gradually diffuse to the walls where they become discharged. During their motion through the gas they also engage in ion–molecule reactions. By proper choice of neutral reactant concentrations, the reactions may be speeded up such that the ions reach ion–molecule reaction equilibria. The relative ion concentrations are monitored by allowing some of the gas to bleed out through a very narrow slit (1 × 0.01 mm) into an evacuated chamber, where the ions are captured by electric fields and subjected to conventional mass spectrometric analysis and detection.

Results and Discussion

(a) Description of Reaction Systems in Which Equilibria $R^+ + B = RB^+$ Were Observed. The required ions R^+ were generated in ~4 torr of methane. The ultimate ions in pure methane are[12] CH_5^+ and $C_2H_5^+$. The ions R^+ were generated by reactions of CH_5^+ and $C_2H_5^+$ with suitable reagent gases added to the methane. As an example we will discuss the setup involved in the measurement of the following equilibrium: i-$C_3H_7^+ + CH_2Cl_2 = i$-$C_3H_7ClCH_2Cl^+$ (see Figure 1). To create the isopropyl cation some 70 mtorr of propane were added to 4 torr of methane. This results in a very fast conversion of the CH_5^+ and $C_2H_5^+$ to $C_3H_7^+$ by reactions[12] 6 and 7. In the presence of small amounts of B = CH_2Cl_2, (6) and (7) are followed by (8), i.e., the formation of

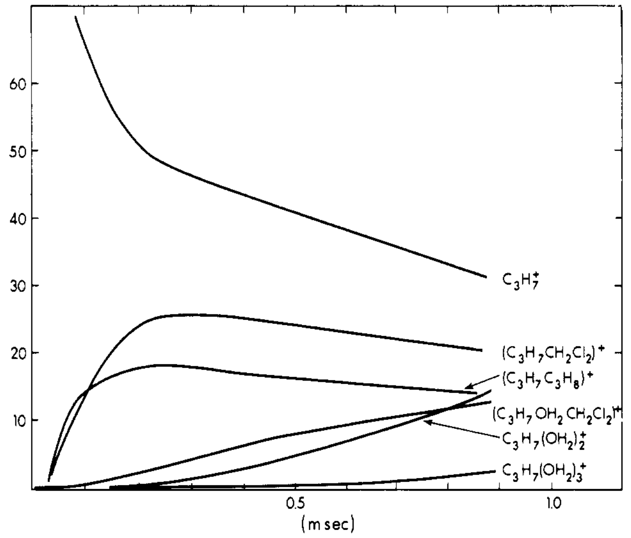

Figure 1. Ion intensities in percent of total ion current of major ions, observed after an ionizing electron pulse in 4 torr of CH_4 containing 72 mtorr of C_3H_8 and 1.16 mtorr of CH_2Cl_2. Temperature −4 °C. i-$C_3H_7^+$ is obtained by reactions of the ultimate ions in methane, CH_5^+, and $C_2H_5^+$ with propane. The iPr$^+$ engages in the following reaction: $C_3H_7^+ + CH_2Cl_2 = C_3H_7ClCH_2Cl^+$, which reaches equilibrium. A side reaction occurs and also reaches equilibrium: $C_3H_7^+ + C_3H_8 = C_3H_7{\cdot}C_3H_8^+$. Both adduct ions are slowly drained by exchange reactions with the strong base H_2O present as a minor impurity.

$$CH_5^+ + C_3H_8 = i\text{-}C_3H_7^+ + H_2 + CH_4 \quad (6)$$

$$C_2H_5^+ + C_3H_8 = C_2H_6 + i\text{-}C_3H_7^+ \quad (7)$$

$$i\text{-}C_3H_7^+ + CH_2Cl_2 = i\text{-}C_3H_7ClCH_2Cl^+ \quad (8)$$

$$i\text{-}C_3H_7^+ + C_3H_8 = i\text{-}C_3H_7{\cdot}C_3H_8^+ \quad (9)$$

the desired chloronium ion. Reaction 8 is third body dependent. Reactions 2 and 3 are complete in microseconds and therefore CH_5^+ and $C_2H_5^+$ do not appear in Figure 1. The $C_3H_7^+$ ion, initially ~100% of the total ion current, disappears rapidly by reaction 8 forming the chloronium adduct. The adduct formation of $C_3H_7^+{\cdot}C_3H_8$ by (9) is also observed. At times longer than ~0.4 ms the ratio $C_3H_7ClCH_2Cl^+/C_3H_7^+$ becomes constant. This must mean that reaction 8 reaches equilibrium. After a similar time reaction 9 also reaches equilibrium. The concentrations of isopropyl, the chloronium adduct, and the propane adduct are seen to gradually decrease while hydrates are formed. Since water is much stronger base than either methylene chloride or propane, the displacement of these bases by water, present as a minor impurity in the apparatus, leads to reactions 10–12. The

$$C_3H_7{\cdot}CH_2Cl_2^+ + OH_2 = C_3H_7{\cdot}OH_2{\cdot}CH_2Cl_2^+ \quad (10)$$

$$C_3H_7{\cdot}OH_2{\cdot}CH_2Cl_2^+ + OH_2 = C_3H_7(OH_2)_2^+ + CH_2Cl_2 \quad (11)$$

$$C_3H_7{\cdot}C_3H_8^+ + OH_2 = C_3H_7(OH_2)^+ + C_3H_8 \text{ etc.} \quad (12)$$

equilibrium constant for the chloronium equilibrium 8 was obtained by using the constant ratio of the ions $C_3H_7ClCH_2Cl^+$ and

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[12] (a) Munson, M. S. B.; Field, F. H. *J. Am. Chem. Soc.* **1965**, *87*, 3294. (b) n-$C_3H_7^+$ is also produced by reactions 6 and 7. This either isomerizes to i-$C_3H_7^+$ or is converted by hydride abstraction from propane to i-$C_3H_7^+$.

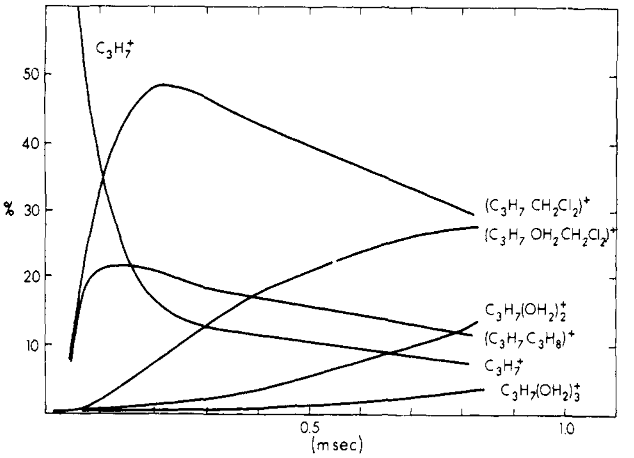

Figure 2. Same reaction mixture and reaction mechanism as in Figure 1, but at the lower temperature (−14 °C). Both equilibria now contain larger equilibrium concentrations of the adduct ions $C_3H_7ClCH_2Cl^+$ and $C_3H_7C_3H_8^+$ relative to $C_3H_7^+$.

$C_3H_7^+$ observed at longer reaction times. Since reaction 8 is much faster than the hydration reaction 10 (see Figure 1), the equilibrium concentrations of the above ions should be little disturbed by the slow removal via (10).

The connentration changes shown in Figure 2 were obtained with the same gas mixture as used in Figure 1 but at a lower (−14 °C) temperature. Correspondingly, the concentration ratio $C_3H_7^+ClCH_2Cl^+/C_3H_7^+$ is much higher, as expected, since reaction 8 is exothermic, i.e., the equilibrium constant K_{10} increases with decreasing temperature. Changes of the methylene chloride pressures by a factor of 2 or more, in separate runs, had no effect on the equilibrium constant. The equilibrium 8 was observed at several different temperatures in between 29 and 20 °C.

The determination of the equilibria 8 described above is fairly typical of the reactions encountered in all determinations of equilibria 1. The t-Bu^+ ion was produced by the addition of small amounts of isobutane to the methane. The c-Pe^+ was produced via hydride abstraction by i-Pr^+ from cyclopentane. The desired reaction sequence was obtained by adding propane in roughly tenfold excess over cyclopentane in the major methane gas. With this mixture i-Pr^+ is produced by reactions 2 and 3 and then i-Pr^+ abstracts H^- from cyclopentane to give c-Pe^+. The hydride abstraction by i-Pr^+ is considerably less exothermic than the direct reactions of CH_5^+ and $C_2H_5^+$ with cyclopentane. Since these more exothermic reactions, in principle, could produce acyclic $C_5H_9^+$ isomers, the milder two-step route was chosen.

The 2-methyl-2-butyl and the 2-norbornyl cations were also produced by milder, two-step processes. Thus Nb^+ was prepared in a mixture of 5 torr of CH_4, 20 mtorr of propane, and 4 mtorr of norbornane. The i-Pr^+, produced by the first two gases, hydride abstracts from norbornane, and this reaction leads to Nb^+. Hydride abstractions involving alkyl cations and various RH have been described by Solomon, Meot-Ner, and Field.[13]

A more complex but still tractable reaction system occurred in the measurement of the equilibria involving Et^+ and CH_2Cl_2. The ions observed are shown in Figure 3. The Et^+ resulting from methane engages in the desired equilibrium reaction 13. However, Et^+ also engages in reaction 14. This normally very slow reaction

$$C_2H_5^+ + CH_2Cl_2 = (C_2H_5CH_2Cl_2)^+ \qquad (13)$$

$$C_2H_5^+ + CH_4 = C_3H_7^+ + H_2 \qquad (14)$$

$$CH_5^+ + CH_2Cl_2 = CH_2Cl^+ + HCl + CH_4 \qquad (15)$$

$$CH_2Cl^+ + CH_2Cl_2 = CH_3Cl + CHCl_2^+ \qquad (16)$$

observed earlier in this laboratory[15] has a positive temperature dependence and at the elevated temperature of the experiments, 252 °C, becomes sufficiently fast to remove a significant fraction of Et^+ (see Figure 3). An analogue computer simulation of reaction systems, very similar to reactions 13 and 14 performed in the earlier work,[2] shows that reaction 14 would cause the $(C_2H_5CH_2Cl_2)^+/C_2H_5^+$ ratio to increase relative to the equilibrium 13 ratio. However, the increase is very small and can be neglected.

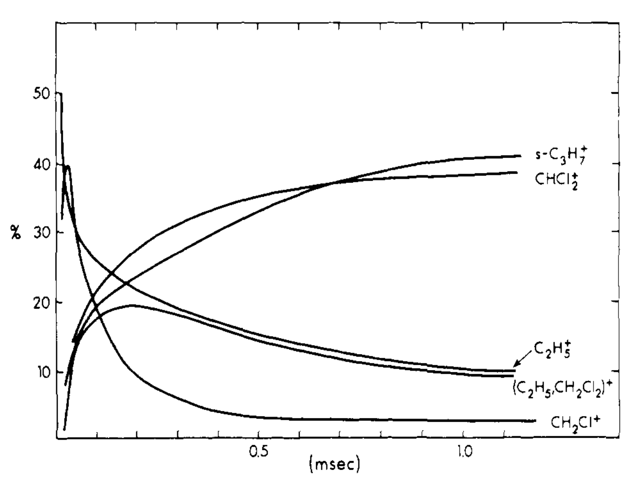

Figure 3. Reactions occurring in the experiments for determination of equilibrium $C_2H_5^+ + CH_2Cl_2 = (C_2H_5CH_2Cl_2)^+$. Ion source pressures: 4 torr of CH_4, 13 mtorr of CH_2Cl_2. Temperature = 252 °C. The $C_2H_5^+$ involved in the equilibrium can also react with CH_4 at this temperature: $C_2H_5^+ + CH_4 = C_3H_7^+ + H_2$. However, this reaction is slower than the equilibrium rates.

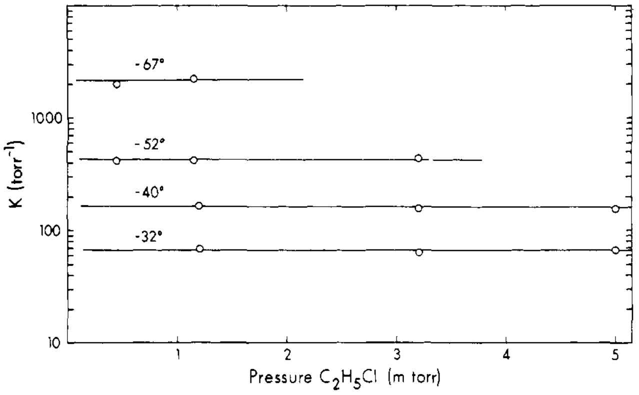

Figure 4. Equilibrium constants for the reaction t-Bu^+ + EtCl = t-BuClEt$^+$. Dependence on pressure of EtCl.

A side reaction that can be observed in Figure 3 is the production of $CHCl_2^+$ by the hydride abstraction 16. From the half-life of (16) in Figure 3 one can estimate a $k_{16} \approx 8 \times 10^{-11}$ molecules^{-1} cm^3 s^{-1}. This reaction was not observed in an ICR study of Lias and Ausloos[16] presumably because it was too slow for detection at the low CH_2Cl_2 pressures used.

The lack of dependence of the equilibrium constants K_1 on the pressure of B is illustrated in Figure 4, for the equilibrium t-Bu^+ + EtCl = BuEtCl$^+$. Similar results were obtained for the other systems.

(b) Binding Energies of Chloronium Ions R′ClR$^+$. The results from the measurements of the equilibrium constants K_1 are summarized in the van't Hoff plots shown in Figures 5–7. The results are divided into three groups. Figure 5 shows a constant B = CH_2Cl_2 and a cnanging R^+, Figure 6 gives a constant R^+ = t-Bu^+ and changing B, and Figure 7 gives results for two different B (CH_3Cl and CH_2Cl_2) and three different ions R^+ (Et^+, i-Pr^+, t-Bu^+).

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Table I. Thermochemical Data for Halonium Ions[a]

reaction	$-\Delta H_1{}^b$ MINDO/3	$-\Delta H_1{}^c$ (exptl)	$\Delta H_1{}^c$ (alt)	$-\Delta S_1$, cal/deg	$-\Delta G_1{}^9$ (298), kcal/mol
1. $CH_3Cl{\cdot}Me^+ = CH_3Cl + Me^+$	64.2				
2. $CH_3ClEt^+ = CH_3Cl + Et^+$	31.4	30.7[e]	30.7	29.4[e]	22.5[e]
3. $CH_3Cl{\cdot}i\text{-}PR = CH_3Cl + i\text{-}Pr^+$	21.3	22.9[e]	22.4	43.1[e]	10.1[e]
4. $CH_3Cl{\cdot}t\text{-}Bu^+ = CH_3Cl + t\text{-}Bu^+$	13.8	8.4	9.3	19.3	2.6
5. $CH_2Cl_2Et^+ = CH_2Cl_2 + Et^+$		36.0	33.2	45.1	22.6
6. $CH_2Cl_2{\cdot}i\text{-}Pr^+ = CH_2Cl_2 + i\text{-}Pr^+$		15.6	14.9	31.0	6.4
7. $CH_2Cl_2{\cdot}c\text{-}Pe^+ = CH_2Cl_2 + c\text{-}Pe^+$		9.8	10.6	20.2	3.8
8. $CH_2Cl_2{\cdot}t\text{-}Bu^+ = CH_2Cl_2 + t\text{-}Bu^+$		9.5	10.0	22.3	2.8
9. $CH_2Cl_2{\cdot}t\text{-}Pe^+ = CH_2Cl_2 + t\text{-}Pe^+$		9.5	9.8	23.3	2.5
10. $CH_2Cl{\cdot}Nb^+ = CH_2Cl_2 + Nb^+$		10.6	9.8	31.1	1.3
11. $CH_3Cl{\cdot}t\text{-}Bu^+ = CH_3Cl + t\text{-}Bu^+$	13.8	8.4	9.9	19.3	2.6
12. $C_2H_5Cl{\cdot}t\text{-}Bu^+ = C_2H_5Cl + t\text{-}Bu^+$	17.4	9.2	10.6	16.3	4.3
13. $CH_2Cl_2{\cdot}t\text{-}Bu^+ = CH_2Cl_2 + t\text{-}Bu^+$	12.6	9.5	10.0	22.3	2.8
14. $CHCl_3{\cdot}t\text{-}Bu^+ = CHCl_3 + t\text{-}Bu$	10.2	9.1	9.5	23.6	2.1
15. $SO_2F_2{\cdot}t\text{-}Bu^+ = SO_2F_2 + t\text{-}Bu^+$		10.4	11.5	10.4	1.6
16. $CHF_3{\cdot}t\text{-}Bu^+ = CHF_3 + t\text{-}Bu^+$	(44.0)[d]	6.8	7.7	19.8	0.9
17. $CF_4{\cdot}t\text{-}Bu^+ = CF_4 + t\text{-}Bu^+$	(40.1)[d]	3.4	5.7	10.4	0.3

[a] All data without superscripts are from present work; all energies are in kcal/mol. [b] From MINDO/3 calculations of ΔH_f(reactants): $\Delta H_f(Me^+) = 260.3$; $\Delta H_f(Et^+) = 205.7$ (bridged structure); $\Delta H_f(sec\text{-}Pr^+) = 189.7$; $\Delta H_f(t\text{-}Bu^+) = 170.8$; $\Delta H_f(MeCl) = -15.4$; $\Delta H_f(EtCl) = -26.0$; $\Delta H_f(CH_2Cl_2) = -22.3$; $\Delta H_f(CHCl_3) = -26.0$. [c] ΔH(exptl) was obtained from the slope of the van't Hoff plots. ΔH(alt) is an alternate value, considered more reliable, calculated from $\Delta G°_{298}$(exptl) and a $\Delta S(\text{alt}) = (26 + \Delta S°(\text{exptl}))/2$, i.e., the $\Delta S°$(alt) is assumed to be an average of the experimental $\Delta S°$ from the van't Hoff plot and a constant $\Delta S° = 26$ eu. This is an averaging procedure based on the observation that the entropy change for this type of association reactions is often close to ~26 eu. [d] MINDO/3 calculations, present work. The MINDO/3 method is obviously unreliable for fluoronium ions. [e] Previous work from this laboratory.[2]

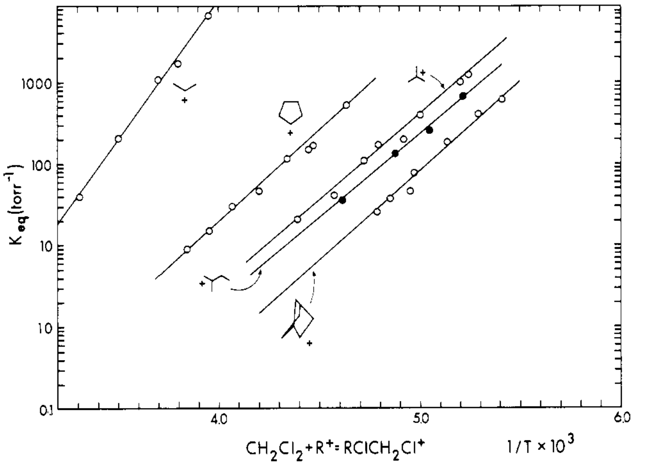

Figure 5. van't Hoff plots of equilibrium constants for the reactions $R^+ + CH_2Cl_2 = (RClCH_2Cl)^+$. Stability of chloronium ions decreases as stabilization of R^+ increases. These results reproduce stability order for R^+: i-Pr, c-Pe^+, t-Bu^+, Nb^+ observed from measurements of chloride affinities of R^+ (Sharma[10]).

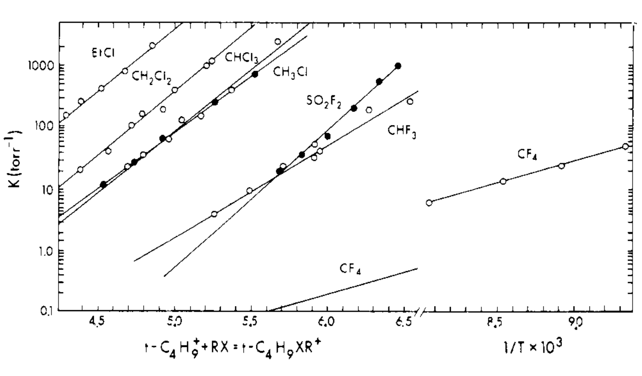

Figure 6. van't Hoff plots of equilibrium constants for the reactions $t\text{-}Bu^+ + B = (t\text{-}BuB)^+$. Stability of adducts decreases in the order B = EtCl, CH_2Cl_2, $CHCl_3 \approx CH_3Cl$, SO_2F_2, CHF_3, CF_4.

It is interesting to note the wide range of temperatures which had to be covered in order to observe the different equilibria 1. Thus a temperature as high as 390 °C was required for the most strongly bonded adduct $C_2H_5{}^+{-}ClCH_3$, while temperatures as low as −160 °C were used in measurements of weakly bonded adducts involving stabilized R^+ like t-Bu^+ and a very weakly nucleophilic B like CF_4 (see Figures 5–7).

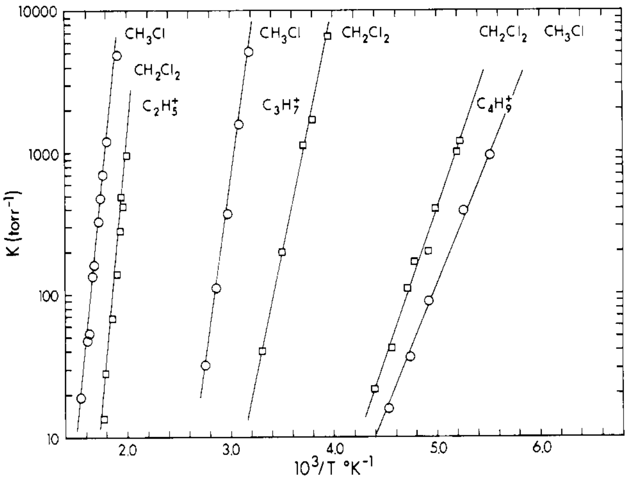

Figure 7. van't Hoff plots of equilibria $R^+ + R'Cl = (RClR')^+$.

The $\Delta H_1°$, $\Delta G_1°(298)$, and $\Delta S_1°$ values obtained from the van't Hoff plots in Figures 5–7 are given in Table I. Results from two equilibria measured earlier[2] are also included.

MINDO/3 predicted $\Delta H_1°$ for a number of reactions were obtained[17] by calculating the MINDO/3 (Dewar[18]) enthalpies of formation of the reactants R^+, R′X, and $(RXR')^+$. The results for these calculations are also given in Table I. McManus[19] has also calculated MINDO/3 energies involving various chloronium ions. Since the geometry optimization procedure is part of the MINDO/3 program,[18] essentially identical results to those of McManus[19] were obtained whenever calculations on the same systems were performed.

Comparing the MINDO results with experiment for the reaction series 1–4, Table I, involving $R^+ = Et^+$, i-Pr^+, t-Bu^+, and CH_3Cl, one finds good agreement particularly for Et^+ and i-Pr^+. This suggests that the MINDO result for $D(Me^+{-}ClMe) = 64.2$ kcal/mol is also reliable to a few kcal/mol. This energy change is too high to be determined experimentally via van't Hoff plots

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(17) Complete geometry optimization was performed. The resulting structures are available on request from one of the authors (P.K.).

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(19) McManus, S. P. *J. Org. Chem.* **1982**, *47*, 3070.

Table II. Methyl Cation Affinities of ClR = $D(\text{Me}^+\text{–ClR})^a$ and $D(\text{R}^+\text{–ClR})$

R	$\Delta H_f(\text{R}^+)^b$	$\Delta H_f(\text{RCl})^c$	$\Delta H_f(\text{MeClR}^+)^d$	$D(\text{Me}^+\text{–ClR})$ expt1^d	$D(\text{Me}^+\text{–ClR})$ (MINDO/3)^e	$D(\text{R}^+\text{–ClR})$ (MINDO/3)^f
Me	261.0	−20.6			64	64
Et	215.6	−26.1	164.4	71	72	38
i-Pr	191.0	−33.6	150.1	77	79	30
t-Bu	166.5	−43.7	136.6	81	85	23

[a] All values in kcal/mol. [b] Rosenstock.[22] [c] Cox and Pilcher.[21] [d] Calculated from ΔH_1, reactions 2–4, Table I, and literature data.[21,22] [e] McManus.[19] [f] Present work.

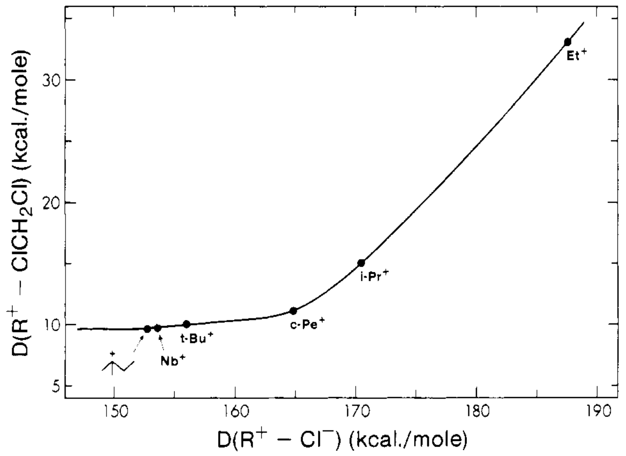

Figure 8. Plot of heterolytic bond dissociation energies $D(\text{R}^+\text{–ClCH}_2\text{Cl})$ vs. $D(\text{R}^+\text{–Cl}^-)$. Data show that $D(\text{R}^+\text{–ClCH}_2\text{Cl})$ decreases as $D(\text{R}^+\text{–Cl}^-)$ decreases, i.e., as stability of R^+ increases. However, for relatively stable ions R^+, $D(\text{R}^+\text{–ClCH}_2\text{Cl})$ is almost constant (R^+ = *i*–Pe$^+$, Nb$^+$, *t*-Bu$^+$, and even c-Pe$^+$). This shows that there is little differential nucleophilic solvation of these R^+ by the weakly nucleophilic solvent molecule CH_2Cl_2.

of the association equilibria 1. An experimental result based on Me cation transfer equilibria[6] which is in agreement with the MINDO/3 value will be reported in the near future. The results for the series $\text{R}^+\text{–ClCH}_3$ show that the bond energy decreases rapidly with increasing stability of R^+, i.e., in the order Me$^+$, Et$^+$, *i*-Pr$^+$, *t*-Bu$^+$. The overall change being from ~64 kcal/mol for Me$^+$ to ~9 kcal/mol for *t*-Bu$^+$. The same type change is also observed in the series $\text{R}^+\text{–ClCH}_2\text{Cl}$ given by reactions 5–10 (Table I). The results for this series are based on the van't Hoff plots of Figure 5 which very graphically display the decrease of stability of $\text{R}^+\text{–ClCH}_2\text{Cl}$ with increasing stability of R^+. It is interesting to note that these results give the stability order Et$^+$, *i*-Pr$^+$, c-Pe$^+$, *t*-Bu$^+$, Nb$^+$, i.e., place the nominally secondary norbornyl cation at a higher stability than the tertiary species, *t*-Bu$^+$. This result is in line with measurements of the gas-phase hydride[10,13] and chloride[10] affinities of the above R^+ ions which have shown that Nb$^+$ has a lower hydride and chloride affinity than *t*-Bu$^+$, i.e., is more stable than *t*-Bu$^+$.

A plot of $D(\text{R}^+\text{–ClCH}_2\text{Cl})$ vs. $D(\text{R}^+\text{–Cl}^-)$, i.e., the chloride affinity of R^+, is shown in Figure 8. The chloride affinities are from ref 10 except that for *t*-Pe$^+$.[20] The decrease of $D(\text{R}^+\text{–ClCH}_2\text{Cl})$ with decrease of $D(\text{R}^+\text{–Cl}^-)$ slows down as the stability of R^+ increases. Thus *t*-Pe$^+$, Nb$^+$, *t*-Bu$^+$, and even c-Pe$^+$ have almost the same $D(\text{R}^+\text{–ClCH}_2\text{Cl})$ values. The differences for the corresponding free energy changes ($-\Delta G_1°$, see Table I) are somewhat larger but still relatively small, i.e., within about 2 kcal/mol. The formation of the chloronium ions $\text{R}^+\text{ClCH}_2\text{Cl}$ can be considered as representing the specific nucleophilic solvation of R^+ by the solvent CH_2Cl_2. Thus, the small changes for the more stable R^+ ions observed above mean that the specific solvation of R^+ by weakly nucleophilic solvents like CH_2Cl_2 is almost equally strong as long as R^+ is a fairly stable cation. Notice that the above generalization would not at all hold for R^+ = Et$^+$ or Me$^+$ (see Figure 8). The above findings are in agreement with deductions made by Arnett[8,9] and others[23] that there is little differential (nucleophilic) solvation of carbocations R^+ in weakly nucleophilic solvents like CH_2Cl_2 and SO_2ClF. A recent comparison[10] of the stabilities of carbocations in the gas phase with Arnett's[8,9] solution data indicates that there can be significant differential nonspecific solvation. Bulky cations like 1-adamantyl$^+$ were found to be significantly less stable when compared to *t*-Bu$^+$ in CH_2Cl_2 and SO_2ClF solution than in the gas phase. This observation was attributed to poor general solvation of ions which, due to their bulky structures, displace significant amounts of the solvent dielectric from the vicinity of the ionic charge center.[10]

Examined above were bonding changes in the series $\text{R}^+\text{–ClR}_0$ where the nature of R^+ was changed while R_0 was kept constant. Bonding changes for the situation $\text{R}_0{}^+\text{–ClR}$ where the leaving cation is kept constant while the nature of RCl is changed are given in Table II for Me$^+$–ClR where R = Me, Et, *i*-Pr, *t*-Bu. These values were obtained from the experimental ΔH_1 for reactions 2–4 (Table I) and literature data.[21,22] Also given in Table II are the MINDO/3 results for the same bonds obtained by McManus.[19] The two sets of results are seen to be very close. Examining the data one finds that $D(\text{Me}^+\text{–ClR})$ increases as R changes in the order R = Me, Et, *i*-Pr, *t*-Bu. Electron donation by R to Cl increases in the above order and should be the factor responsible for the observed Me$^+$–ClR stability increases.

Another series $\text{R}_0{}^+\text{–ClR}$ is present in Table I reactions 11–17, where $\text{R}_0{}^+$ = *t*-Bu$^+$ and RCl = MeCl, EtCl, CH_2Cl_2, CHCl_3. Included for the same $\text{R}_0{}^+$ are three solvent molecules, which contain no chlorine: SO_2F_2, CF_3H, and CF_4. The observed increase of $D(t\text{-Bu}^+\text{–ClR})$ for R = Me to Et is in the same direction as that observed for the series Me$^+$–ClR (Table II).

The changes for *t*-Bu$^+$ and the three chloromethanes, CH_3Cl, CH_2Cl_2, and CHCl_3 (Table I), are small and somewhat erratic, so a significant regular trend cannot be deduced for this series. The corresponding MINDO/3 results predict a small decrease of the *t*-Bu$^+$–ClR bond energy with increased chlorine substitution. This trend, if true, would be in line with the expectation that substituents on R with an electron-withdrawing field-inductive effect, like Cl, will decrease the $\text{R}_0{}^+\text{–ClR}$ bond energy. In fact, this expected trend is observed in the experimental results for the pair $\text{Et}^+\text{–ClCH}_3$, $\text{Et}^+\text{–ClCH}_2\text{Cl}$ and the pair *i*-Pr$^+$–ClCH_3, *i*-Pr–ClCH_2Cl (see Figure 7). While the exact ΔH values are probably not sufficiently accurate to reveal the trend, the position of the van't Hoff lines shows a weaker bond (free) energy for dichloromethane. Thus, the reversal observed for *t*-Bu$^+$ (Figure 7) is unexpected and its cause unclear.

The fluoromethanes CF_3H and CF_4 are seen to bond much more weakly to *t*-Bu$^+$ than the chloromethanes (Table I). This result is expected since the formation of a halonium ion on combination with R^+ causes the participating halide atom to acquire some positive charge. The greater electronegativity of fluorine relative to chlorine results in weaker bonding $\text{R}^+\text{–XR}'$ for the fluoronium ion. This electronegativity effect overpowers the greater ability of fluorine to form covalent bonds. Me$^+$ affinity studies[6] reveal the same trend. Thus $D(\text{Me}^+\text{–ClMe})$ was determined to be some 10 kcal/mol higher than $D(\text{Me}^+\text{–FMe})$. The *t*-Bu$^+$–$\text{CF}_4$ bond energy is found to be lower than that of *t*-Bu$^+$–CF_3H (Table I, Figure 6) which is expected since the

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(20) On the basis of the hydride affinity of Field,[13] $\Delta H_f(t\text{-Bu}^+)$ = 166.5 kcal/mol[22] and $\Delta H_f(t\text{-PeCl})$ = −48.4 kcal/mol.

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electron-withdrawing field-inductive effect of one more fluorine substituent in the CF_4 adduct should destablize the ion.

SO_2 and SO_2ClF are important solvents of low nucleophilicity. The present results for SO_2F_2, reaction 15, Table I and Figure 6, show that the SO_2F_2 bonding to $t\text{-Bu}^+$ is significantly weaker than that of CH_2Cl_2. Measurements of the Me^+ bonding to SO_2, SO_2ClF, and SO_2F_2 from this laboratory (methyl cation affinities)[6] show the bonding decreasing in the order SO_2, SO_2ClF, SO_2F_2. The same order may be expected also for bonding to more stable ions like $t\text{-Bu}^+$. On this basis one may expect that the bonding of $t\text{-Bu}^+$ to SO_2ClF will be similar to that for CH_2Cl_2. Assuming that this is the case one would expect that a plot of $R^+\text{–}SO_2ClF$ bonding energies would be similar to the $R^+CH_2Cl_2$ plot on Figure 7, and this would mean that little differential specific nucleophilic solvation by SO_2ClF can be expected for ions R^+ which are fairly well stabilized, i.e., ions that fall in the flat region of the plot in Figure 7. This is a result that is anticipated from Arnett's[8,9] measurements of R^+ ion stabilities in SO_2ClF solution.

The bond dissociation energies $D(R^+\text{–}ClR)$ predicted by MINDO/3 are given in Table II. The fact that MINDO/3 was successful is predicting the $D(R^+\text{–}ClMe)$ energies (see Table I) lends credence also to the present data, for which experimental determinations were not made. The calculation shows that $D(R^+\text{–}ClR)$ decreases as the stability of R^+ increases, i.e., in the order R = Me, Et, *i*-Pr, *t*-Bu. These results can be compared with the trends already discussed above, i.e., the rapid decrease of $D(R^+\text{–}ClMe)$ in the above order (Table I) and the increase of $D(Me^+\text{–}ClR)$ in the above order (Table II). In the symmetric adducts R_2Cl^+, these two effects occur in opposition; however, the weakening of $D(R^+\text{–}ClMe)$ with an increase of R^+ stability is the stronger effect which leads to the net weakening of $D(R^+\text{–}ClR)$ predicted by the calculation.

Acknowledgment. This work was supported by a grant from the Canadian Natural Sciences and Engineering Research Council.

Registry No. CH_3Cl, 74-87-3; Me^+, 14531-53-4; Et^+, 14936-94-8; $i\text{-Pr}^+$, 19252-53-0; $t\text{-Bu}^+$, 14804-25-2; Nb^+, 24321-81-1; CH_2Cl_2, 75-09-2; $CHCl_3$, 67-66-3; SO_2F_2, 2699-79-8; CHF_3, 75-46-7; CF_4, 75-73-0; C_2H_5Cl, 75-00-3; $c\text{-Pe}^+$, 25076-72-6; $t\text{-Pe}^+$, 17603-15-5; $CH_3Cl\cdot t\text{-Bu}^+$, 81971-25-7; $CH_2Cl_2\cdot Et^+$, 37160-91-1; $CH_2Cl_2\cdot i\text{-Pr}^+$, 96164-25-9; $CH_2Cl_2\cdot c\text{-Pe}^+$, 96164-26-0; $CH_2Cl_2\cdot t\text{-Bu}^+$, 96193-86-1; $CH_2Cl_2\cdot t\text{-Pe}^+$, 96164-27-1; $CH_2Cl_2\cdot Nb^+$, 96164-28-2; $CH_3Cl\cdot Me^+$, 24400-15-5; $C_2H_5Cl\cdot t\text{-Bu}$, 96164-29-3; $CHCl_3\cdot t\text{-Bu}^+$, 96164-30-6; $SO_2F_2\cdot t\text{-Bu}^+$, 96164-31-7; $CHF_3\cdot t\text{-Bu}^+$, 96164-32-8; $CF_4\cdot t\text{-Bu}^+$, 96164-33-9; $CH_3Cl\cdot Et^+$, 24400-21-3; $CH_3Cl\cdot t\text{-Pr}^+$, 24400-25-7.

Formation of Ionic Transition-Metal Carbonyl Cluster Fragments by Ion–Molecule Reactions. 1. The $Cr(CO)_6$ and $Fe(CO)_5$ Systems

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Abstract: Fragment ions formed by dissociative ionization of $Cr(CO)_6$ and $Fe(CO)_5$ react readily with their respective neutrals to give ionic cluster fragments of the type $M_x(CO)_y^+$. The M^+ and $M(CO)_x^+$ reactant ions give rise to different ionic cluster fragments which undergo further reaction with neutral $M(CO)_y$. In this paper, we propose the reactivity of the ionic cluster fragments is related to the degree of coordination unsaturation. Plots of the relative reaction rate vs. electron deficiency can give some indication of the structure of the cluster fragments. This interpretation of the results suggests that some cluster fragments have multiple metal–metal bonds and/or carbonyl ligands acting as 4-electron donors. The present work emphasizes the ion–molecule reaction sequence and the degree of coordination saturation/unsaturation of the ionic cluster fragments.

The study of the chemical and physical properties of transition-metal clusters is a rapidly expanding research field.[1] The rapid growth in this area can be attributed to the development of new experimental techniques which permit detailed studies at the molecular level. For example, studies on the reactivities of single crystals provide more detailed information than methods which probe the average reactivities of bulk material.[2] The recent studies by several research groups on small bare metal clusters represent steps to refine even further these studies, i.e., the modeling of reactive sites at the molecular level.[3] It is hoped that such studies will provide important insight into the properties of transition-metal clusters which has been unobtainable from bulk studies. Over the past several years we have been studying the ion–molecule reaction chemistry of ionic transition-metal cluster fragments. The objectives of these studies include investigating the reactivities of metal ions with other metal-containing species, characterizing these clusters with both spectroscopic methods and chemical reactivities, and utilizing these clusters as models for catalytic reactions, e.g., C–H and C–C bond-insertion reactions. In this report, the general ion-molecule reaction sequence for cluster formation for the $Cr(CO)_6$ and $Fe(CO)_5$ systems is presented.

Several reviews have appeared in the literature on the synthesis and characterization of small metal clusters, and throughout the development of ion cyclotron resonance (ICR) spectrometry, the chemistry of transition-metal ions has been an active research area.[4-14] In an early study with ICR, Beauchamp and Foster

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