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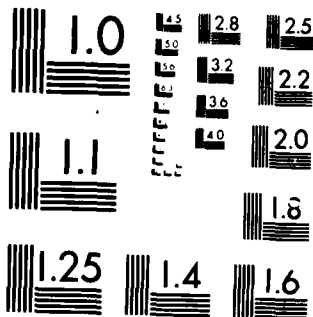
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STUDIES OF NEGATIVE ION REACTIONS : SOLVATED IONS AND STRONG ACIDS

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Abstract : The reactions of several negative ion species with up to three solvate molecules have been studied in a variable temperature selected ion flow tube. The reactions include association of some species of interest in the stratosphere and some proton transfer reactions of the strong and "super" acids.

1. Introduction

We have used a simple tightly enclosed electron impact ion source to generate both simple and solvated negative ions which can then be injected into a selected ion flow tube (SIFT). In the case of the solvated species, the core ions include OH^- , NO_3^- , and HSO_4^- , and the solvates are H_2O , HNO_3 , and H_2SO_4 . Although collisional dissociation of the injected solvated ions occurs to some extent in all but the most strongly bound clusters, useful number densities of several interesting solvated species can be obtained. We discuss here some reactions of both simple and solvated negative ions, including association of $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_m(\text{HNO}_3)_n$ with HCl and of NO_3^- with HNO_3 , together with several reactions of strong Bronsted acids and their anions.

2. Experimental

The AFGL SIFT [3,4,5] is similar to that described by Adams and Smith [6]. The ion source is a stainless steel box measuring 2.5 by 1.5 by 1.5 cm. Electrons generated by an external filament of thoriated iridium or rhenium are accelerated by a potential of about 150V and enter the box through a hole 0.1 cm in diameter located at the center of a 2.5 by 1.5 cm face. A repeller electrode is located at the back of the source box. Primary negative ions are produced by dissociative attachment of both primary and secondary electrons. Subsequent ion-neutral collisions in the source generate higher order, e.g solvated, ions, which then exit the box through a hole 0.1 cm in diameter in the face opposite the repeller. Pressure in the

source may be as high as a few tenths of a torr. Sulfuric acid was admitted to the source by passing a carrier gas through glass wool saturated with the acid. The 'super' acids were simply heated to about 55°C where their vapor pressure is high enough to allow controlled flow. Nitric acid vapor was generated from a liquid mixture of 1 part HNO₃ and 2 parts H₂SO₄ by volume.

3. Results and Discussion

Clustering in Stratospheric Ions

In situ ion composition measurements [7,8] have shown that the dominant negative ions in the stratosphere are NO₃⁻(HNO₃)_n and HSO₄⁻(H₂SO₄)_m(HNO₃)_n. The species HCl is observed as a ligand in stratospheric ions and is a convenient one for laboratory study because of its high vapor pressure. We have measured rate coefficients [9] for the association of HCl with HSO₄⁻(H₂SO₄)_m(HNO₃)_n for m=0 to 3 and n=0,1. At the lowest temperature (153K) and in either H₂ or He buffer, the rate coefficients for reactions of the unsolvated and singly solvated ions ranged from about 0.6(-26) to 2(-26) cm⁶s⁻¹, while those for the doubly and triply solvated ions were below 0.04(-26) cm⁶s⁻¹. The temperature coefficients of the clustering reactions, defined as n in the expression $k_T = k_{300}(300/T)^n$, were found to increase with increasing degree of solvation. A total of three ligands was found to bond strongly to HSO₄⁻.

In all instances of the clustering of HSO₄⁻ core ions to HCl, the effective two-body rate coefficients varied linearly with pressure, indicating that the measurements were made in the low-pressure limit of three-body reactions. In contrast with these results, the effective two-body rate coefficient for the clustering of NO₃⁻ with HNO₃ was found to be independent of pressure above 0.3 torr, and this reaction is therefore in the high pressure limit under these conditions. The fact that the rate coefficient, which is 2.5(-10) cm³s⁻¹ at 300K, is considerably lower than the collision limit has significant consequences for deriving stratospheric nitric acid concentrations from ion composition data. Using the present result, the nitric acid concentration at 40.8 km is about 65% higher than was estimated [10] assuming the collision limited rate coefficient.

Ion Reactions of Some Strong Acids

In accord with precepts now over 60 years old, chemists are accustomed to think of acids in solution as being either good proton donors, as suggested by Bronsted and Lowry, or as good electron acceptors, as suggested by Lewis [11]. The application of the Lewis model to gas phase ion chemistry has been little explored, but the Bronsted/ Lowry model has been tested extensively. The gas phase acidity of a proton donor HX is defined as the enthalpy of the reaction in which the acid dissociates to form a proton and X^- , i.e.,

$$\Delta H_{\text{acid}}^0 = D(H-X) + IP(H) - EA(X) \quad (1)$$

In eq.(1), $D(H-X)$ is the dissociation energy of HX, $IP(H)$ is the ionization potential of H, and $EA(X)$ is the electron affinity of X. Using this definition, stronger acids have lower values of ΔH_{acid}^0 . Gas phase acidities of a large number of molecules have recently been tabulated [12]. The strongest acid listed in this compilation is HI, for which $\Delta H_{\text{acid}}^0 = 314.6$ kcal/mol. The proton transfer reaction



is exothermic if

$$EA(X) + D(H-Y) \geq EA(Y) + D(H-X). \quad (2)$$

We have measured rate coefficients for several reactions involving strong acids in order to establish their relative acidities and to determine lower limits for the electron affinities, $EA(X)$. Of particular interest are the species metaphosphoric acid (HPO_3), sulfuric acid (H_2SO_4), and the so-called "super" acids, trifluoromethylsulfonic acid (usually called triflic acid, CF_3SO_3H), and fluorosulfonic acid (FSO_3H).

The results of these measurements are given in Table 1. These results may be summarized as follows. Triflic acid transfers a proton rapidly to each of the anions listed as reactants in reactions 1 to 5 and in addition undergoes an association reaction with FSO_3^- . In its reaction with $NO_3^- \cdot HNO_3$, both solvated and unsolvated product ions are observed.

Triflic acid is therefore a stronger acid than HI, HPO_3 , FSO_3H , and H_2SO_4 . In reactions 6,7, and 9, fluorosulfonic acid transfers a proton to I^- , PO_3^- , and HSO_4^- , and is therefore a stronger acid than HI, HPO_3 , and H_2SO_4 . Reactions 11 and 12 show that H_2SO_4 is a stronger acid than HI and HPO_3 . The failure of HI to transfer a proton to PO_3^- in reaction 16 suggests that HPO_3 is a stronger acid than HI. The order of relative acidities is then $\text{CF}_3\text{SO}_3\text{H} > \text{FSO}_3\text{H} > \text{H}_2\text{SO}_4 > \text{HPO}_3 > \text{HI}$. The results in Table 1, together with literature values for the other required parameters, can be used in eq.(1) to conclude that the gas phase acidities of $\text{CF}_3\text{SO}_3\text{H}$ and FSO_3H are similar and are both ≤ 297 kcal/mol.

The proton transfer reactions in Table 1 are a manifestation in the gas phase of acid-base chemistry familiar in liquid solutions. Proton transfer to an electron, which is completely equivalent to dissociative attachment, may also be considered as an acid-base reaction in which the electron is acting as a Bronsted base. It is of interest that dissociative attachment in the strong Bronsted acids has recently been discovered to be a rapid reaction [13].

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Table I. Rate Coefficients for Reactions of some Strong Acids.

Reaction			Rate Coefficient ($10^{-9}\text{cm}^3\text{s}^{-1}$)	
1. I^-	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + \text{HI}$			2.4
2. PO_3^-	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + \text{HPO}_3$			3.2
3. FSO_3^-	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + \text{FSO}_3\text{H}$	75% 70%		2.5
	$\rightarrow \text{CF}_3\text{SO}_3^-(\text{FSO}_3\text{H})$	25% 30%		
		0.4 0.8 torr		
4. HSO_4^-	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + \text{H}_2\text{SO}_4$			2.8
5. $\text{NO}_3^-(\text{HNO}_3)$	$+ \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^- + 2\text{HNO}_3$	50%		2.6
	$\rightarrow \text{CF}_3\text{SO}_3^-(\text{HNO}_3) + \text{HNO}_3$	50%		
6. I^-	$+ \text{FSO}_3\text{H} \rightarrow \text{FSO}_3^- + \text{HI}$			2.0
7. PO_3^-	$+ \text{FSO}_3\text{H} \rightarrow \text{FSO}_3^- + \text{HPO}_3$			1.5
8. CF_3SO_3^-	$+ \text{FSO}_3\text{H} \rightarrow \text{CF}_3\text{SO}_3^-(\text{FSO}_3\text{H})$			1.2
9. HSO_4^-	$+ \text{FSO}_3\text{H} \rightarrow \text{FSO}_3^- + \text{H}_2\text{SO}_4$			1.3
10. $\text{NO}_3^-(\text{HNO}_3)$	$+ \text{FSO}_3\text{H} \rightarrow \text{FSO}_3^- + 2\text{HNO}_3$	15%		1.3
	$\rightarrow \text{FSO}_3^-(\text{HNO}_3) + \text{HNO}_3$	85%		
11. I^-	$+ \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{HI}$			1.9
12. PO_3^-	$+ \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + \text{HPO}_3$			2.4
13. FSO_3^-	$+ \text{H}_2\text{SO}_4 \rightarrow \text{FSO}_3^-(\text{H}_2\text{SO}_4)$			2.4
14. CF_3SO_3^-	$+ \text{H}_2\text{SO}_4 \rightarrow \text{CF}_3\text{SO}_3^-(\text{H}_2\text{SO}_4)$			1.5
15. $\text{NO}_3^-(\text{HNO}_3)$	$+ \text{H}_2\text{SO}_4 \rightarrow \text{HSO}_4^- + 2\text{HNO}_3$	<15%		2.4
	$\rightarrow \text{HSO}_4^-(\text{HNO}_3) + \text{HNO}_3$	>85%		
16. PO_3^-	$+ \text{HI} \rightarrow \text{PO}_3^-(\text{HI})$			0.0068

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