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This chapter provides a review of recent research on the reactions of negative ions with neutral molecules at thermal energies. Included are sections on the temperature dependence of associative detachment, vibrational excitation in associative detachment, negative ion reactions with H_2SO_4 and N_2O_5, reactions with acetonitrile, reactions of chlorine-containing species, reactions of O_2^- and its hydrates, electron affinity determinations, isotope effects involving proton transfer, and reactions of H_3O^-.

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22b. TELEPHONE NUMBER *(Include Area Code)*
(617)861-3124

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Swarms of Ions and Electrons in Gases

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Reactions of Negative Ions

Albert A. Viggiano* and John F. Paulson
Air Force Geophysics Laboratory
Hanscom AFB, Massachusetts 01731

*Air Force Geophysics Scholar

A. Introduction

Traditionally, negative ion-molecule reactions have been much less studied than those of positive ions. This is due to the fact that the most popular type of ion source, electron impact, produces a much greater variety of positive ions than negative ions and usually in greater abundances. Thus, in order to make workable signals of many types of negative ions, ion sources in which ion-molecule reactions take place have to be used.

The flowing afterglow has been ideally suited to the study of negative ion reactions since in it there exists a region where primary ions can be converted easily into secondary ions /1/. More recently, relatively gas tight electron impact sources, in which the pressure can be a few torr, have been used in selected ion flow tubes (SIFTs) to generate a variety of negative ions. In addition, ion beam experiments, /2/, /3/ and ion cyclotron resonance mass spectrometers, /4/, /5/ have been used to study a number of negative ion-molecule reactions. The latter instrument has been used to a great degree to establish a scale of gas phase acidities /6/. In this review we will cover the research on negative ion reactions performed using swarm experiments in the last five years. The emphasis will be on giving a broad overview of the most recent work in order to show the variety of measurements that can be made with these systems. The work presented covers a wide spectrum of results, including studies of vibrational product distributions and temperature dependences of associative detachment reactions, many studies involving atmospheric species, as well as those relating to electron affinity determinations and isotope exchange. The work involving H_3O^- shows that by choosing conditions carefully one can study species that are difficult to produce. Two main areas are left out of this review: the effects of solvation and the reactions of organic anions. The former topic has recently been reviewed by Bohme /7/ and the latter by DePuy and Bierbaum /8/.

B. Associative Detachment

Associative detachment is an important process in controlling the electron density in a variety of natural plasmas, such as the earth's ionosphere and interstellar space, and has been a much studied process for many years. In spite of this, much new information has become available recently. This new information involves the first studies of the temperature dependence of the rate coefficients of these reactions /9/ and of the infrared emissions from the neutral products of the reactions /10/-/14/. These studies have yielded new insights into the reaction mechanisms as well as details of the kinematics involved. In addition, much recent work has been done on the theoretical aspect of these reactions /15/.

The reactions whose temperature dependences were studied fell into two classes, those which were slow and those for which associative detachment was only one of several channels. These reactions could then be expected to have a significant dependence on temperature in either the rate coefficient or branching ratio. Table 1 lists the results of this study. The temperature dependences are the results of least squares calculations to power law dependences.

For the reactions involving only associative detachment, the temperature dependence was found to be $T^{(-0.75\pm0.1)}$ in all three cases. The authors /9/ concluded that this represented mainly the temperature dependence of the lifetime of the collision complex with respect to dissociation back into reactants. This result should be compared with the theories of Bates /16/ and Herbst /17/, which predict a complex lifetime varying as $T^{-0.5}$ for atomic-diatomic systems.

Among these associative detachment reactions, a particularly interesting one is that of S^- with O_2. This is an example of an insertion reaction, in which one of the reactants must insert itself between two atoms already bonded together. The standard model for an insertion reaction was thought to be a two step process /18/ which is written for this reaction as,

$$S^- + O_2 \rightarrow SO^- + O \qquad [1]$$

$$SO^- + O \rightarrow SO_2 + e \qquad [2]$$

where the products of the first step never separate. The criterion for this to be allowed is that the first step is exothermic. In this example, step 1 is endothermic by 8.7 kcal $mole^{-1}$ and therefore might not be expected to occur. An alternate explanation of this process as an addition reaction to form an isomer of SO_2 also fails, as this is endothermic.

Table 1. Rate Coefficients for Associative Detachment Reactions /9/

Reaction	$k(T)(cm^3\ s^{-1})$
$O^- + NO \rightarrow NO_2 + e$	$3.1(-10)^*(300/T)^{0.83}$
$S^- + CO \rightarrow COS + e$	$2.3(-10)(300/T)^{0.64}$
$S^- + O_2 \rightarrow SO_2 + e$	$4.6(-11)(300/T)^{0.72}$
$O^- + C_2H_2 \rightarrow C_2H_2O + e$	$1.1(-9)(300/T)^{0.39}$
$O^- + C_2H_2 \rightarrow$ products	$1.94(-9)$
$O^- + C_2H_4 \rightarrow C_2H_4O + e$	$5.7(-10)(300/T)^{0.53}$
$O^- + C_2H_4 \rightarrow$ products	$9.0(-10)(300/T)^{0.43}$

*3.1 (-10) means 3.1×10^{-10}

The authors /9/ then proposed that the reaction could be explained in terms of the insertion model if the kinetic energy gained during the collision was taken into account. In order to overcome the endothermicity, the reactants must come within 1.94Å of each other. This leads to a reaction efficiency of 8.4%, which compares well with the measured value of 6.2%, lending credence to this explanation. The temperature dependence of this reaction can then still be explained by a change in the complex lifetime.

The reactions of O^- with C_2H_2 and C_2H_4 are fast and have the associative detachment channel as a main channel. The overall rate of the reaction with C_2H_2 was found to be independent of temperature, although the branching ratio was found to have a significant temperature dependence. The reaction of O^- with C_2H_4 was found to have a slight temperature dependence, but the branching ratio was found not to change significantly with temperature. The rate coefficient for the associative detachment channel for each of these reactions was found to vary as $T^{(-0.45\pm0.06)}$.

Over the past several years the flowing afterglow has been used to study the chemiluminescence associated with a number of reactions, many of which were associative detachment reactions. Included in the associative detachment reactions are the reactions of O^- with CO /10/ and of the halide negative ions with hydrogen and deuterium atoms /11/-/14/. The most complete study to date is that of Smith and Leone on the reactions of F^- with H and D /14/, and the present discussion will emphasize these results. The reaction of F^- with H is sufficiently exothermic to produce HF with up to 5 quanta of vibrational energy, and the reaction of F^- with D can produce DF with up to 7 vibrational quanta. The nascent vibrational energy product distributions found for these reactions are shown in Table 2. For the H reaction, it was found that the population in each vibrational level increased up to v = 4 and then decreased for v = 5. The F^- reaction with D also showed a large amount of product vibrational excitation, although more uniformly distributed as a function of v than the H analog. Smith and Leone /14/ were also able to get some information on the rotational energy distribution of the DF product by studying this reaction in an argon buffer, where the rotational energy quenching rate was slower than in helium. They found a large amount of rotational excitation, equal to about 13% of the available energy.

Associative detachment reactions are an extreme example of a reaction in which there is a large difference in the reduced mass of the products and reactants. Smith and Leone /14/ have pointed out that many aspects of the product distributions can be explained by classical kinematics. Due to the low mass of the outgoing electron, essentially all of the incoming orbital angular momentum must end up in the product neutral. This leads to the unique case in which the entrance channel impact parameter maps directly into the rotational quantum number of the diatomic product. The maximum allowed J then depends on the vibrational level in question and the overall energetics of the reaction. As stated above, Smith and Leone /14/ have qualitatively observed this high level of rotational excitation for the F^- reaction with D in an argon buffer. The observed falloff in population at the highest vibrational level in both the H and D reactions is then explained by the fact that the highest rotational levels are not energetically accessible for states with a large amount of vibrational excitation, and consequently collisions with large impact parameters (large orbital angular momentum) cannot form the product neutral in a high vibrational level and still conserve angular momentum.

Table 2. Relative Product Vibrational Populations from the F^- + H, D Reactions /14/

$F^- + H \rightarrow HF(v) + e$		$F^- + D \rightarrow FD(v) + e$	
v	nascent distribution	v	nascent distribution
1	0.00 ± 0.06	1	0.08 - 0.07
2	0.09 ± 0.01	2	0.09 ± 0.01
3	0.21 ± 0.01	3	0.15 ± 0.02
4	0.41 ± 0.02	4	0.11 ± 0.02
5	0.30 ∓ 0.02	5	0.15 ± 0.01
		6	0.24 ± 0.03
		7	0.18 ± 0.02

In contrast to the fact that the high level of rotational excitation can be explained classically, the high degree of vibrational excitation must be explained quantum dynamically. Smith and Leone /14/ argue that the F^- + H(D) reaction can best be explained by the virtual state model rather than the resonant state model because there exists an open s-wave electron detachment exit channel. In the former model, transitions are facilitated due to a breakdown in the Born-Oppenheimer approximation. The increased nuclear velocity associated with higher vibrational levels then aids the Born-Oppenheimer breakdown, and qualitatively one can expect an increase in the transition rate for this state. Model calculations by Gauyacq /15/ support these arguments. At present, however, there is no explanation for the differences in the product vibrational distributions for H and D.

C. Atmospheric Negative Ion Chemistry

In the past several years a large effort has gone into understanding the ion chemistry of the atmosphere, especially the stratosphere. This interest has been fueled by the advent of balloon-borne mass spectrometers that have yielded the first detailed height profiles of both positive and negative ions in the stratosphere /19/, /20/. In order to explain the results, many of which were unexpected, laboratory measurements had to be performed. This section will deal with the most recent laboratory measurements that pertain to negative ions of atmospheric interest.

The first in-situ measurements of stratospheric negative ions revealed the presence of a series of ions that could be best fit as $R^- (HR)_m(HNO_3)_n$ where HR had a mass of 98 ± 2 amu /21/. Arnold and Henschen /21/ speculated that HR was sulfuric acid. In order to test this hypothesis, Viggiano et al./22/ studied a number of positive and negative ion reactions with H_2SO_4. In order to get sulfuric acid into the gas phase in a controlled manner, they used a furnace in which dry nitrogen was passed through glass wool covered with several drops of concentrated H_2SO_4. The flow conditions were set such that the flow was viscous, and the H_2SO_4 flow was then proportional to the square root of the N_2 flow. In this manner, they were able to measure the relative rates of the reactions but were unable to set absolute values, since the absolute concentration of sulfuric acid in the flow tube was not known. However, they noted that the ratio of the rate coefficients for the fastest reactions was the same as would be expected for the collision rates based on the masses of the respective reactant ions. By then setting the fastest rate equal to the collision rate, the rate coefficients were put on an absolute basis. Since the time of publication of the results, the dipole moment of H_2SO_4 has been measured, and the rate coefficients have been revised accordingly /23/. The revised results are listed in Table 3.

Table 3. Reaction Rate Coefficients for H_2SO_4 Reactions at 343K /23/

Reaction	k(cm^3 s^{-1})x10^9	$\frac{k_{meas}}{k_{theor}}$
1. $O^- + H_2SO_4 \rightarrow HSO_4^- + OH$	4.2	(1)*
2. $Cl^- + H_2SO_4 \rightarrow HSO_4^- + HCl$	2.7	0.9
3. $NO_3^- + H_2SO_4 \rightarrow HSO_4^- + HNO_3$	2.6	1.0
4. $I^- + H_2SO_4 \rightarrow HSO_4^- + HI$	1.9	0.9
5. $NO_3^-(HNO_3) + H_2SO_4 \rightarrow HSO_4^-(HNO_3) + HNO_3$	2.3	1.1
6. $NO_3^-(HNO_3)_2 + H_2SO_4 \rightarrow HSO_4^-(HNO_3)_2 + HNO_3$	1.1	0.6

* defined as 1

The most important results from an atmospheric viewpoint are the reactions of H_2SO_4 with $NO_3^-(HNO_3)_n$ ions. The latter ions had previously been thought to be the terminal negative ions in the stratosphere, and the fast reactions of these ions with sulfuric acid indicated that HR was correctly identified by Arnold and Henschen /21/. In fact, these measurements have provided the only means at present for determining the gaseous sulfuric acid concentration in the stratosphere /24/. The laboratory studies indicated that sulfuric acid should not play a role in the positive ion chemistry of the stratosphere, and this conclusion is supported by more recent in-situ results. In addition to the atmospheric implications, the reaction of I^- with H_2SO_4 puts a lower limit to the electron affinity of HSO_4 at 4.5 eV.

Another important species in the stratosphere is N_2O_5. Two studies were made of the reactions of atmospheric ions with N_2O_5 /25/, /26/. The results of the negative ion reactions in these studies are listed in Table 4. All the reactions were found to be fast to produce NO_3^- except those involving hydrates of NO_3^-. These results imply that N_2O_5 will speed the conversion rate of primary negative ions in the stratosphere to NO_3^- core ions. The important reactions from this point of view are those of CO_3^-, O_2^- and its hydrates, and NO_2^- and its hydrates, all of which are precursors to NO_3^- in the stratosphere. Particularly interesting is the reaction with CO_3^- since in the mesosphere the conversion of CO_3^- to NO_3^- is slow. The rapidity of this reaction as well as that of the reaction of CO_3^- with HNO_3 ensures rapid production of NO_3^- core ions in the stratosphere. The lack of reaction of the hydrates of NO_3^- with N_2O_5 indicates that the barrier in the reaction of N_2O_5 with H_2O is not overcome in the presence of the NO_3^- core. This last result also holds for positive ion hydrates.

Table 4. Rate Coefficients of Negative Ions Reacting with N_2O_5

Reaction	$k(cm^3s^{-1})$	Ref
$F^- + N_2O_5 \rightarrow NO_3^- + FNO_2$	1.1(-9)	25
$Cl^- + N_2O_5 \rightarrow NO_3^- + ClNO_2$	9.4(-10)	25
$Br^- + N_2O_5 \rightarrow NO_3^- + BrNO_2$	5.9(-10)	25
$I^- + N_2O_5 \rightarrow NO_3^- + INO_2$	5.9(-10)	25
$CO_3^- + N_2O_5 \rightarrow NO_3^- + NO_3 + CO_2$ $\rightarrow NO_3^- + NO_2 + CO_3$	2.8(-10)	25
$NO_2^- + N_2O_5 \rightarrow NO_3^- + 2NO_2$	7.0(-10)	25
$Cl^- + N_2O_5 \rightarrow NO_3^- + ClNO_2$	9.3(-10)	26
$Cl^-(H_2O) + N_2O_5 \rightarrow$ products	8.2(-10)	26
$O_2^- + N_2O_5 \rightarrow$ products	1.1 (-9)	26
$O_2^-(H_2O) + N_2O_5 \rightarrow$ products	1.0(-9)	26
$O_2^-(H_2O)_2 + N_2O_5 \rightarrow$ products	9 (-10)	26
$NO_2^- + N_2O_5 \rightarrow NO_3^- + 2NO_2$	6 (-10)	26
$NO_2^-(H_2O) + N_2O_5 \rightarrow$ products	5(-10)	26
$NO_3^-(H_2O) + N_2O_5 \rightarrow$ products	<1(-11)	26
$NO_3^-(H_2O)_2 + N_2O_5 \rightarrow$ products	<1(-11)	26

Another interesting subset of the N_2O_5 reactions are those with the halide ions. These are all fast and produce NO_3^- and the nitryl halide. The fast reaction of I^- with N_2O_5 has been exploited in order to study the thermal decomposition rate of N_2O_5 /27/. In this study, the flowing afterglow was used in a novel way as a detector for neutral kinetics. Employing this technique of selective chemical ionization, Viggiano et al./27/ studied the thermal decomposition of

N_2O_5 over a pressure range of 10 to 800 torr and a temperature range of 285 to 384K. The results of this study and that by Connell and Johnston /28/ have been combined by Malko and Troe /29/ and compared to the latest theories on unimolecular decomposition.

CH_3CN has been found to play an important role in the positive ion chemistry of the stratosphere. A study was made by Paulson and Dale /30/ using a SIFT in order to see if CH_3CN could also enter into the negative ion chemistry of the stratosphere. The results of this work are shown in Table 5.

Table 5. Rate Coefficients for Reactions of CN Containing Compounds at 297 K /30/

Reaction	$k(cm^3 s^{-1})$
$O^- + CH_3CN \rightarrow CH_2CN^- + OH + 0.54$ eV	3.5(-9)
$\rightarrow OH^- + CH_2CN + 0.85$	<5(-12)
$OH^- + CH_3CN \rightarrow CH_2CN^- + H_2O + 0.89$	3.3(-9)
$\rightarrow CN^- + CH_3OH + 1.00$	<5(-12)
$OH^-(H_2O) + CH_3CN \rightarrow CH_2CN^- + 2H_2O - 0.19$	3.1(-9)
$\rightarrow CH_2CN^-(H_2O) + H_2O$	2.6(-9)
$OH^-(H_2O)_2 + CH_3CN \rightarrow$ products	slow
$CH_2CN^-(H_2O) + CH_3CN \rightarrow CH_2CN^-(CH_3CN) + H_2O$	>5(-10)
$CN^- + CH_3CN + He \rightarrow CN^-(CH_3CN) + He$	3.5(-12)*
$Cl^- + CH_3CN + He \rightarrow Cl^-(CH_3CN) + He$	2.5(-12)*
$O_2^- + CH_3CN + He \rightarrow O_2^-(CH_3CN) + He$	3.7(-11)*
$CH_2CN^- + CH_3CN + He \rightarrow CH_2CN^-(CH_3CN) + He$	1.3(-12)*
$NO_2^- + CH_3CN + He \rightarrow NO_2^-(CH_3CN) + He$	8.5(-12)*
$NO_3^- + CH_3CN + He \rightarrow NO_3^-(CH_3CN) + He$	7.8(-12)*
$CO_3^- + CH_3CN + He \rightarrow CO_3^-(CH_3CN) + He$	1.1(-12)*
$CN^- + HNO_3 \rightarrow NO_3^- + HCN$	2.0(-9)
$CH_2CN^- + HNO_3 \rightarrow NO_3^- + CH_3CN$	1.4(-9)
$CH_2CN^- + NO_2 \rightarrow NO_2^- + CH_2CN$	1.0(-9)

*Two-body rate coefficients at a He pressure of 0.4 torr (1.3×10^{16} cm^{-3}).

In the reactions of acetonitrile with both O^- and OH^-, only the proton transfer channel was observed, although hydrogen atom transfer in the reaction with O^- and nucleophilic displacement in the reaction with OH^- are also exothermic. The latter reaction would lead to $CH_3OH + CN^-$. Reaction with $OH^-(H_2O)$ produced both m/e 40 i.e., CH_2CN^- and m/e 58, written here as $CH_2CN^-(H_2O)$. The ratio of these product ions in the limit of zero reactant flow is 1.22. Production of CH_2CN^- is slightly endothermic, based upon current thermochemical information. Production of m/e 58 might be regarded as nucleophilic displacement if, as suggested by Caldwell et al./31/, the m/e 58 ion product is written not as $CH_2CN^-(H_2O)$ but as $CN^-(CH_3OH)$. With further addition of CH_3CN to the flow tube, however, the m/e 58 species reacts further and is replaced with m/e 81, $CH_2CN^-(CH_3CN)$. This suggests that m/e 58 is $CH_2CN^-(H_2O)$ which then undergoes a solvent switching reaction with further addition of CH_3CN. Reaction of $OH^-(H_2O)_2$ with CH_3CN is slow. The other reactions of CH_3CN listed in Table 5 are three-body association processes. The fate of CH_2CN^- and of CN^- in the stratosphere is determined by the rapid reactions of both of these species with HNO_3 and by the reaction of CH_2CN with NO_2. Based upon the rate coefficients for these reactions and upon recent measurements of stratospheric number densities for HNO_3 and NO_2, the lifetimes of CH_2CN^- and CN^- are about 3 seconds at 35 km, compared to ion lifetimes of thousands of seconds, indicating that these should be minor species, as has been observed /19/, /20/.

Two recent studies pertain to the ion chemistry of the mesosphere. The first of these was made to determine the role of chlorine-containing species in this region /32/. The results are listed in Table 6. HCl was found to react rapidly with O^-, O_2^-, NO_2^- and CO_4^- producing Cl^- (or $ClHO_2^-$ in the latter case). This indicates that these reactions are likely to be the source of Cl^- in the 60-80 km region of the atmosphere. The reaction of CO_3^- with HCl was found to be slow, presumably beause the reaction is endothermic. In contrast, ClO^- was predicted not to be an important species in the atmo sphere. This is due to the fact that the rate constant for ClO^- production from the reaction of Cl^- with O_3 has a small upper limit and that ClO^- was found to react rapidly with NO, NO_2, and O_3. The electron affinity of ClO was found to be 1.95 ± 0.25 eV in the same study.

Table 6. Reactions of Chlorine Containing Species at 300K /32/

Reaction	$k(cm^3\ s^{-1})$
$O^- + CCl_4 \rightarrow ClO^- + CCl_3$	$(1.4 \pm 0.4) \times 10^{-9}$
$O^- + HCl \rightarrow Cl^- + OH$	$(2.0 \pm 0.6) \times 10^{-9}$
$O_2^- + HCl \rightarrow Cl^- + HO_2$	$(1.6 \pm 0.5) \times 10^{-9}$
$NO_2^- + HCl \rightarrow Cl^- + HNO_2$	$(1.4 \pm 0.4) \times 10^{-9}$
$CO_4^- + HCl \rightarrow ClHO_2^- + CO_2$	$(1.2 \pm 0.4) \times 10^{-9}$
$CO_3^- + HCl \rightarrow$ products	$\leq 3 \times 10^{-11}$
$ClO^- + NO \rightarrow NO_2^- + Cl$	$(2.9 \pm 0.9) \times 10^{-11}$
$ClO^- + NO_2 \rightarrow NO_2^- + ClO$	
$\rightarrow Cl^- + NO_3$	$(3.2 \pm 1.6) \times 10^{-10}$
$\rightarrow NO_3^- + Cl$	
$ClO^- + SO_2 \rightarrow Cl^- + SO_3$	$(1.3 \pm 0.4) \times 10^{-9}$
$ClO^- + CO_2 \rightarrow$ products	$\leq 1 \times 10^{-13}$
$ClO^- + O_3 \rightarrow Cl^- + 2O_2$	$(7 \pm 3.5) \times 10^{-11}$
$\rightarrow O_3^- + ClO$	
$Cl^- + O_3 \rightarrow ClO^- + O_2$	$\leq 5 \times 10^{-13}$

The other study pertaining to mesospheric negative ion chemistry involves silicon-containing species. These measurements were made after a rocket-borne mass spectrometer found an ion at mass 76 that could not be identified with any conventional ions. The results of the rocket flight and the laboratory results are reported by Viggiano et al./33/. An important conclusion was that O_3^- and CO_3^- react rapidly with SiO to produce SiO_3^-. The absolute values of the rate coefficients could not be determined because the flow of SiO could not be measured. The other important laboratory result was that SiO_3^- did not react with NO, NO_2, CO, CO_2, O, O_3, or Cl_2, the most important trace species that could be expected to react with SiO_3^- in the mesosphere. The absence of reaction with these neutrals suggests that they are endothermic and places a lower limit of 4.7 eV on the dissociation energy of the bond between O^- and SiO_2. The authors concluded that the mass 76 ion was probably SiO_3^- and went on to speculate that very heavy ions found in the same flight may be ions of the type $SiO_3^- (SiO_2)_m (MgO)_n (FeO)_o$...formed by electron attachment to particles resulting from meteor ablation. This hypothesis is based on the large stability found for SiO_3^-.

Recently, there has been a study by Fahey et al. /34/ that has looked at the largely unexplored area of tropospheric ion chemistry. This research involves the reactions of $O_2^-(H_2O)_n$ with n = 0 to 4. The study was carried out in a variable temperature flowing afterglow modified so that the reactant ions were created in a high pressure region (27 torr) which was separated from the main flow tube by a membrane having an aperture 0.4 cm in diameter. In this manner, the cluster ions could be produced with a minimum amount of H_2O, which minimized the effects of secondary reactions. The technique had the additional advantage of ensuring that the reactant ions were formed in the source region and not in the reaction region. The results of this study are listed in Table 7.

Table 7. Reaction Rate Coefficients for $O_2^-(H_2O)_n$ Reactions /34/

Reaction	k(cm^{3}s^{-1})	Temp.(K)
$O_2^- + O_3 \rightarrow O_3^- + O_2$	7.8(-10)	335
$O_2^-(H_2O)+O_3 \rightarrow O_3^- + O_2 + H_2O$	8.0(-10)	292-335
$O_2^-(H_2O)_2+O_3 \rightarrow O_3^-(H_2O)+O_2+H_2O$	7.8(-10)	235-292
$O_2^-(H_2O)_3+O_3 \rightarrow O_3^-(H_2O)_2+O_2+H_2O$	~6.4(-10)	181-235
$O_2^-(H_2O)_4+O_3^- \rightarrow O_3^-(H_2O)_3+O_2+H_2O$	~4.6(-10)	181
$O_2^-(H_2O)+NO \rightarrow O_2^-(NO)+H_2O$	2(-10)	211-300
$O_2^-(H_2O)_2+NO \rightarrow O_2^-(NO)(H_2O)+H_2O$	1.5(-10)	176-300
$O_2^-(H_2O)_3+NO \rightarrow O_2^-(NO)(H_2O)_2+H_2O$	1.5(-10)	176-211
$O_2^-(H_2O)_4+NO \rightarrow O_2^-(NO)(H_2O)_3+H_2O$	1.2(-10)	176-184
$O_2^-(H_2O)_5+NO \rightarrow O_2^-(NO)(H_2O)_4+H_2O$	1.2(-10)	184
$O_2^-+SO_2 \rightarrow SO_2^-+O_2$	1.9(-9)	303
$O_2^-(H_2O)+SO_2 \rightarrow SO_4^-+H_2O$	1.8(-9)	303-304
$O_2^-(H_2O)_2+SO_2 \rightarrow$ products	1.7(-9)	207-304
$O_2^-(H_2O)_3+SO_2 \rightarrow$ products	1.7(-9)	207-210
$O_2^-(H_2O)_4+SO_2 \rightarrow$ products	1.6(-9)	207
$O_2^-(H_2O)+CO_2 \rightarrow CO_4^-+H_2O$	>5.2(-10)	295
$O_2^-(H_2O)_2+CO_2 \rightarrow$ products	7(-11)	292
$O_2^-(H_2O)_3+CO_2 \rightarrow$ products	<1(-12)	187-213
$O_2^-(H_2O)_4+CO_2 \rightarrow$ products	<1(-12)	187-213

In the cases in which there is an exothermic exchange of ligands (NO, SO_2, or CO_2 for H_2O), the reactions were all fast, even for the higher hydrates. This could be expected since there are no steric barriers for ligand exchange. The identity of the ion formed in the $O_2^- (H_2O)_n$ reaction with NO is probably the peroxy isomer of NO_3^-, although rearrangement into the more stable form could not be ruled out. The most surprising result of this study was that $O_2^- (H_2O)_n$ ions reacted rapidly with O_3 to produce O_3^- with one less water molecule attached. This process might involve either the transfer of an oxygen atom or the simultaneous transfer of both charge and one or more water molecules. Studies using ^{18}O labeling in the reactant ion showed that only the latter process occurred. The speed of these ligand exchange and charge exchange reactions at large degrees of hydration is in contrast to similar studies involving ion-atom exchange. In the latter case reactivity typically decreased significantly with increased hydration /7/. The findings in this study ensure that the primary $O_2^- (H_2O)_n$ ions expected in the earth's troposphere will quickly react to form more evolved ions and that O_2^- hydrates will not be a major species when ambient tropospheric ions are measured.

D. Electron Affinity Determination

One of the major applications of negative ion-molecule reactions is for electron affinity determination. In the last several years, a number of swarm studies have involved the determination of electron affinities. The determination of electron affinities in a swarm experiment can be done in a variety of ways. A direct method is that of bracketing. This involves studying a number of charge exchange reactions with compounds of known electron affinities. The reactions involved are

$$A^- + B \rightarrow B^- + A \qquad [3]$$

and

$$C^- + A \rightarrow A^- + C. \qquad [4]$$

A fast reaction implies the reactant neutral has the higher electron affinity. By studying a number of such reactions for both A^- and A one can then bracket the electron affinity of species A if the electron affinities of the other species are known. A less direct form of bracketing involves studying more complex reactions than charge exchange, and then by knowing the thermochemistry of the other species involved, one can again put limits on the electron affinity.

An alternative to this method is to study an equilibrium process and derive the electron affinity of one of the negative species from the measured thermochemistry. One may study the equilibrium directly or determine the equilibrium constant by measuring both the forward and reverse rate coefficients independently.

In this manner a number of studies in recent years have yielded electron affinity determinations. In some of the studies the determination of an electron affinity (or limit to it) was an added bonus, as in the studies involving sulfuric acid /22/ and ClO/32/ mentioned in the atmospheric section of this paper. In addition, there have been several studies where the determination of the electron affinity was the prime purpose /35/-/38/. The most recent electron affinity determinations in swarm experiments are listed in Table 8 along with the technique. In some cases, such as HSO_4 and UF_6, only lower limits could be placed. Rather tight limits, as low as 0.1 eV, can be obtained in favorable cases, such as SF_4, with careful attention given to the reactions studied.

Table 8. Recent Electron Affinity (EA) Determinations

Molecule	EA (eV)	Method	Reference
SF_6	1.0 ± 0.2	bracketing	37
SF_4	2.35 + 0.1	bracketing	36
UF_6	>3.61	bracketing	35
HO_2	1.16 ± 0.15	equilibrium constant	38
HSO_4	>4.5	bracketing	22
ClO	1.95 ± 0.25	bracketing	32

One particularly interesting aspect of the above studies not related to electron affinity determinations warrants further discussion. It is usually assumed in flowing afterglow studies that the ambipolar diffusion coefficient is a constant independent of degree of reaction. Streit and Newton /35/, /39/ have found that this is not the case for UF_6 reactions. UF_6^- probably has a much smaller free diffusion coefficient than the lighter reactants used in the study. As the reaction proceeds, the ambipolar diffusion coefficient of the reactant ion in the flowing afterglow increases as the reactant ion is replaced by the slower diffusing UF_6^- /39/. Thus as the flow of UF_6 increases, the decline in the primary signal deviates from linearity in the normal plot of the logarithm of the ion signal versus reactant neutral flow. The effect is that, upon addition of small amounts of UF_6, the decline in the primary signal is more than if only reaction occurred because the ambipolar diffusion coefficient is increasing. Upon large additions of UF_6, the ambipolar diffusion coefficients reach constant values, and the decline in the primary is a straight line. This problem does not occur in a SIFT as charged particles of only one sign are present.

E. Isotope Effects Involving Proton Transfer

Proton transfer is one of the most basic types of ion-molecule reactions. Many studies of proton transfer reactions have been used to establish tables of gas phase acidities and proton affinities /6/, /40/. In this section two studies involving the basic nature of proton transfer will be discussed. Both of these involve the use of isotopically labelled species to help elucidate the reaction mechanism.

The first study to be discussed involves the measurements of the rate coefficients for hydrogen-deuterium exchange between HO^- (and DO^-) with a variety of weakly acidic neutrals, MD(and MH) /41/. The results of this study are listed in Table 9. Grabowski et al. /41/ have pointed out that there is only a weak correlation of the H-D exchange rate with the relative acidity of the exchange reagent. The mechanism used to explain these data is

$$\mathrm{DO^- + MH \rightarrow \underset{I}{[DO^-(MH)]} \rightarrow \underset{II}{[(DOH)M^-]} \rightarrow \underset{III}{[HO^-(MD)]} \rightarrow HO^- + MD.} \qquad [5]$$

The rate of the H-D exchange is then determined by several factors. Molecules with either large dipole moments or large polarizabilities will generally form longer lived ion-molecule complexes and, therefore, will have a better chance for reaction. The slowness of the DO^- reaction with ethylene is an example where the low initial bond strength of the complex causes the reaction to be slow, the reaction efficiency being less than 0.02 percent. In contrast, the analogous reaction with ammonia leads to a complex with large initial bond strength and to a reaction efficiency of 18 percent.

Table 9. Rate Coefficients for H-D Exchange Reactions at 299K /41/

Reaction	$k \times 10^{10}$ ($cm^3 s^{-1}$)	k/k_c*	Reaction	$k \times 10^{10}$ ($cm^3 s^{-1}$)	k/k_c*
$HO^- + D_2$	0.68	0.060	$HO^- + C_6D_6$	7.5	0.38
$DO^- + H_2$	0.38	0.024	$DO^- + C_6H_6$	6.6	0.34
$HO^- + HD$	0.35	0.027	$DO^- + CH_4$	≤ 0.002	<0.0002
$DO^- + HD$	0.15	0.012	$DO^- + C_2H_4$	≤ 0.002	≤ 0.0002
$HO^- + ND_3$	2.7	0.13	$DO^- + CH_3NH_2$	5.7	0.28
$DO^- + NH_3$	3.8	0.18	$DO^- + (CH_3)_2NH$	7.5	0.38
$HO^- + D_2O$	12	0.50	$DO^- + H_2CO$	exchange observed	
$DO^- + H_2O$	18	0.74			

*k_c means the collision rate

Once a long lived complex is formed, the reaction rate is determined by the rate of intramolecular proton transfer. This rate is determined primarily by two factors, the relative basicity of OD^- and M^- and the relative bond strength of HOD to M^- and that of OD^- to MH (the bond strengths of complex I and II, respectively). These two factors then determine the relative energies of the OD^- (MH) and M^- (HOD) complexes which play a major role in determining the rate of the reaction. Faster rates result when OD^- is the stronger base and the M^- (HOD) complex has the stronger bond. Both effects facilitate proton transfer.

Another effect that has an influence on the reaction efficiency is multiple proton transfer within the collision complex. This problem of intramolecular proton transfer is treated in another study from the same laboratory /42/. This study involved the reactions of amide and hydroxyl with SO_2, CO_2, N_2O and CS_2. The results are listed in Table 10. The observation of unlabeled hydroxide products in the reactions involving $H^{18}O^-$ reactants shows that an intramolecular proton transfer is occurring.

Table 10. Reactions of OH^- and NH_2^- /42/

Reaction	k(cm^3 s^{-1})
$NH_2^- + SO_2 \rightarrow (66.5\%)\ SO_2^- + H_2N$	2.94(-9)
$\rightarrow (26.0\%)\ NSO^- + H_2O$	
$\rightarrow (7.5\%)\ HO^- + HNSO$	
$NH_2^- + CO_2 \rightarrow NCO^- + H_2O$	9.29(-10)
$NH_2^- + N_2O \rightarrow (72.1\%)\ N_3^- + H_2O$	2.88(-10)
$\rightarrow (27.9\%)\ HO^- + HN_3$	
$NH_2^- + CS_2 \rightarrow (54\%)\ NCS^- + H_2S$	1.8(-9)
$\rightarrow (46\%)\ HS^- + HNCS$	
$H^{18}O^- + S^{16}O_2 \rightarrow H^{16}O^- + S^{16}O^{18}O$	1.25(-9)
$H^{18}O + C^{16}O_2 \rightarrow H^{16}O^- + C^{16}O^{18}O$	5.69 (-10)
$D^{18}O + C^{16}O_2 \rightarrow D^{16}O^- + C^{16}O^{18}O$	6.33 (-10)
$H^{18}O^- + N_2{}^{16}O \rightarrow H^{16}O^- + N_2{}^{18}O$	1.16 (-11)
$H^{34}S^- + C^{32}S_2 \rightarrow H^{32}S^- + C^{32}S^{34}S$	1.53 (-11)

Grabowski /42/ has set up a simple statistical model to help elucidate some of the mechanistic detail of the reactions involving $H^{18}O^-$ and $H^{34}S^-$. In this model, once a complex is formed it can either undergo an intramolecular proton transfer or dissociate into products which may or may not be the initial reactants. The model can then be used to predict the reaction efficiency as a function of the ratio of the proton transfer rate to the dissociation rate. The results of this calculation pertaining to the situation where there are three equivalent heavy atoms (e.g., $H^{18}O^- + CO_2$) are shown in Figure 1. The maximum reaction efficiency is 2/3 since two of the heavy atoms are equivalent. Using this graph one finds that on the average 2 to 3 proton transfers occur in the re-

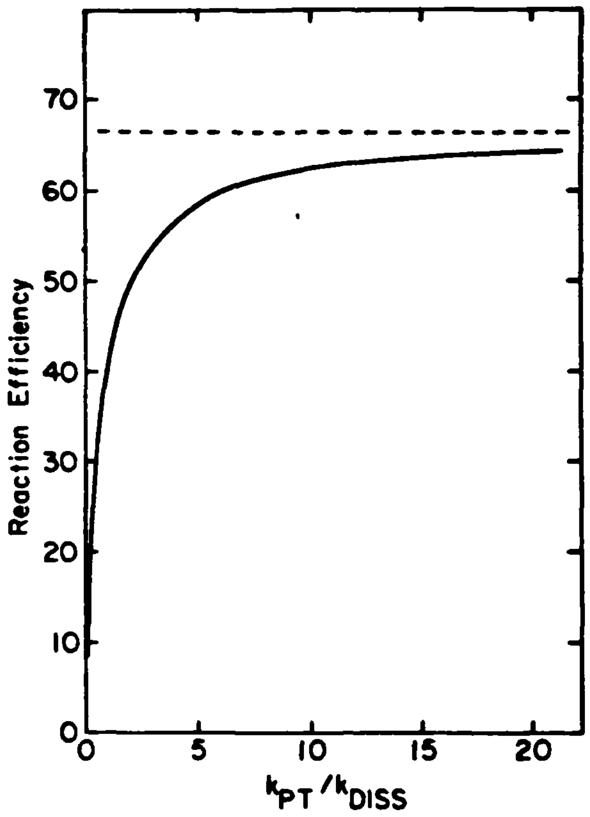

Fig. 1. A plot of the calculated reaction efficiency as a function of the ratio of proton transfer to dissociation rate coefficients for the reactions of $H^{18}O^-$ with SO_2 and CO_2 and the reaction of $H^{34}S^-$ with CS_2. The dashed line is the statistical limit for the reaction efficiency in the event of complete randomization of the proton. Reprinted by permission /42/.

action of $H^{18}O^-$ with CO_2 and 11 to 12 in the reaction with SO_2. The fact that more proton transfers occur in the case of SO_2 is due to the fact that the CO_2 bond energy is less than the SO_2 bond energy. This leads to a reduced reaction efficiency as explained above. By doing experiments in which the hydrogen was replaced by deuterium, the author concluded that the lifetime of the complexes with respect to dissociation, rather than the proton transfer rate, controlled the exchange, since this substitution neither slowed the reaction nor changed the reaction efficiency.

F. Reaction of H_3O^-

The ion H_3O^- has been observed in ion beam experiments /43/ where it is formed in the endothermic reaction

$$OH^-(H_2O) + H_2 \rightarrow H_3O^- + H_2O \qquad [6]$$

and in an ion cyclotron resonance (ICR) apparatus /5/ from the exothermic reaction

$$OH^- + H_2CO \rightarrow H_3O^- + CO \qquad [7]$$

The dissociation energy $D(H^- - H_2O)$ is known to be about 17 ± 3 kcal mol^{-1} from the beam experiments and from molecular orbital calculations /44/. An attempt to observe H_3O^- produced in the reaction between OH^- and H_2CO in a SIFT was unsuccessful /45/. The ions H_3CO^- and $H_3CO_2^-$ were observed, however, and are thought to result from the reactions

$$\begin{aligned} H_3O^- + H_2CO &\rightarrow H_3CO^- + H_2O \qquad [8] \\ &\rightarrow H_3CO_2^- + H_2 \end{aligned}$$

which have also been observed in the ICR /5/. When $OD^-(D_2O)$ reacted with H_2CO, no evidence was obtained for the formation of H_2DO^-, and the only ion product was $H_2DCO_2^-$, which corresponds to a solvent switching reaction.

G. Conclusions

In the past several years, a wide range of experimental work has been done on negative ion-molecule reactions. The developement of the SIFT apparatus for use with negative ions has greatly expanded the type of experiments that can be performed, as it has for positive ions. As many of the more straight-forward reactions have been studied, experimenters have turned to novel techniques to perform their experiments. Those reported here include the study of vibrational product distributions, use of a membrane ion source region to study large cluster ions, and the study of neutrals difficult to work with, such as H_2SO_4 and N_2O_5. Information has even been obtained on undetected ions such as H_3O^-. All this information has given new insights into the basic mechanisms of ion-molecule reactions as exemplified by the work on proton transfer reactions and associative detachment.

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