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Dissociative attachment reactions of electrons with strong acid molecules

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Using the flowing afterglow/Langmuir probe (FALP) technique, we have determined (at variously 300 and 570 K) the dissociative attachment coefficients β for the reactions of electrons with the common acids HNO_3 (producing NO_2^-) and H_2SO_4 (HSO_4^-), the superacids FSO_3H (FSO_3^-), $\text{CF}_3\text{SO}_3\text{H}$ (CF_3SO_3^-), ClSO_3H (ClSO_3^- , Cl^-), the acid anhydride (CF_3SO_2)₂O (CF_3SO_3^-), and the halogen halides HBr (Br^-) and HI (I^-). The anions formed in the reactions are those given in the parentheses. The reactions with HF and HCl were investigated, but did not occur at a measurable rate since they are very endothermic. Dissociative attachment is rapid for the common acids, the superacids, and the anhydride, the measured β being appreciable fractions of the theoretical maximum β for such reactions, β_{max} . The HI reaction is very fast ($\beta \sim \beta_{\text{max}}$) but the HBr reaction occurs much more slowly because it is significantly endothermic. The data indicate that the extreme acidity of the (Bronsted-type) superacids has its equivalence in the very efficient gas-phase dissociative attachment which these species undergo when reacting with free electrons. The anions of the superacids generated in these reactions, notably FSO_3^- and CF_3SO_3^- , are very stable (unreactive) implying exceptionally large electron affinities for the FSO_3 and CF_3SO_3 radicals.

I. INTRODUCTION

The properties of acids in the liquid phase have been discussed in detail and are well understood.¹ In this paper, we are concerned with the properties and behavior of acid molecules in the gas phase, specifically with their interactions with low energy (thermal) electrons in low temperature (afterglow) plasmas. All but one of the molecules investigated in this study contain hydrogen and are strong Bronsted acids. Both in the gas phase and in solution, a Bronsted acid, XH , will donate a proton to any base, Y^- ,



provided that the acid XH is a stronger acid than HY —or equivalently, that the base X^- is a weaker base than Y^- . The acids examined here are exceedingly strong and include some so-called superacids (which are stronger than 100% sulfuric acid²) e.g., fluorosulfonic acid, FSO_3H , and triflic acid, $\text{CF}_3\text{SO}_3\text{H}$.

When molecules of these strong acids are introduced in the vapor phase into a gaseous plasma, they undergo dissociative attachment reactions with the free electrons in the plasma, viz.



Comparison of reaction (2) with reaction (1) shows that dissociative attachment may be viewed equivalently as a Bronsted acid/base reaction, with the electron acting as the proton acceptor or base.

The energetic requirements of reaction (2) are analyzed simply. When an electron combines with a proton, it liber-

ates 13.6 eV or 313.5 kcal/mol (the ionization energy of the hydrogen atom). Thus reaction (2) will be exothermic for acids with heats of deprotonation ($\text{XH} \rightarrow \text{X}^- + \text{H}^+$) less than 313.5 kcal/mol. Since heats of deprotonation range typically from 300 to 400 kcal/mol,³ only the strongest acids can undergo the dissociative attachment reaction (2).

No comprehensive study has been made of dissociative attachment reactions for acid molecules at thermal energies. Fehsenfeld *et al.*⁴ have studied the nitric acid reaction:



They determined the rate coefficient β for reaction (3) to be $(5 \pm 3) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ at 300 K using a flowing afterglow/mass spectrometer technique. Note that the product ion is NO_2^- (NO_3^- production is endothermic by $\sim 11 \text{ kcal mol}^{-1}$ ⁴ and so it cannot occur at a significant rate under thermal conditions). Although large, $\beta(\text{HNO}_3)$ is several times smaller than the upper-limit (collisional) rate coefficient β_{max} for such reactions.⁵ A somewhat smaller $\beta(\text{HNO}_3)$ of $(1.4 \pm 0.7) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ was determined by Wecker and Schindler using an electron cyclotron resonance technique.⁶ We discuss the HNO_3 reaction and the β_{max} concept further in Sec. III.

Recently, we have developed our flowing afterglow/Langmuir probe (FALP) technique to study electron attachment reactions at thermal energies. Using this technique, we have previously determined the attachment coefficients for several species including some halocarbons (e.g., CCl_4 , CCl_3F , CF_3Br , etc.), SF_6 , C_7F_{14} , and C_6F_6 .⁷⁻⁹ In some cases (e.g., CCl_4 , SF_6), the measured β values are close to β_{max} , but when $\beta < \beta_{\text{max}}$, then generally β increases with temperature indicating an activation energy E_a for these reactions. Thus we have determined the E_a for several such reactions.

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A comparison of liquid phase and gas phase behavior of the strong acids referred to above has obvious attractions. Thus we have now studied, using the FALP technique, attachment reactions of the hydrogen halides, HF, HCl, HBr, and HI, the common acids, HNO₃ and H₂SO₄, the superacids FSO₃H, ClSO₃H, CF₃SO₃H, and also the anhydride of triflic acid, (CF₃SO₂)₂O.

II. EXPERIMENTAL

The FALP technique has been described in detail previously.^{10,11} In brief, an afterglow plasma is created in a fast-flowing helium carrier gas by means of an upstream microwave-cavity discharge. Metastable helium atoms are destroyed by adding sufficient argon to the afterglow in the upstream region, and then an appropriate concentration of an attaching gas is added downstream. This results in an increase in the axial gradient of the plasma electron number density n_e . The gradient of n_e is determined using a movable Langmuir probe and the electron attachment coefficient β is determined from this gradient knowing the number density of the attaching molecules in the plasma. Further details of the experiments and the method of analysis are given in Smith *et al.*⁷ and Smith and Adams.¹² Measurements were made at 300 K for all the species included in the study (except H₂SO₄) and also at 510 K for some of the species. The full temperature range currently available using the FALP (80–600 K), could not be utilized because of condensation problems and because of decomposition problems in some cases.

Because of the very large β for many attachment reactions, it is convenient to dilute the attaching gases with helium in order to facilitate measurements of their very small flow rates into the plasma (small number densities of the attaching gas molecules are desirable in the plasma, since otherwise the gradient of n_e is too large). We routinely use this approach for gases and vapors which are not reactive with stainless steel surfaces, e.g., CCl₄, SF₆.⁷ Clearly this is not possible for most of the species included in the present study and thus we were forced to flow the "neat" gases and vapors into our calibrated capillary flow measurement system. The relatively small pressures at the input and across the capillary, and the sparsity of information concerning the viscosities of these species, meant that the derived flow rates of attaching gases into the plasma were not as accurately determined as is usually the case in our experiments. This reflects directly on the accuracy of the derived β values (see Table I). For the HI measurements, we were able to use our helium dilution approach. For the H₂SO₄ experiments, we could not measure the H₂SO₄ flow rate directly because of the very low vapor pressure of H₂SO₄ at 300 K. The reservoir containing H₂SO₄ had to be heated and the vapor transferred into the afterglow plasma by a carrier.¹³ A limit to the H₂SO₄ number density was obtained in the following manner. We monitored the change in the plasma positive ion (He⁺, Ar⁺, and H₃O⁺) signals by the downstream mass spectrometer as H₂SO₄ was added to the FALP. These changes are related to the H₂SO₄ number density by the rate coefficients for the reaction of H₂SO₄ with these positive ions. Use of the rate coefficients measured by Viggiano *et al.*^{13,14} then allowed a

TABLE I. Attachment rate coefficients for the reactions of electrons with the molecules indicated at the temperatures indicated.

Attaching molecule	Product ion	$\beta(\text{cm}^3 \text{s}^{-1})$	
		300 K	510 K
HNO ₃	NO ₂ ⁻	$5 \pm 2 (-8)^a$	b
H ₂ SO ₄	HSO ₄ ⁻	b	$>5 (-8)$
FSO ₃ H	FSO ₃ ⁻	$6 \pm 6 (-8)$	$1.2 \pm 1.2 (-7)$
CF ₃ SO ₃ H	CF ₃ SO ₃ ⁻	$1.0 \pm 1.5 (-7)$	b
(CF ₃ SO ₂) ₂ O	CF ₃ SO ₃ ⁻	$1.0 \pm 1.5 (-7)$	$2 \pm 2 (-7)$
ClSO ₃ H	ClSO ₃ ⁻ ^c	d	d
	Cl ⁻		
HBr	Br ⁻	$3.3 \pm 1 (-12)$	$2.8 \pm 1 (-10)$
HI	I ⁻	$3.5 \pm 1 (-7)$	$3.5 \pm 1 (-7)$
HCl	Cl ⁻	$<1 (-11)^e$	$<1 (-11)^e$
HF	F ⁻	$<1 (-11)^e$	$<1 (-11)^e$

^a $5 \pm 2 (-8)$ means $5 \pm 2 \times 10^{-8}$.

^b Not studied.

^c The products are in the approximate ratio Cl⁻:ClSO₃⁻; 2:1, see the text.

^d The measured rate coefficients are of the order of $1 (-8)$. However it appears that the ClSO₃H was heavily contaminated with HCl and SO₃, see the text.

^e These reactions are highly endothermic.

lower limit to be placed on the H₂SO₄ number density in the flow tube and thus a lower limit to be placed on the β for the attachment reaction of electrons with H₂SO₄.

For the HNO₃ experiments, the HNO₃ vapor was taken directly from a mixture of H₂SO₄/HNO₃ in the concentration ratio 2:1. The FSO₃H, ClSO₃H, CF₃SO₃H, and (CF₃SO₂)₂O vapors were taken off the liquids supplied by the Aldrich Chemical Company, the HF, HCl, and HBr were supplied by the Matheson Company and we synthesized the HI from the reaction of KI with H₃PO₄.

III. RESULTS AND DISCUSSION

A. General comments

The summarized data are presented in Table I and its footnotes. Note that the β values range from $3.5 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$ for HI at 300 K and $2 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$ for (CF₃SO₂)₂O at 510 K to $3.3 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ for HBr at 300 K. The theoretical maximum value for the electron capture rate coefficient β_{max} has been derived from the de Broglie wavelength of the electron as $\beta_{\text{max}} \approx 5 \times 10^{-7} (300/T)^{1/2} \text{ cm}^3 \text{s}^{-1}$.⁵ All of the β at 300 K fall short of the value predicted by this approach. A more sophisticated theoretical treatment by Klots¹⁵ assumes that the electron-molecule interaction is dominated by the polarization potential and β_{max} is then formulated in terms of the polarizability of the molecule. The calculation of β_{max} using the Klots formulation is not straightforward; however estimates show that the β_{max} values at 300 K are about half of the $5 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$ predicted by the simpler approach referred to above. Neither of these theories, however, accounts for the effects of a permanent dipole moment of the attaching molecule. Therefore they give only a rough estimate of β_{max} for the molecules under consideration here since the acids studied all have large dipole moments. In any event, $\beta(\text{HI})$ and $\beta[(\text{CF}_3\text{SO}_2)_2\text{O}]$ are very large and are close to the values of

β_{\max} expected from the Klots theory. When $\beta < \beta_{\max}$ this is often due to activation barriers to the reaction as noted above and/or because the dissociative attachment reaction is somewhat endothermic. Examples of both types of behavior are evident in the present study, the results of which we discuss under the following headings 1. HNO_3 , 2. H_2SO_4 , the sulfonic acids and $(\text{CF}_3\text{SO}_2)_2\text{O}$, and 3. the hydrogen halides.

1. HNO_3

Our value of $\beta(\text{HNO}_3)$ at 300 K is in good agreement with that obtained by Fehsenfeld *et al.*⁴ The reaction which yields NO_2^- as the product ion [Eq. (3)] is exothermic by 7 kcal mol⁻¹,⁴ yet $\beta(\text{HNO}_3)$ is significantly smaller than β_{\max} . This could be a manifestation of a small activation energy E_a for the reaction which would only need to be about 1 kcal mol⁻¹. This is in the range of the E_a we have found for other dissociative attachment reactions.^{7,8} We could not study this reaction at 510 K since HNO_3 decomposed at this temperature. This reaction has been discussed fully by Fehsenfeld *et al.*⁴

2. H_2SO_4 , the sulfonic acids and $(\text{CF}_3\text{SO}_2)_2\text{O}$

All of these species undergo rapid dissociative attachment with thermal electrons. The H_2SO_4 reaction proceeds thus:



As stated above, only a lower limit to $\beta(\text{H}_2\text{SO}_4)$ could be obtained and only at 510 K. At 300 K, H_2SO_4 condensed on the walls of the inlet system to the FALP and therefore the reaction could not be studied at this temperature. $\beta(\text{H}_2\text{SO}_4) \geq 5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ at 510 K which again is a substantial fraction of β_{\max} for the reaction. Reaction (4) proceeds rapidly and $\Delta H^\circ \leq 0$, as shown by the thermochemistry. Benson¹⁶ gives the bond dissociation energy $D(\text{H}-\text{OSO}_3\text{H}) = 103.5 \text{ kcal mol}^{-1}$ and Viggiano *et al.*^{13,14} give a limit to the electron affinity as $\text{EA}(\text{HSO}_4^-) \geq 103.5 \text{ kcal mol}^{-1}$. Combining these values implies that $\Delta H^\circ \leq 0$.

The fluorosulfonic acid reaction is also fast and proceeds thus:



generating the fluorosulfonate anion. In this case, we were able to determine $\beta(\text{FSO}_3\text{H})$ at both 300 and 510 K. Although the absolute error on each β value is quite large, it is the systematic error in the flow measurement that accounts for most of this error, and so the relative values of β at the two temperatures are much more certain. Therefore, it is clear that $\beta(\text{FSO}_3\text{H})$ is larger by a factor of about 2 at the higher temperature (see Table I). The increasing rate coefficient with increasing temperature is very probably a manifestation of a small E_a in the reaction, since the attachment reaction is appreciably exothermic (i.e., $\text{E.A.}(\text{FSO}_3^-) > D(\text{FSO}_3-\text{H})$ Viggiano *et al.*¹⁷). That this is so is also indicated by the fact that the electron attachment reaction (5) is very fast and the reverse associative detachment reaction is immeasurably slow.^{17,18}

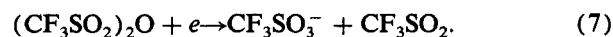
The triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) experiments were difficult to perform because of the extremely "sticky" nature of this

acid in the stainless steel system. No attempt was made to study the reaction at temperatures above 300 K. At 300 K, $\beta(\text{CF}_3\text{SO}_3\text{H})$ is large, perhaps somewhat greater than $\beta(\text{FSO}_3\text{H})$. The uncertainty comes from measuring the flow rates of these highly reactive substances. The reaction produces the triflate anion thus:



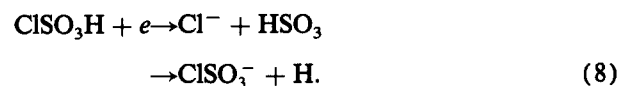
Considering the error limits, $\beta(\text{CF}_3\text{SO}_3\text{H})$ at 300 K could be very close to β_{\max} for this reaction. Again as with FSO_3H , the reaction is exothermic.^{17,18}

The reaction of electrons with triflic anhydride proceeds thus:



The only ionic product of the reaction is the triflate anion, CF_3SO_3^- . The reaction is again very rapid and the β at 510 K is about a factor of 2 greater than that at 300 K. Thus at 510 K, $\beta[(\text{CF}_3\text{SO}_2)_2\text{O}]$ probably approaches β_{\max} . So $(\text{CF}_3\text{SO}_2)_2\text{O}$ is an excellent scavenger of thermal electrons from plasmas.

The results of our measurements of β for chlorosulfonic acid, ClSO_3H , were initially very surprising. At 300 K, the measurements of $\beta(\text{ClSO}_3\text{H})$ were rather variable around a value of $10^{-8} \text{ cm}^3 \text{ s}^{-1}$, that is about an order of magnitude less than the β values for the other strong acids. Also, the reaction apparently resulted in two product ions



The Cl^- product ion was dominant, i.e., $\text{Cl}^- : \text{ClSO}_3^- :: 2:1$. Similar results were obtained both for β and the product ratio at 510 K. The apparently small $\beta(\text{ClSO}_3\text{H})$ was appreciated when we discovered that chlorosulfonic acid is heavily contaminated with the HCl and SO_3 from which it is synthesized² and therefore that the reactant gas flowing into the afterglow plasma was presumably predominantly a mixture of HCl and SO_3 . The measured β values of approximately $10^{-8} \text{ cm}^3 \text{ s}^{-1}$ (rather than the expected $\sim 10^{-7} \text{ cm}^3 \text{ s}^{-1}$) indicate that the vapor above the liquid ClSO_3H surface may have contained only about 10% of ClSO_3H molecules. Since HCl is not reactive with electrons at 300 K (see Table I), the Cl^- product most likely originates from the ClSO_3H reaction (8). This indicates that $D(\text{Cl}-\text{SO}_3\text{H}) \leq \text{E.A.}(\text{Cl}) = 83.4 \text{ kcal mol}^{-1}$. (There was no obvious increase in the Cl^- product with increasing temperature.) There is independent evidence that the $\text{Cl}-\text{SO}_3\text{H}$ bond is indeed relatively weak.² (Note that no F^- was observed in the FSO_3H reaction where the $\text{F}-\text{SO}_3\text{H}$ bond is very strong.) While it cannot be excluded that the Cl^- product originates from an unknown impurity or decomposition product, in all likelihood the ClSO_3^- results from electron attachment to ClSO_3H .

3. Hydrogen halides

As expected from considerations of the energetics, no measurable attachment occurred for HF and HCl , even at 510 K. The reactions:





are endothermic by 57.0 and 18.8 kcal mol⁻¹, respectively.^{19,20}

The HBr and HI reactions are considerably more interesting. Simple dissociative attachment occurs in both cases:



As can be seen in Table I, $\beta(\text{HBr})$ is very small at 300 K and is about two orders of magnitude greater at 510 K. This is a manifestation of the appreciable endothermicity of this dissociative attachment reaction.¹⁸ It is worthy of note that a value of 9.6×10^{-11} cm³ s⁻¹, lying between our values at the two temperatures, was obtained using the electron cyclotron resonance technique with an approximately thermal distribution of electron energies.²¹

The HI reaction (12) is extremely rapid. The $\beta(\text{HI})$ at 300 K of 3.5×10^{-7} cm³ s⁻¹ is as large as any we have measured. That $\beta(\text{HI})$ is so large indicates that the reaction cannot be significantly endothermic. A detailed study of these hydrogen halide reactions, which includes measurements of the reverse ion-atom rate coefficients, has been carried out using our selected ion flow tube (SIFT) apparatus,²² and a full account of this work will be presented in another publication.¹⁸

IV. SUMMARY AND CONCLUSIONS

In this study, we have shown that the common acids HNO₃ and H₂SO₄, and the superacids FSO₃H and CF₃SO₃H react rapidly with free electrons in thermal plasmas. Indeed, the measured rate coefficients β are appreciable fractions of the theoretical maximum rate coefficient β_{max} indicating that these reactions cannot be significantly endothermic. In all of these cases, the reactions are dissociative and, except for the HNO₃ reaction, which results in NO₂⁻ and OH (the NO₃⁻ + H product channel is endothermic because of these acids, only HNO₃ has a lower heat of deprotonation than H), these acids behave as Bronsted acids producing H atoms and, respectively, HSO₄⁻, FSO₃⁻, and CF₃SO₃⁻ ions. For the hydrogen halides, dissociative attachment is very endothermic for HF and HCl and so is not observed in our experiments. The HBr dissociative attachment reaction is appreciably endothermic and therefore proceeds only slowly at thermal energies. In contrast, the HI reaction is very fast and the measured β values, together with data on the reverse ($\text{I}^- + \text{H} \rightarrow \text{HI} + e$) associative detachment reaction, indicate that the reaction is very close to thermoneutral (i.e., $\Delta H^\circ \sim 0$). That these dissociative attachment reactions proceed with high probability when they are exothermic, tempts us to describe them in similar terms to ion-molecule proton transfer reactions. Exothermic proton transfer reactions of positive and negative ions with molecules are also invariably fast.²³ These dissociative attachment reactions may be considered to proceed via the donation of a proton to the incoming electron thus producing the appropriate anion and an H atom.

The rapid reactions observed here between Bronsted acids and thermal electrons demonstrate the extreme acidity of these acids. The present study therefore suggests that the stability of the CF₃SO₃⁻ and FSO₃⁻ ions should be particularly great. Our independent studies of the reactivity of these ions using the SIFT technique^{17,18} support this conclusion. These results are consistent with both the CF₃SO₃ and FSO₃ radicals having large electron affinities, exceeding those of the halogen atoms.

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