

The reactions of F^+ ions at thermal energies

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Abstract. The rate coefficients and product ions have been determined for the reactions of F^+ ions with some fifteen molecular gases at 300 K using a SIFT apparatus. The reactant gases were N_2 , CO, CO_2 , H_2 , D_2 , NO, O_2 , C_6H_6 , C_2H_4 , C_2H_2 , CH_4 , NH_3 , H_2O , H_2S and OCS. The mechanisms of the reactions are interpreted in terms of the accessible electronic states of the parent molecular ions formed in the (predominantly) charge transfer processes that occur. For two reactions, the electronic states of the product ions have been identified experimentally; for the other reactions, the states of the product ions have been inferred in the light of the available data obtained from photoelectron spectroscopy studies.

1. Introduction

Fluorine atoms have an exceptionally large ionization energy, smaller than only helium and neon atoms, and hence F^+ ions have a large recombination energy. In its ground state, F^+ is a closely-spaced triplet with recombination energies of 17.42 eV (3P_2), 17.47 eV (3P_1) and 17.48 eV (3P_0). Since these energies are appreciably greater than the ionization energies of all the stable molecules, charge transfer is energetically possible with all molecular gases and therefore it is likely that F^+ will be very reactive with most molecular species. However, it is well known that energetics alone do not control the course of ion/molecule reactions (for example, the very exothermic charge transfer process $He^+ + H_2 \rightarrow H_2^+ + He$ is very inefficient at room temperature (Ikezoe *et al* 1986)).

A previous study has been carried out on the reactions of F^+ ions with a number of simple molecules at room temperature (Hamdan *et al* 1986). We have undertaken a complementary study of the reactions of this energetic ion with a variety of molecular gases, including the simple non-polar diatomics N_2 and H_2 (possessing high ionization energies) and NO and O_2 (possessing low ionization energies), several polyatomic hydrocarbons including C_2H_2 and C_6H_6 , and some polar molecules, including H_2O and NH_3 . Ten of the fifteen reactions discussed here have been studied by Hamdan *et al* (1986). There are, however, a number of differences in the results between the two studies. This is particularly so for the ion products. In addition to the differences, we present here a detailed discussion of the results which tries to explain the formation of the observed product ions and the rate coefficients (determined at 300 K) in terms of the accessible ionic states of the reactant molecule. A further objective of the study was to explore the nature of the reactions in terms of how they were influenced by properties of the reactant molecules, i.e. ionization and dissociation energies, atomicities, dipole moments etc. This study formed part of a wider systematic study of the reactions of the atomic halogen ions F^+ , Cl^+ , Br^+ and I^+ , the results of which will be reported in a subsequent paper (Mayhew and Smith 1990).

2. Experiment

The SIFT apparatus has been discussed in detail in other publications (see the recent detailed review by Smith and Adams 1988) and only the salient features will be mentioned here. F^+ ions were generated from CF_3Br in an electron impact ion source and, after mass selection by a quadrupole mass filter, injected into pure helium carrier gas whence they were convected along the flow tube. Reactant gases were introduced in controlled amounts into the F^+ /carrier-gas swarm; the loss of the reactant F^+ ions and the appearance of the ion products of the reaction were monitored by a downstream mass spectrometer/detection system. The rate coefficients and the ion product distributions were then determined in the usual manner (Adams and Smith 1976). A point to note is that the detection mass spectrometer was operated at the lowest resolution possible whilst still maintaining clear separation of the product ions. Nevertheless, it was usually necessary to correct the product distributions for mass discrimination.

The F^+ ions were generated in both low pressure and high pressure electron impact ion sources. We presume that the F^+ ions were generated initially in their spin-orbit states in relative concentrations according to their statistical weights (5:3:1, favouring the 3P_2 ions). Since the F^+ ions do not suffer collisions with CF_3Br in the low pressure source, the F^+ entering the helium carrier gas presumably had a statistical mix of their spin-orbit states. In the high pressure source, collisions do occur and some redistribution amongst the states may result. However, the energy splitting is so small that the distribution between the states could be maintained near-Boltzmann in collisions with the helium atoms of the carrier gas. In any event, no difference in the reactivity of the F^+ ions as generated in either of the two types of ion source was observed with any of the molecules included in this study. (Note that differences in the reactivity of Br^+ ions have been observed in previous studies (Hamdan *et al* 1984) and in our study (Mayhew and Smith 1990) which has been attributed to Br^+ ions in their different spin-orbit states. However, the spin-orbit splitting in Br^+ ions is greater than for F^+ ions).

3. Results and discussion

The rate coefficients and product ion distributions for the reaction of F^+ ions with some fifteen different molecules are given in table 1. For the purposes of discussion the reactions have been presented in four groups. Groups (i) N_2 , CO, CO_2 , H_2 and D_2 and (ii) NO and O_2 comprise the essentially non-polar molecules which have relatively large and small ionization energies respectively. Group (iii) comprises the polyatomic hydrocarbons CH_4 , C_2H_2 , C_2H_4 and C_6H_6 and group (iv) comprises the dipolar molecules NH_3 , H_2O , H_2S and OCS. As will be seen, it is the physical properties of the molecules, in particular the availability of electronic states within the parent ions, that play an important role in determining the course of the reactions.

3.1. The N_2 , CO, CO_2 and H_2 reactions (group (i))

The reactions of F^+ with N_2 , CO and CO_2 all proceed at the gas kinetic (collision) rate, i.e. the measured rate coefficients, k , are equal to the collisional rate coefficients, k_c , calculated using the Langevin theory (Gioumousis and Stevenson 1958), and the single product ion of each reaction is the parent ion of the reactant molecule (N_2^+ ,

Table 1. Rate coefficients (k) and product ion distributions for the reactions of F^+ with a series of molecules at 300 K. The ionization energies of the reactant molecules in eV are given in parentheses. The recombination energies of the F^+ ground state are 17.42 eV (3P_2), 17.47 eV (3P_1) and 17.48 eV (3P_0).

Reactant molecule	Products ^a	k (cm ³ s ⁻¹) ^b	k_c (cm ³ s ⁻¹)
CO ₂ (13.72)	CO ₂ ⁺ (100)	1.2 (-9)	1.0 (-9)
CO (14.01)	CO ⁺ (100)	9.6 (-10)	9.7 (-10)
H ₂ (15.43)	<u>H</u> ⁺ (5), HF ⁺ (35) <u>H</u> ₂ ⁺ (60)	8.8 (-10)	1.6 (-9)
D ₂ (15.46)	<u>D</u> ⁺ (5), DF ⁺ (35) <u>D</u> ₂ ⁺ (60)	7.0 (-10)	1.2 (-9)
N ₂ (15.58)	N ₂ ⁺ (100)	9.0 (-10)	9.2 (-10)
NO (9.25)	NO ⁺ (100)	9.8 (-10)	9.6 (-10)
O ₂ (12.06)	O ⁺ (6), O ₂ ⁺ (85) <u>FO</u> ⁺ (9)	8.4 (-10)	8.6 (-10)
C ₆ H ₆ (9.24)	C ₃ H ₃ ⁺ (16), C ₄ H ₄ ⁺ (55) C ₅ H ₅ ⁺ (6), C ₆ H ₆ ⁺ (23)	2.0 (-9)	1.9 (-9)
C ₂ H ₄ (10.50)	<u>C</u> ₂ H ₂ ⁺ (27), C ₂ H ₃ ⁺ (66) <u>C</u> ₂ H ₄ ⁺ (6)	1.4 (-9)	1.4 (-9)
C ₂ H ₂ (11.40)	C ₂ H ⁺ (14), C ₂ H ₂ ⁺ (86)	1.4 (-9)	1.3 (-9)
CH ₄ (12.62)	CH ₃ ⁺ (100)	1.6 (-10)	1.3 (-9)
NH ₃ (10.15)	NH ⁺ (5), NH ₂ ⁺ (83) <u>NH</u> ₃ ⁺ (8), FH ⁺ (4)	2.0 (-9)	2.2 (-9)
H ₂ S (10.47)	S ⁺ (12), HS ⁺ (88)	8.2 (-10)	1.7 (-9)
OCS (11.19)	S ⁺ (90), OCS ⁺ (10)	1.5 (-9)	1.7 (-9)
H ₂ O (12.61)	<u>O</u> ⁺ (17), <u>OH</u> ⁺ (6) HF ⁺ (11), H ₂ O ⁺ (66)	3.1 (-9) ^c	2.3 (-9)

^a An ionic product which is underlined requires a neutral product molecule to be formed involving the fluorine atom (see text for details). Note that the ion product C₂H₂⁺ in the C₂H₄ reaction is possible if either H₂ or HF is formed as the neutral product. Product percentages are given in brackets.

^b Rate coefficients in the form $A(-B)$ represent $A \times 10^{-B}$ cm³ s⁻¹.

^c A greater uncertainty is associated with this value because of the appearance in the product ion spectrum of the secondary ion H₃O⁺ with the same mass as F⁺.

CO⁺, CO₂⁺). It seems likely that all three reactions proceed via exothermic resonant charge transfer into the vibrationally excited A ²Π states of the ions (Berkowitz 1979), for which there is a reasonable Franck-Condon overlap with the ground state of the precursor neutral molecule. The proposed N₂⁺(A ²Π_u) and CO⁺(A ²Π) product ions should be able to fluoresce into the \tilde{X} ²Σ_g⁺ and \tilde{X} ²Σ⁺ states of the ions, respectively, so strong fluorescence in the visible region of the spectrum should be observable in these reactions. It would be instructive to seek this fluorescence experimentally. Similarly, the CO₂⁺(A ²Π_u) state should make a radiative transition to a vibrationally excited level of the CO₂⁺(\tilde{X} ²Π_g) ground state.

The F⁺ reaction with H₂ (and D₂) is apparently more complex; three ionic products are evident, H₂⁺(60%), HF⁺(35%) and H⁺(5%), and the k is large but less than k_c ($\approx 0.6k_c$; see table 1). In this reaction, the Franck-Condon overlap is poor between the ground electronic state of H₂ and the available vibrational levels of the H₂⁺(\tilde{X} ²Σ_g⁺) ground ionic state at the recombination energy of F⁺ of 17.42 eV (see figure 1). However, in view of the large k , this reaction cannot be proceeding as 'simple charge transfer at a distance' but rather via an intimate collision. This deduction is also supported by

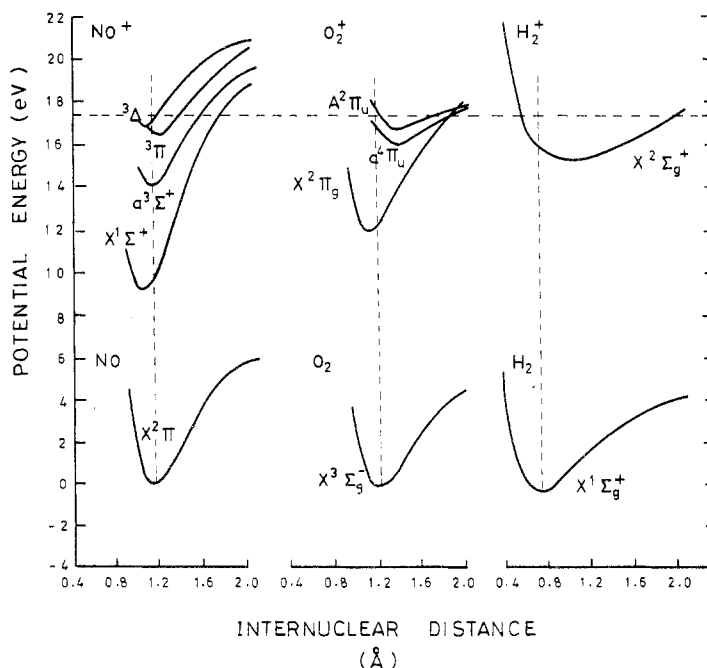


Figure 1. Potential energy curves of the ground electronic states of neutral NO, O₂ and H₂ and the ions NO⁺, O₂⁺ and H₂⁺, and some excited electronic states of NO⁺ and O₂⁺. The vertical broken lines are included to indicate the relative internuclear spacings of the neutral and ionic potential curves. The horizontal broken line is drawn at an energy of 17.42 eV, the recombination energy of F⁺ ions.

the observation that the H⁺ product channel is only exothermic if an HF molecule is formed (i.e. H⁺ + HF is the required product channel). The data interpretation for this reaction was complicated in that H₃⁺, HeH⁺ and H₂F⁺ appeared in the ion product mass spectrum. The H₃⁺ and H₂F⁺ product ions are formed in the secondary reactions of H₂⁺ and HF⁺ with H₂. The appearance of HeH⁺ is interesting in that it indicates that the H₂⁺ product ions are vibrationally excited ($v \geq 3$) whence they react with He atoms to form HeH⁺ (Chupka and Russell 1968). The exothermicity of the F⁺ + H₂ → H₂⁺ + F channel of 2 eV is clearly sufficient to populate H₂⁺ ($v \geq 3$). Thus the scheme for the reaction of F⁺ with H₂ in a helium bath gas is complex as is illustrated in figure 2. Note that the ion product distribution for the D₂ reaction mirrors that for the H₂ reaction; also note that the measured $k \approx 0.6k_c$.

3.2. The NO and O₂ reactions (group (ii))

Both these reactions proceed at the collisional rate (i.e. $k = k_c$). The only observed product for the NO reaction is NO⁺; the major product of the O₂ reaction is O₂⁺ (85%) with minor products FO⁺ (9%) and O⁺ (6%). For the channel producing O⁺ to be exothermic, a neutral FO molecule must be formed.

The production of NO⁺ in its ground vibronic state would necessitate the large reaction exothermicity (8.2 eV) to appear as translational energy of the product NO⁺ ion and the F atom. This is quite improbable and it is much more likely that resonant charge transfer occurs into an excited state of NO⁺. The total available recombination

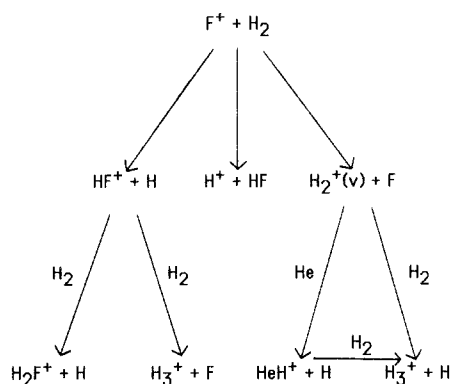


Figure 2. Scheme of the $F^+ + H_2$ reaction in helium bath gas. $H_2^+(v)$ indicates vibrationally excited H_2^+ . Note that H^+ , H_3^+ and H_2F^+ do not react with H_2 at a significant rate.

energy of F^+ ions (~ 17.42 eV) allows for the production of ions in a number of electronic states (see figure 1) such as the $a^3\Sigma^+$, and $b^3\Pi$ and $w^3\Delta$ states. The small Franck-Condon factors which describe the transition from the ground state of NO to the $a^3\Sigma^+(v)$ ensure that production of ions in that state is improbable. In this regard, production of NO^+ ions in the $w^3\Delta$ state is favoured. The photoelectron spectrum of NO (Edqvist *et al* 1971) also indicates that $NO^+(w^3\Delta)$ would be produced efficiently with photons of energy ~ 17.4 eV (comparable with the available F^+ recombination energy).

Noting that the $NO^+(w^3\Delta)$ ions would be metastable to radiative transitions to the $NO^+(X^1\Sigma^+)$ ground state, we deduced that the energetic metastable state of NO^+ would be present in the flow tube. It is known that Ar atoms undergo charge transfer with NO^+ ions in the $a^3\Sigma^+$ state (Glosik *et al* 1978, Dotan *et al* 1979) (and presumably the other triplet state ions do also), thus:



the rate coefficient being dependent on the NO^+ internal energy. Therefore Ar is a monitor gas for the metastable NO^+ ions. Note that for $NO^+(a^3\Sigma^+, v=0)$, reaction (1) is endothermic by 0.09 eV and hence the reaction has a thermal rate coefficient $\sim 3.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, somewhat less than k_c . The exciting result here is that on the introduction of Ar into the NO^+ ion swarm formed by the $F^+ + NO$ reaction, a fraction of the NO^+ ions was observed to react rapidly with argon ($k \sim 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). Clearly this indicates that at least part of the NO^+ product ions were formed in an electronically excited state above the $a^3\Sigma^+$ electronic state. That all the NO^+ ions do not react with Ar is explained by the fact that quenching of the $(NO^+)^*$ occurs in collisions with the NO in the flow tube (to predominantly the ground state of the NO^+ ion).

The occurrence of the (albeit) minor product ions $O^+(+FO)$ and $FO^+(+O)$ in the F^+ and O_2 reaction indicates that at least a fraction of the F^+ collisions with O_2 are intimate since chemical bonds are broken and made. Nevertheless, it is unlikely that the major O_2^+ ion is formed in the ground vibronic state because of the considerable exothermicity for that reaction. It therefore seems probable that the O_2^+ is formed in an excited electronic state; both the $4\Pi_u$ (high vibrational levels) and the $A^2\Pi_u$ (low vibrational levels) (see figure 1) have favourable Franck-Condon factors (Edqvist *et al* 1970) for their production, although this may not be relevant if the $F^+ + O_2$ reaction

is intimate, i.e. an $(\text{FO}_2^+)^*$ complex is formed prior to $\text{O}_2^+ + \text{F}$ production. The $a^4\Pi_u$ is metastable and should survive in the flow tube and again Ar is a potential monitor gas for O_2^+ ions in these states (Glosik *et al* 1978, Dotan *et al* 1979). On addition of Ar to the O_2^+ ion swarm, Ar^+ ions were observed, presumably resulting from the reaction:



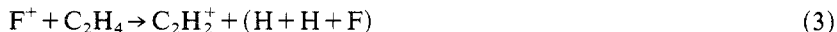
Thus a fraction at least of the O_2^+ ions formed in the $\text{F}^+ + \text{O}_2$ reaction are in electronically excited states.

3.3. The C_6H_6 , C_2H_4 , C_2H_2 and CH_4 reactions (group (iii))

The C_6H_6 , C_2H_4 and C_2H_2 reactions with F^+ are all very efficient ($k = k_c$ in all cases); the CH_4 reaction is much less efficient (see below).

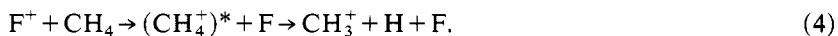
Four product ions are observed in the C_6H_6 reaction (see table 1), including the parent ion C_6H_6^+ (23%). The major product ion is C_4H_4^+ (55%). (This channel is exothermic by 3.89 eV assuming C_2H_2 is the neutral fragment). Interestingly it has been shown that this ion is a major fragment of the unimolecular decay of $(\text{C}_6\text{H}_6^+)^*$ formed by 30 eV electron impact on C_6H_6 (Ausloos 1981). This implies that the F^+ and C_6H_6 reaction proceeds via electron transfer first producing excited $(\text{C}_6\text{H}_6^+)^*$ which then largely fragments to the observed ionic products and neutral molecules and partly relaxes (radiatively) to stable C_6H_6^+ .

The C_2H_4 reaction also apparently proceeds via dissociative charge transfer, although the C_2H_2^+ product channel:



must result in the formation of either H_2 (exothermic by 4.3 eV) or HF (exothermic by 5.7 eV) to satisfy the energetics. It is interesting to note that no state of C_2H_4^+ with favourable Franck-Condon factors to the ground state of C_2H_4 exists at the 17.4 eV recombination energy of the F^+ ion (Rabalais 1977). Nevertheless reaction (3) proceeds at the collisional rate. This may indicate that reaction (3) proceeds via an intimate collision of the reactants forming a transient $(\text{FC}_2\text{H}_4)^+$ ion. This does not need to be invoked for the $\text{F}^+ + \text{C}_2\text{H}_2$ reaction, since C_2H_2^+ ($^2\Sigma_g^+$, v) can be produced by charge transfer with good Franck-Condon overlap with the ground state of C_2H_2 (Turner *et al* 1970). Perhaps significantly, the major product ion of the reaction is C_2H_2^+ (86%) (see table 1).

The CH_4 reaction is interesting in that only one fragment product ion, CH_3^+ , is observed and the reaction is inefficient ($k = 0.1k_c$, see table 1). Presumably the reaction proceeds via charge transfer to an electronic state of CH_4^+ which is either repulsive or fully predissociated:

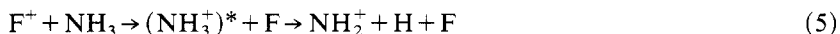


This reaction is exothermic by 3.1 eV. This may account for the relative inefficiency of the process, perhaps indicating poor Franck-Condon overlap. It is worthy of note that the vibrational bands in the photoelectron spectrum (PES) of CH_4 between the energies 12.6 eV to ~16 eV appear to be superimposed on a dissociative continuum (Rabalais 1977). Yet again, the parallels between the PES results and the results of the present experiments are clear.

3.4. The NH_3 , H_2O , H_2S and OCS reactions (group (iv))

The reactions of these very polar molecules proceed rapidly, the k for the NH_3 , H_2O and OCS reactions being equal (within the errors) to the collisional rate coefficients calculated using the average dipole orientation (ADO) theory (Su and Bowers 1979) (see table 1). The k for the H_2S reaction is, however, somewhat less efficient (see below).

Four product ions are observed in the NH_3 reaction, the parent ion NH_3^+ (8%) being only a minor product. NH_2^+ (83%) is the major product. It is of note that the second band in the photoelectron spectra of NH_3^+ , between 14.7 and 17.8 eV, appears to consist partly of a continuum and it has been suggested that dissociation of the excited $(NH_3^+)^*$ occurs (Rabalais *et al* 1973). Therefore in the F^+ reaction with NH_3 , the major process is probably:



although it should be noted that a minor product channel FH^+ (4%) is observed which implies an intimate (chemical) interaction between F^+ and NH_3 in a fraction of the collisions. Similarly, in the H_2O reaction, the minor ion product channels HF^+ (11%), O^+ (17%) and OH^+ (6%) for the latter pair of which the formation of HF is required to satisfy the energetics, also imply an intimate (chemical) reaction, even though the major ion product is H_2O^+ (66%).

The H_2S reaction proceeds at a rate significantly slower than collisional (i.e. $k \sim 0.5k_c$), in agreement with the k measured by Hamdan *et al* (1986). Significantly, there is no bound electronic state of H_2S^+ in the available energy region around 17.45 eV (Karlsson *et al* 1976). The reaction proceeds to produce the fragment ions SH^+ (88%) and S^+ (12%) and, like the CH_4 reaction, the reaction may be proceeding by the formation of a $(H_2S^+)^*$ which dissociates to the observed products (there is no necessity to invoke the production of neutral H_2 or HF in this reaction).

The OCS reaction is rapid and results in the fragmentation of the molecule producing S^+ (90%) as the major product and presumably neutral CO :



The parent ion OCS^+ (10%) is only a minor product. (Note that $CS^+ + FO$ is an energetically possible channel but it is not observed.) It seems likely that reaction (6) proceeds via charge transfer producing the excited OCS^+ ($\tilde{B}^2\Sigma^+$) ion (minimum energy required is 16.04 eV), which has been shown to be largely predissociated (Eland 1973), presumably to $S^+ + CO$.

4. Summary and concluding remarks

These studies of the reactions of energetic F^+ ions with a wide variety of molecular gases apparently proceed largely (but not exclusively) by charge transfer. We have attempted to explain the formation of the observed product ions in terms of the electronic states of the parent molecular ions which are energetically accessible in the reaction, and by drawing from available data on the photoelectron spectra of the reactant molecules. Thus the reactions often proceed via the formation of excited electronic states of the parent molecular ions which may be bound and may radiate to lower states (e.g. the N_2^+ and CO^+ product ions of the N_2 and CO reactions), or may be metastable as is the case for the NO^+ and O_2^+ product ions of the NO and O_2 reactions, or may be immediately repulsive (e.g. the CH_3^+ ion product of the CH_4

reaction). Thus we have detected the excited NO^+ and O_2^+ ions in the flow tube using the 'monitor gas' method. Optical radiation should be emitted from the excited ion products of some of these reactions and then spectroscopic studies would assist further in the detailed elucidation of the reaction mechanisms.

Acknowledgments

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