Reactions of $F_2^{+\cdot}$ with aromatic compounds in an ion trap mass spectrometer

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Abstract

The reaction of $F_2^{+\cdot}$ with aromatic compounds in the gas phase has been shown to proceed by way of two competing reactions: single electron transfer and addition–elimination.

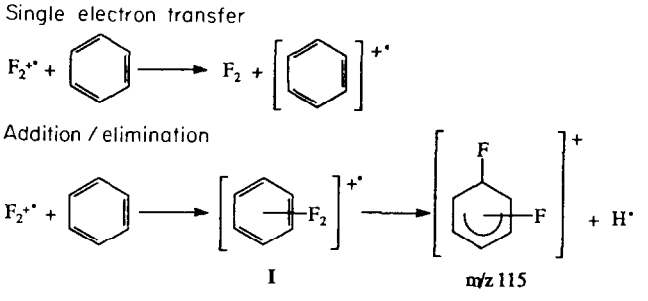
Introduction

Recent advances in mass spectrometry permit the study of ion–molecule reaction mechanisms in the gas phase. An ion trap mass spectrometer (ITMS) allows the isolation of ions with specific mass-to-charge ratio (*m/z*) and the subsequent reaction of these ions with neutral molecules. The course of the reaction may be monitored with time [1, 2]. For example, when $Cl_2^{+\cdot}$ is allowed to react with aromatic compounds in an ITMS, the initial process observed is charge transfer to produce Cl_2 and an aromatic cation radical – a single electron transfer or SET reaction [3]. The aromatic cation radical can then undergo further reaction, either fragmentation or reaction with residual neutral compounds in the ITMS.

The reactions of molecular halogen species in the gas phase have not been widely studied. In this work, we have examined the reaction of the fluorine cation radical ($F_2^{+\cdot}$) with aromatic compounds using the ITMS.

Results and discussion

When $F_2^{+\cdot}$ is formed in the presence of aromatic compounds in an ITMS, two major competing processes occur. These are single electron transfer (SET) and addition–elimination (A/E) as outlined in Scheme 1. The intermediacy of the cation radical **I** is postulated; its lifetime must be very short. The signal at *m/z* 116 cannot be attributed to **I**; its abundance corresponds



Scheme 1.

to the expected ^{13}C signal. A plot of the disappearance of $F_2^{+\cdot}$ (*m/z* 38) and the appearance of the benzene cation radical (*m/z* 78) and of the benzene–fluorine cation radical with the loss of a hydrogen atom (*m/z* 115) is depicted in Fig. 1. The simultaneous increase of *m/z* 78 ($M^{+\cdot}$) and *m/z* 115 ($M+F_2^{+\cdot}-H^{\cdot}$) is strongly suggestive of competitive processes. Thus, the benzene cation radical ($M^{+\cdot}$) is not a precursor to the difluorinated species, nor does it result from fragmentation of the fluorine addition product. If the formation of the difluorinated product were through initial charge transfer followed by attack of the resulting aromatic cation radical on residual fluorine gas, the appearance curves would be sequential, not simultaneous.

The results of the reaction $F_2^{+\cdot}$ with various aromatic compounds are listed in Table 1, the major product ions formed after 100 ms being given. Single electron transfer reactions are commonly observed in the gas phase; all of the compounds studied showed some reaction via this pathway. Strongly electron-donating substituents give large amounts of the SET product

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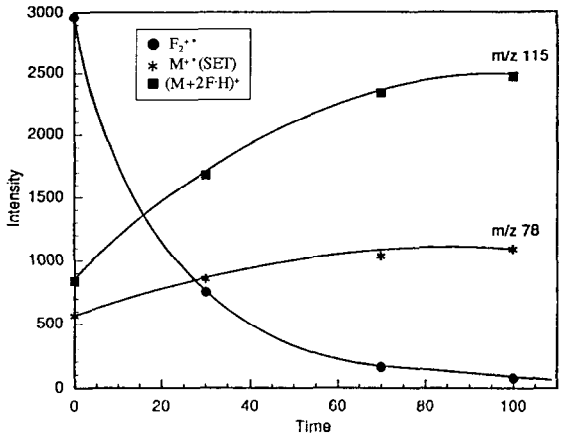
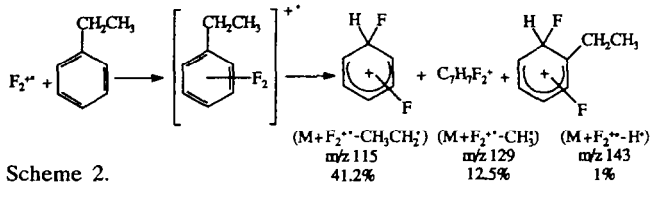


Fig. 1. Plots of intensity versus time for the reaction of benzene and $F_2^{+\cdot}$.

which are resistant to subsequent fragmentation. As the electron-donating ability of the substituent decreases, other processes such as fragmentation and addition–elimination reactions increase.

The competing addition–elimination reaction is especially interesting since gas-phase aromatic compounds seldom undergo addition to the nucleus. In all cases, the aromatic ion formed is difluorinated. The neutral species eliminated from the aromatic compound was often H$^{\cdot}$, but the substituent or a portion of the substituent on the aromatic compound was also eliminated. The distribution of the addition–elimination product ions detected for ethyl benzene is given as an example (Scheme 2).



Scheme 2.

Figure 2 shows the mass spectrum generated after a 150 ms reaction with $F_2^{+\cdot}$ and ethyl benzene. The ions resulting from single electron transfer (*m/z* 106) and from addition–elimination, *m/z* 115 $(M+F_2^{+\cdot}-CH_3CH_2^{\cdot})$, *m/z* 129 $(M+F_2^{+\cdot}-CH_3^{\cdot})$ and *m/z* 143 $(M+F_2^{+\cdot}-H^{\cdot})$, are observed. The most abundant addition–elimination product (*m/z* 115) results from the addition of $F_2^{+\cdot}$ to the aromatic nucleus with the elimination of $C_2H_5^{\cdot}$. This suggests that one fluorine atom adds at the most electron-rich carbon bearing the ethyl group which is subsequently lost. The product ion at *m/z* 129 is particularly interesting. Benzyl-substituted species undergo ring-expansion to tropyllium ions in the gas phase. The addition product probably loses a methyl radical with concomitant ring-expansion to form the ion at *m/z* 129. Elimination of H$^{\cdot}$, resulting in the ion at *m/z* 143, is minor as expected on the basis of the low stability of a hydrogen radical-leaving group. Dimerization reactions are also observed. The ion at *m/z* 221 corresponds in mass to $(2M+F_2^{+\cdot}-CH_3CH_2^{\cdot})$. The dimerization reaction appears to be sequential, based on the appearance curves of the ions detected with time (Fig. 3). The SET and A/E reactions occur simultaneously while formation of the dimer is observed after a time delay.

As the substituent on the aromatic ring becomes more electron-withdrawing the stability of the SET product decreases and fragmentation occurs. In fact, for the most electron-withdrawing group, NO_2, the predominant reaction is fragmentation (Table 1). It might also be noted that in this case that there is practically no competing addition–elimination reaction.

It is tempting to compare the chemistry of $F_2^{+\cdot}$ in the gas phase with that of F_2 in solution. In this study, we have determined that $F_2^{+\cdot}$ adds to the aromatic substrate followed by loss of a neutral radical to give a difluorinated species. In the synthesis of 5-fluorouracil, the addition of F_2 followed by the elimination of HF

TABLE 1. Effect of aromatic compound on reaction pathway after 100 ms reaction time[a]

Compound	SET (%)	A/E (%)	Dimer (%)	Fragmentation (%)	Unreacted $F_2^{+\cdot}$ (%)
1,3-Benzodioxole	77	13	0	2	8
Anisole	61	37	1	<1	<1
o-Xylene	50	40	0	2	8
Ethyl benzene	37	54	<1	2	6
Toluene	27[b]	66	<1	3	3
Benzene	16	78	3	1	2
Chlorobenzene	28	50	6	12	5
Methyl benzoate	9	44	0	33	14
Trifluoromethylbenzene	3	70	0	22	5
Nitrobenzene	10	2	0	60	28

[a]Percentages determined from total ion current.
[b]Includes molecular ion and tropylium ion percentages.

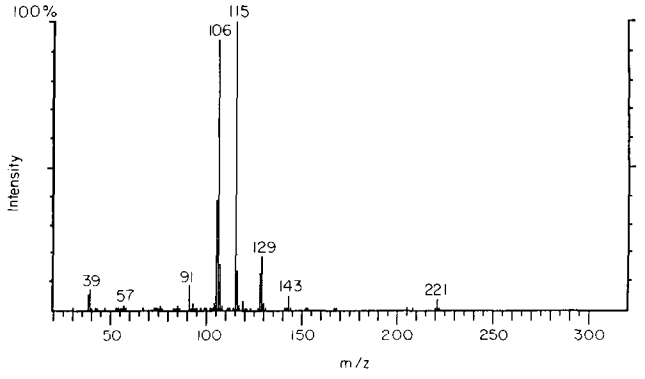


Fig. 2. Mass spectrum generated after 150 ms reaction of ethyl benzene and $F_2^{+\cdot}$.

has been proposed [4]. Although both processes involve initial addition, the excited intermediate decomposes differently in the gas phase.

Experimental

The data were acquired on a Finnigan-MAT ITMS instrument (San Jose, CA). The instrument design and operation of ion selection have been thoroughly discussed elsewhere [5–11]. A mixture of 10% fluorine in helium (Spectra Gases, Inc., Newark, NJ) was introduced via a pulsed gas introduction valve (IOTA ONE, General Valve Co., Fairfield, NJ). The pulsed gas introduction of fluorine was optimized for the formation of $F_2^{+\cdot}$ (*m/z* 38) and a 140 μs valve opening was used for all experiments. By using the pulsed valve, the concentration of residual fluorine after ionization was greatly diminished, reducing its interference in subsequent reactions. There was no effect of F_2 concentration (defined by the pulse time) on the competitive mechanisms or the disappearance of $F_2^{+\cdot}$. The rate of disappearance of $F_2^{+\cdot}$ was linear ($t_{1/2}=17\pm1$ ms) and unaffected by the fluorine pressure.

The aromatic compounds, obtained from Aldrich, were introduced continuously into the ITMS through a controlled leak valve at an optimized uncalibrated gauge pressure reading of 1.8×10^{-6} Torr. Helium was introduced through a second leak valve such that the total pressure reading was 1.2×10^{-5} Torr. The pressures reported have been taken directly from ion gauge readings. Helium buffer gas has been shown to increase instrument performance (sensitivity) by collapsing the ion beam toward the center of the trap, thus reducing the spread of ions. The helium buffer gas pressure did however affect the reaction mechanisms. Low helium pressure favored the SET mechanism and high helium pressure favored the addition–elimination mechanism. At low helium pressures the ions in the trap are further apart, hence there are fewer collisions and the electron-transfer mechanism is favored. At higher helium pressures, more collisions occur between ions and molecules in the ITMS and the addition–elimination reaction is enhanced. Helium pressure also affected subsequent ion–molecule reactions such as dimerization.

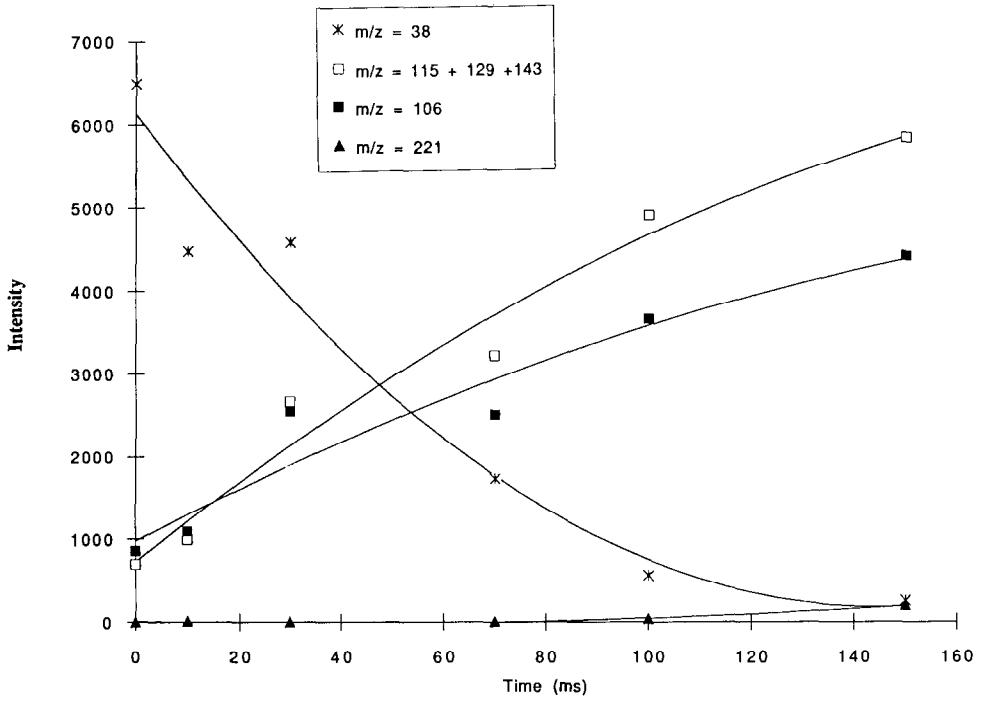


Fig. 3. Plots of intensity versus time for the reaction of ethyl benzene and $F_2^{+\cdot}$.

The ITMS routinely operates at temperatures between 25 °C and 100 °C. At source temperatures greater than 100 °C, the sensitivity decreased dramatically. However, within the working temperature range, the product distribution between the single electron transfer products and those arising from addition–elimination was unaffected by source temperature.

The scan function for the reaction of the fluorine cation with the aromatic compound involved ionization, ion isolation, reaction time and product mass spectrum generation. The start triggered the sequence beginning with a 140 μs pulse of fluorine gas into the trap followed by a 29 ms ionization pulse. Standard 70 eV electron ionization was used. After a 1.1 ms settling time, the fluorine radical cation (m/z 38) was isolated by ramping the RF voltage and then applying a DC voltage, followed by ramping the RF and DC voltages back to their initial settings so that all the ions formed by reaction of $F_2^{+\cdot}$ and neutral molecules were stored. Isolation of the single mass to charge ion took 3.2 ms. Mass spectra were generated at several points within 1–200 ms after isolation. For a 'zero time' reaction, the multiplier was activated and the RF scan initiated as soon as the isolation sequence was complete and represents approximately 3–5 ms elapsed time. The source temperature was maintained at 30 °C for all experiments. Data were collected using various combinations of aromatic reactant pressures and helium buffer gas pressures.

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