

# Combined ab Initio MO and Experimental Studies on the Unimolecular HF Loss from Protonated Fluorobenzene in the Gas Phase<sup>†</sup>

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**Abstract:** The unimolecular loss of hydrogen fluoride from protonated fluorobenzene was studied by chemical ionization mass spectrometry and MP2/6-31G\* ab initio MO calculations. Kinetic energy release measurements point to the existence of three distinct pathways. In addition to direct HF loss from the fluorine-protonated molecule, the calculations reveal the coexistence of 1,1- and 1,2-elimination processes, both derived from ring-protonated isomers. The structures and energetics of the relevant minima and transition structures have been determined, and the combined experimental/theoretical findings point to a unique situation in which protonation of the same precursor molecule by different Brønsted acids affords identical products via three different reaction channels.

## Introduction

The topic of protonation of benzene derivatives is of long-standing interest in chemistry in general and organic mass spectrometry in particular.<sup>1,2</sup> Numerous studies have established the thermochemistry and kinetics of these protonation reactions<sup>3–7</sup> with special emphasis on the problem of site-selectivity in substituted benzenes.<sup>8,9</sup>  $\sigma$ -Complexes are nowadays accepted as the most stable form, both in solution and in the gas phase.<sup>1</sup> In a monosubstituted benzene derivative, five different protonation sites are of chemical significance: (i) ring protonation in the ortho, meta, and para positions (1, 2, and 3, respectively), (ii) ipso protonation (4), and (iii) direct protonation of the functional group X (5) (Chart I).

Other structures, for example the “face-on”<sup>3</sup> and “side-on”<sup>10</sup>  $\pi$ -complexes, have also been discussed in the literature and found to correspond to energy-rich transition structures. On the basis of a computational approach, a “ring-walk” mechanism<sup>11</sup> was suggested for the interconversion of the ring-protonated isomers 1–4 via hydrogen-bridged transition structures (in analogy to 6) to account for the experimentally observed hydrogen equilibration.<sup>12</sup> For X = F, various theoretical studies based on both semiempirical<sup>9,13–15</sup> and ab initio<sup>9,16–18</sup> MO calculations indicate energy barriers between 7 and 20 kcal/mol for this reaction.

In the case of fluorobenzene (X = F), which forms the subject of the present study, according to 6-31G\*\* calculations<sup>18</sup> structure 3 has been found to be the most stable C<sub>6</sub>H<sub>6</sub>F<sup>+</sup> isomer reflecting the para-directing nature of a fluoro substituent for the case of electrophilic attack. Mason et al. estimated the relative stabilities of the isomers 1, 2, 4, and 5 by the MNDO method and also by ab initio MO calculations employing the 4-31G basis set.<sup>9</sup> In an early ab initio MO study using the minimal STO-3G basis set, the possibility of fluorine migrations via the fluorine-bridged transition structure (TS) 7 was considered (Chart II).<sup>16</sup> Similar transition structures have been located by MNDO calculations<sup>14,15</sup> and were used to explain the experimentally observed<sup>19</sup> elimination of CF<sub>2</sub> from protonated polyfluorobenzenes. To the best of our knowledge, there exist no ab initio MO studies evaluating the energy barriers connecting the ring-protonated ions 1–4 with the fluorine-protonated isomer 5.

The loss of HF is the main process in the unimolecular as well as the collision-induced decomposition of protonated fluorobenzene. In previous experiments<sup>9</sup> using methane as a reagent gas in chemical ionization, the bimodal distribution of the kinetic energy release (KER) associated with the unimolecular HF loss was interpreted in terms of two different processes: (i) direct pro-

Chart I

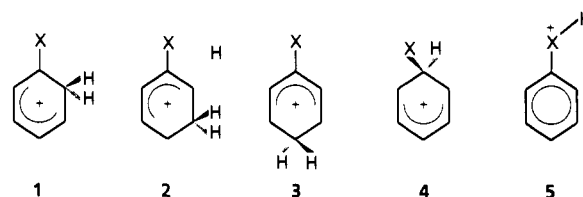
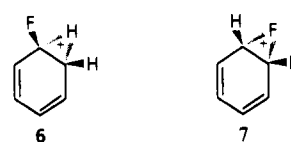


Chart II



tonation of the fluorine atom, leading to an intermediate having a long carbon–fluorine bond [C<sub>6</sub>H<sub>5</sub><sup>+</sup>...FH] (this ion/dipole complex serves as a precursor for the loss of HF) and (ii) the formation of a ring-protonated species, followed by first equilibration of the hydrogen atoms via the “ring-walk” mechanism and then transfer of a proton from a ring position to the fluorine atom.

In the present study, the results of refined measurements of the KER for the HF loss from protonated fluorobenzene are reported and the data are combined with detailed ab initio MO

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<sup>†</sup> Dedicated to Professor John L. Holmes on the occasion of his 60th birthday.

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**Table I.** Comparison of Proton Affinities (kcal/mol) of Various Protonation Sites of Fluorobenzene giving Rise to the  $C_6H_6F^+$  Isomers 1–5<sup>a</sup>

	protonation of $C_6H_5F$ at the position				
	ortho 1	meta 2	para 3	ipso 4	fluorine 5
MNDO	175.1	168.4	176.1	160.3	162.4
4-31G	184.4	178.5	186.6	170.1	138.8
exptl	181.8 <sup>b</sup>				131.8–143.8

<sup>a</sup>Data are taken from refs 9 and 27. <sup>b</sup>This value corresponds to a ring-protonated isomer or fluorobenzene.

calculations; the latter are used to estimate the thermochemistry of minima and transition structures relevant to the ground-state potential energy surface of protonated fluorobenzene. Based on these findings, we will present a reaction mechanism which is consistent with past and present observations.

### Experimental Section

Fluorobenzene was protonated in a chemical ionization source (electron energy 100 eV; repeller voltage ca. 0 V) of a modified VG Instruments ZAB/HF AMD four-sector tandem mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector), which has been described in detail elsewhere.<sup>20</sup> Several reagent gases of different proton affinities were applied, using a very large excess of the protonation agent (source housing pressure ca.  $10^{-4}$  mbar). The ions were selected by means of B(1), and the KER of the unimolecular HF loss from protonated fluorobenzene, occurring in the field-free region preceding the first electric sector, was recorded by scanning E(1) at an energy resolution such that the half-width of the parent ion was always <2 eV; this experiment will be referred to as an E(1) scan. Due to the composite nature of the peaks for the HF loss from protonated fluorobenzenes (vide infra), the KER for the HF loss had to be analyzed by deconvolution. For this purpose we used a least-squares fit of the peak shape with a sum of three Gaussian-type functions.<sup>21</sup> For the determination of kinetic isotope effects in the metastable ion spectra of labeled precursor ions, the species of interest were selected by means of B(1)/E(1) at a mass resolution  $m/\Delta m = 3000$ , and the fragmentation processes, occurring in the field-free region preceding the second magnet, were monitored by scanning B(2); this experiment will be referred to as a B(2) scan. In contrast to an E(1) scan, the B(2) scan provides a resolution high enough to separate the signals corresponding to HF and DF losses. The fourth sector was not used in the present study. All spectra were accumulated and on-line processed either with the VG 11/250 or the AMD-Intectra DP10 data system; 5–50 scans were averaged to improve the signal-to-noise ratio.

### Computational Details

The ab initio MO calculations of the  $C_6H_6F^+$  structures relevant to this study were performed on a CONVEX 230 computer with the GAUSSIAN 90 program package.<sup>23</sup> The standard polarized split valence basis sets (3-21G\* and 6-31G\*)<sup>24</sup> have been used for the geometry optimization of relevant points of the potential energy surface without applying any symmetry constraints. Stationary points were characterized by analyzing the second derivative of the HF/3-21G\* calculated Hessian force-constant

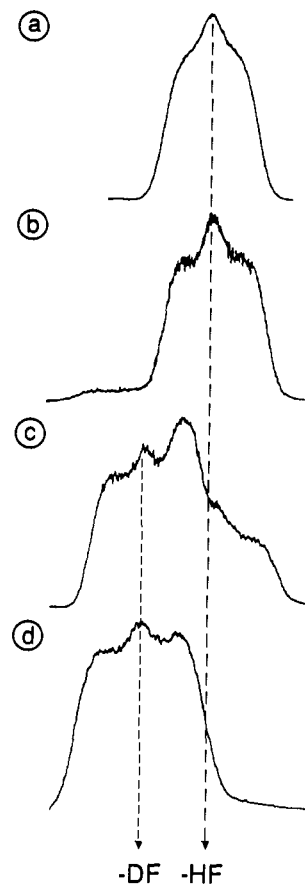
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(21) The composite peak shown in Figure 1a was modeled by three Gaussian functions  $G(E) = \sum_{i=1}^3 c_i \exp[-(E/a_i)^{n_i}]$ . For the analysis of the broad component ("flat-top"), two Gaussian functions were used; in order to account for instrumental effects, one of these Gaussian functions was chosen with a negative  $c_i$ . The kinetic energy release for the broad component was calculated from the peak width at the horns. For the small component, the power  $n_i$  was found to be close to  $n_i = 2$ ; this indicates that the assumptions made in the review article on KER by Holmes and Terlouw (ref 22) are justified in the present case. The KER for this component given in the text refers to  $T_{0.5}$ .

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**Figure 1.** Unimolecular losses of HF and DF from protonated fluorobenzene and isotopomers following protonation with hydrogen as reagent gas (a)  $C_6H_5F/H_2$ ; (b)  $C_6H_5F/D_2$ ; (c)  $C_6D_5F/H_2$ ; (d)  $C_6D_5F/D_2$ .

matrix. The effect of electron correlation energy was taken into account by performing second-order Møller-Plesset<sup>25</sup> (MP2) perturbation calculations. The geometries have only been reoptimized at the MP2/3-21G\* level of theory; geometry optimization of a system as big as  $[C_6H_6F]^+$  with the more common<sup>26</sup> MP2/6-31G\* procedure were not feasible as they exceed our computational facilities. However, single-point MP2 calculations have been performed with the 6-31G\* basis on both the MP2/3-21G\* and the HF/6-31G\* optimized geometries. If not stated otherwise, the relative stabilities of the various structures refer to the MP2/6-31G\*//6-31G\* level of theory; energies are given in kcal/mol and are relative to the ortho-protonated fluorobenzene isomer 1. The calculated harmonic frequencies of the species are available from the authors upon request.

### Results and Discussion

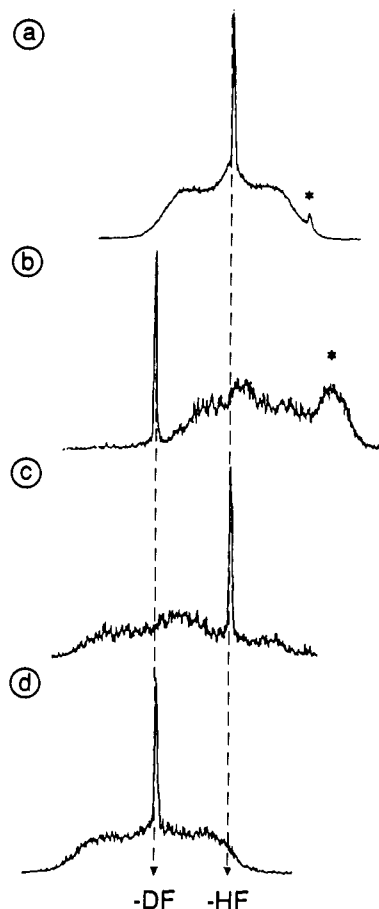
When fluorobenzene (for proton affinities (PA), see Table I) is protonated using molecular hydrogen (PA = 101 kcal/mol<sup>27</sup>) as reagent gas, unimolecular loss of HF from  $C_6H_6F^+$  is observed. The kinetic energy releases associated with this reaction are given for the various isotopomers in Figure 1.

The metastable ion (MI) spectra (E(1) scan) show a composite peak shape<sup>22</sup> consisting of a broad component with  $T_{0.5} = 424$  meV and a narrower one ( $T_{0.5} = 16$  meV) for the HF loss. The complete deconvolution of the KER for the partially labeled ions is not possible because of the overlap of the signals for HF/DF losses, as shown in Figures 1b and 1c. The spectrum of the fully deu-

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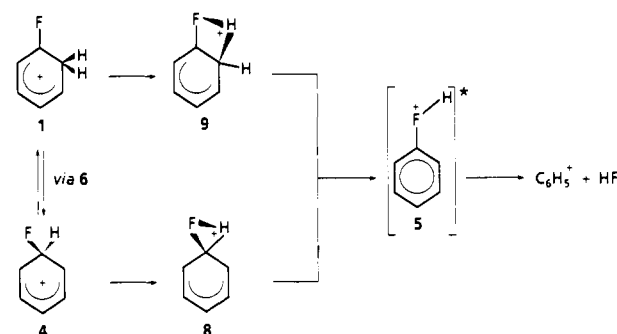
**Figure 2.** Unimolecular losses of HF and DF from protonated fluorobenzene and isotopomers following protonation with methane as reagent gas: (a)  $C_6H_5F/CH_4$ ; (b)  $C_6H_5F/CD_4$ ; (c)  $C_6D_5F/CH_4$ ; (d)  $C_6D_5F/CD_4$ . Signals labeled with an asterisk correspond to artifact peaks. These are due to the following: (i) In a the  $^{13}C$  contribution of  $M^{++}$  to the isobaric  $MH^+$  signal gives rise to the unimolecular losses of  $F^+$ , HF, and HF/ $H^+$ , respectively. The ratio of  $M^{++}/MH^+$  is 10–15 depending on the reactant gas pressure. (ii) In b the artifact arises from  $CHD_3$  loss from the  $^{13}C$  isotopomer of  $C_7H_5D_4^+$ . This ion is presumably formed by exothermic ion/molecule reactions of  $C_6H_5DF^+$  with  $CD_4$  or of  $C_6H_5F$  with  $CD_5^+$  (losses of DF).

terated ion  $C_6D_6F^+$  (Figure 1d) is close to that of the unlabeled compound (Figure 1a). The investigation (B(2) scan) of the mixed deuterated ions  $C_6X_6F^+$  ( $X = H, D$ ) reveals the existence of a kinetic isotope effect: after statistical correction for the number of hydrogen/deuterium atoms in an equilibrated  $C_6X_6F^+$  system ( $X = H, D$ ), the ratio of the HF/DF losses from both  $[C_6H_5F]D^+$  and  $[C_6D_5F]H^+$  gives a value of 2.5.

When  $CH_4$  (PA = 132 kcal/mol) is used as reagent gas, the KER signal is changed dramatically (Figure 2a). In addition to the bimodal component, a third peak with an extremely small kinetic energy release component ( $T_{0.5} = 1.3$  meV) appears. According to Mason's arguments,<sup>9</sup> the narrow peak can be assigned to the HF loss from the directly fluorine-protonated ion **5**. As will be demonstrated further below, this interpretation is also in keeping with the ab initio MO results.

The unimolecular HF/DF losses from protonated fluorobenzene and its isotopomers are shown in Figure 2a–d. From the study of the partially labeled ions an unambiguous assignment is possible for the narrow component; this signal is due to the direct protonation of the fluorine atom followed by loss of HX and DX, respectively, without a hydrogen scrambling process. For example, in the protonation of  $C_6H_5F$  with  $CD_4$  (Figure 2b) the narrow peak corresponds to DF loss, while the product formed from fluorobenzene- $d_5$  and  $CH_4$  (Figure 2c) has a narrow component which corresponds exclusively to the loss of HF. However, due to the hydrogen exchange processes of the ring-protonated species (see below) and the overlaps in the KER spectra of partially

Scheme I



deuterium labeled ions, no further insight into the mechanism(s) of the unimolecular HF and DF losses from the ring-protonated isomers can be extracted from the experiments using methane as reagent gas.

The comparison of the KERs in Figures 1 and 2 indicates that at least three different processes contribute to the unimolecular HF loss from protonated fluorobenzene. As one process (narrow component in Figure 2) can be assigned to the direct protonation of the fluorine atom, the two components of the KERs shown in Figure 1 have to involve ring-protonated isomers.

At this stage it is perhaps appropriate to begin the discussion with some speculations on chemically feasible possibilities: (i) Ring-opened isomers can be readily excluded on thermochemical grounds as the energetically most stable open-chain structures are lying at least 60 kcal/mol higher in energy than **1**.<sup>1,2</sup> Similarly, the possibility of carbon-skeleton rearrangement products or the involvement of highly excited states are not taken into account. (ii) HF loss from protonated fluorobenzene may give rise to two electronic states of the resulting phenyl cation. In fact, according to ab initio calculations at the MCSCF/6-31G\* level,<sup>28</sup> the singlet/triplet gap in the phenyl cation ( $^1A_1 \rightarrow ^3B_2$ ) is as small as 5 kcal/mol. While the existence of both (singlet and triplet) electromers of protonated fluorobenzene can not be excluded rigorously, an electronic configuration in which five electrons in the  $\pi$ -orbitals of the aromatic ring and one electron is located in a  $\sigma$ -orbital of a hydrogen atom is quite unlikely.<sup>29</sup> (iii) A high-energy degenerated fluorine migration (i.e.,  $4 \rightarrow 7$ ) may be the origin of a different kinetic energy release. (iv) Finally, HF elimination may proceed from the ortho- and ipso-protonated fluorobenzene isomers **1** and **4**, and these 1,2- and 1,1-eliminations may compete with each other. Due to the fact that **1** and **4** are connected via the low-energy hydrogen "ring-walk" mechanism, a competition between the 1,1- and 1,2-elimination modes is reasonable, provided that the activation barriers of the dissociation steps are of comparable heights.

In order to distinguish between scenarios iii and iv, we have performed ab initio MO calculations on the singlet potential energy surface (PES) of  $C_6H_6F^+$ . The energetics and structures of the meta- and para-protonated fluorobenzenes **2** and **3** have been studied previously.<sup>9,18</sup> As they are not relevant for the loss of HF, we have restricted ourselves to that part of the PES which is directly connected with the HF elimination channel, starting with the ortho-protonated system **1** (Scheme I).

**A. Minima on the PES.** The ortho-protonated fluorobenzene **1** has been found to correspond to the most stable form of the isomers relevant to the present study; this holds true at all computational levels (Table II). **1** is characterized by positive eigenvalues only in the hessian matrix. The lowest frequency (188  $cm^{-1}$ ) corresponds to a "rocking" vibration of the out-of-plane hydrogen atoms of the methylene group. The HF/6-31G\* optimized geometry of **1** is shown in Figure 3 and reflects the

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(29) For the fluorine protonated ion-dipole complex **5** a triplet is also conceivable. However, this situation is not relevant for the KER, as the symmetry-allowed dissociations of both the singlet and triplet ion-dipole complexes of **5** are expected to give rise to a small kinetic energy release.

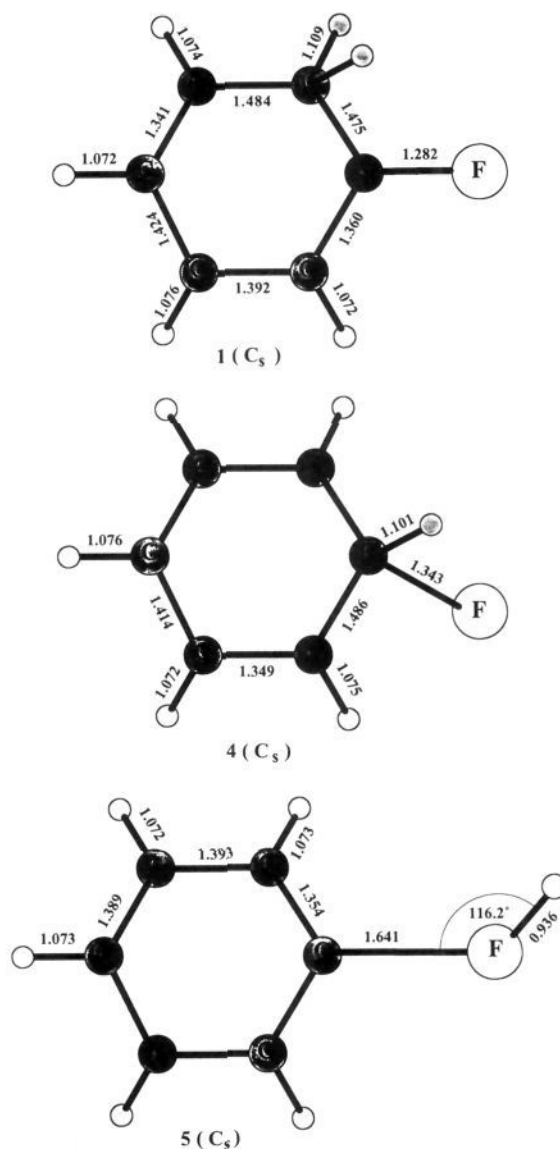
**Table II.** Calculated SCF and MP2 Total Energies ( $E_{\text{tot}}$ , hartrees) and Relative Stabilities ( $\Delta E$ , kcal/mol)

ion	NIMAG <sup>a</sup>	HF/3-21G*// HF/3-21G*	HF/6-31G*// HF/6-31G*	MP2/3-21G*// MP2/3-21G*	MP2/6-31G*// MP2/3-21G*	MP2/6-31G*// HF/6-31G* <sup>b</sup>
1	0	-328.039 007 0.0	-329.864 189 0.0	-328.680 054 0.0	-330.766 452 0.0	-330.765 968 0.0
4	0	-328.009 647 18.4	-329.837 668 16.1	-328.646 685 20.9	-330.736 211 19.9	-330.735 562 19.1 (19.0)
5	0	-327.988 480 31.7	-329.793 073 44.6	-328.635 736 27.8	-330.713 252 33.4	-330.712 406 33.6 (32.3)
6	1	-327.983 663 34.7	-329.816 434 29.9	-328.633 911 28.9	-330.731 585 21.9	-330.731 131 21.9 (20.2)
7	1	-327.957 791 50.9	-329.779 565 53.1	-328.608 805 44.7	-330.692 853 46.2	-330.692 508 46.1 (45.7)
8	1	-327.917 454 76.3	-329.730 39 83.9	-328.584 214 60.1	-330.662 312 60.4	-330.669 119 60.8 (57.6)
9	1	-327.910 902 80.4	-329.725 379 87.1	-328.567 243 70.8	-330.666 900 63.2	-330.665 774 62.9 (58.6)
10	1	-327.986 282 33.1	-329.790 743 46.1	-328.633 727 29.1	-330.711 403 34.9	-330.710 341 34.9 (33.2)

<sup>a</sup>NIMAG = number of imaginary frequencies. <sup>b</sup>The relative energies given in parentheses are corrected for the zero-point vibrational energies; the latter are uniformly scaled by a factor of 0.894.

substituent effects mentioned earlier. The C–C bond lengths to the protonated carbon atom are elongated to 1.48 Å, and the associated C–C–C bond angle decreases from 120° to 116°. The hydrogen atoms of the methylene group are lying in a plane perpendicular to the aromatic ring with a C–H bond length of 1.109 Å and a H–C–H bond angle of 104°. The effect of protonation on the other C–H bonds is very small, as they remain almost unperturbed as compared to fluorobenzene. A similar situation is found for the ipso-protonated fluorobenzene **4** (Figure 3b). The C–F bond is slightly elongated to a value of 1.34 Å, whereas the length of the associated C–H bond increases significantly to 1.10 Å. The F–C–H bond angle amounts to 71° with an H–F distance of 2.00 Å. **4** is found to be less stable than **1** by 19.1 kcal/mol at the highest level of theory used. This value is only slightly dependent on the level of theory applied. Hehre and Hiberty<sup>16</sup> reported a value of 19.4 kcal/mol calculated using the minimal basis set. Our HF/3-21G\* calculation gives a value of 18.4 kcal/mol. Mason<sup>9</sup> reported an energy difference of 14.8 kcal/mol for the two isomers **1** and **4**, and this value is also reproduced by further extension of the basis (14.4 kcal/mol at HF/6-31G\*). We have found that the effects of correlation energy for the structures and relative stabilities of the two “classical” Wheland<sup>30</sup> or Pfeiffer–Wizinger<sup>31</sup> complexes **1** and **4** are quite small. At the MP2/3-21G\* level of theory the energy difference is computed to be 20.9 kcal/mol, and this value remains almost insensitive to the extension of basis set as indicated in Table II (MP2/6-31G\*//MP2/3-21G\*, 19.9 kcal/mol, and MP2/6-31G\*//HF/6-31G\*, 19.1 kcal/mol). From this convergence we conclude that a sufficient description of the geometry of the C<sub>6</sub>H<sub>6</sub>F<sup>+</sup> system is obtained at the SCF level. Actually, for all isomers studied, the difference between MP2/6-31G\*//HF/6-31G\* and MP2/6-31G\*//MP2/3-21G\* calculated total energies is smaller than 1 kcal/mol.

The fluorine-protonated isomer **5** (Figure 3) can be described as an ion–dipole complex<sup>32</sup> between a singlet phenyl cation and neutral hydrogen fluoride. As compared to a normal C–F bond (1.36 Å)<sup>18</sup> the C–F distance in **5** is much longer. At the UHF/3-21G\* level, a distance of 1.60 Å is computed, which after inclusion of electronic correlation (MP2/3-21G\*) elongates slightly to 1.62 Å. Almost the same bond length (1.64 Å) is calculated with the larger 6-31G\* basis set. In contrast to other substituent-protonated benzene derivatives,<sup>33</sup> the H–F bond is in a plane vertical to the plane of the benzene ring with a C–F–H bond angle of 116°. Irrespective of the level of calculation, the ion–



**Figure 3.** HF/6-31G\* optimized geometries of the minima **1**, **4**, and **5** (bond lengths in angstroms, bond angles in degrees).

dipole complex **5** is always higher in energy than all ring-protonated isomers. As already mentioned above for the isomers **1** and **4**, for **5** similar conclusions can be drawn from the energy

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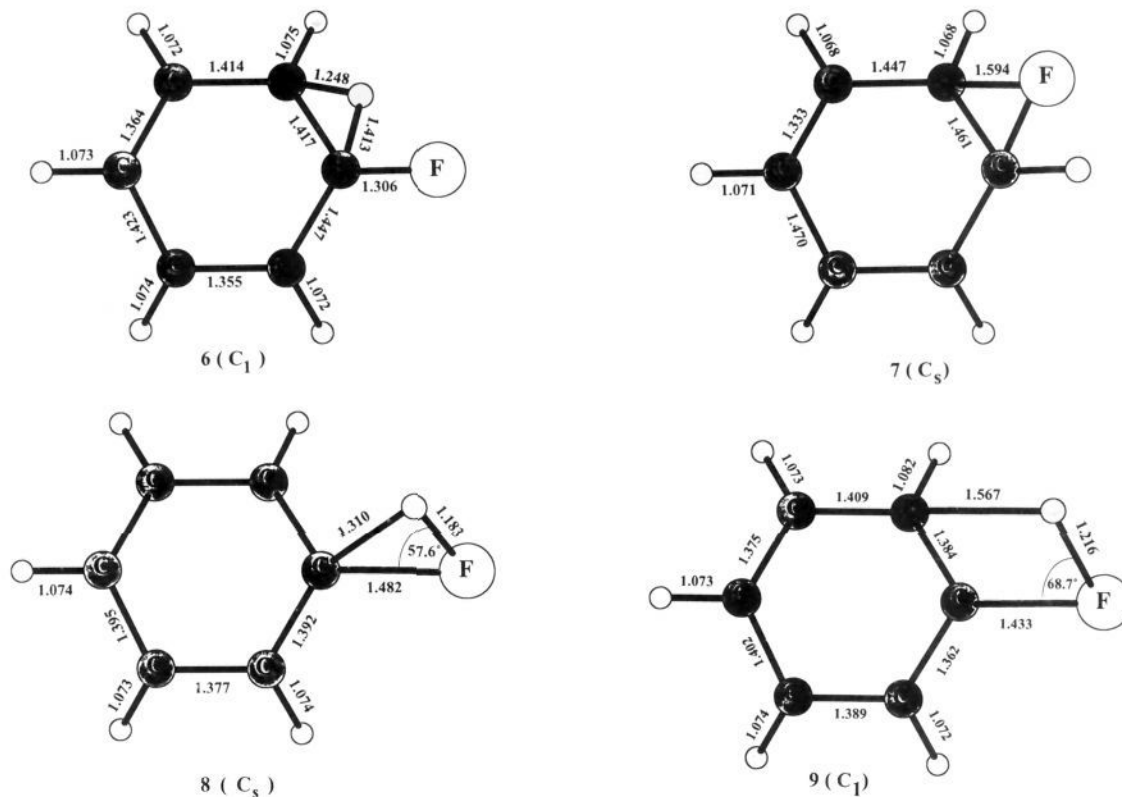


Figure 4. HF/6-31G\* optimized geometries of transition structures 6, 7, 8, and 9 (bond lengths in angstroms, bond angles in degrees).

convergence with respect to the size of the basis set and the correlation effects. At the highest level of theory used, **5** is lying 33.6 kcal/mol above **1**. The relative stability of **5** with respect to the isolated molecules, i.e., the phenyl cation and hydrogen fluoride, is computed to be 6.7 kcal/mol. This value is of the magnitude expected for ion-dipole interactions with *delocalized* cations and is within the range of the experimental data.<sup>9,27</sup>

**B. Transition Structures.** The interpretation that HF is quite weakly bound to the phenyl cation in the ion-dipole complex **5** is supported by the existence of a very small rotational barrier. At the MP2/6-31G\*//HF/6-31G\* level of theory we located a transition structure (**10**) which is only 1.3 kcal/mol higher in energy than the corresponding minimum **5**. The geometry of **10** is almost identical to that of **5** with the two exceptions: (i) in **10** the H-F substructure is lying in a plane with the aromatic ring and (ii) the C-F bond of **10** is slightly elongated by 0.008 Å. The analysis of the second derivative of the force constant matrix shows an imaginary frequency of  $-234\text{ cm}^{-1}$  associated with the rotation around the C-F axis.

The ortho- and the ipso-protonated isomers **1** and **4** are connected via a 1,2-hydrogen migration. The geometry of the corresponding transition structure (**6**) is given in Figure 4. **6** has a "classical" topology with a bridging hydrogen atom located over one C-C bond almost perpendicular to the aromatic ring.<sup>2,16</sup> The corresponding C-H bond distances are 1.41 Å to the fluorine-bearing carbon atom (C-1) and 1.25 Å to C-2; the C-C bond of the bridging center is elongated to 1.42 Å. All other bonds and angles are nearly unperturbed with the exception of those involving the fluorine and the ortho hydrogen atoms, which are shifted out of the "benzene" plane by 8° and 4°, respectively. The imaginary frequency associated with the hydrogen movement has a value of  $-1182\text{ cm}^{-1}$ . The SCF-calculated energy barrier for the process **1** → **6** decreases significantly by inclusion of correlation energy and reaches 21.9 kcal/mol at the highest level of theory used in the present study. This is in good agreement with previous calculations<sup>13,14,16</sup> and experimental findings,<sup>2</sup> which place the height of the barrier of the hydrogen equilibration in protonated benzenes to an interval of 5–20 kcal/mol.

Similarly to **6**, the degenerated ipso-ipso fluorine migration via transition structure **7** (Figure 4) can also contribute to the hydrogen equilibration preceding XF loss (X = H, D). In addition, this path may also be involved in the intramolecular energy redistribution in protonated fluorobenzene. Transition structure **7** is characterized by an imaginary frequency of  $-492\text{ cm}^{-1}$ , reflecting the drastic elongation of the C-F bond to 1.59 Å. This geometry change is also accompanied by an increase of the corresponding C-C bond length to 1.46 Å. As compared to the hydrogen bridge in **6**, the fluorine bridge in **7** does not lie directly over a ring bond. The computed relative energy of **7** (46.1 kcal/mol) is in surprisingly good agreement with previous MNDO results.<sup>14,15,34</sup>

In addition to **7**, a further fluorine-bridged transition structure (**11**), structurally almost identical to **7**, has been found. However, in comparison to **7**, the C-F bond of this energy-rich species (75.5 kcal/mol relative to **1**) is shortened to 1.45 Å, whereas the corresponding C-C bond is broken, as indicated by a C-C distance of 1.93 Å. The fluorine atom is shifted toward the CC plane. We assign isomer **11** to a fluorine ring insertion product; the imaginary frequency of  $-805\text{ cm}^{-1}$  is in keeping with a movement toward a fluorepinium ion, analogous to the oxepine structure described previously in a different context.<sup>16</sup>

For the unimolecular loss of HF from protonated fluorobenzene, the two transition structures **8** and **9** are crucial as they connect the ring-protonated isomers with the ion-dipole complex **5**. Both transition structures, corresponding to formal 1,1- and 1,2-elim-

(34) For a more recent discussion on fluorine-bridged cations, see: Shalar, T. A.; Morton, T. H. *J. Am. Chem. Soc.* **1991**, *113*, 6771.

(35) Gross, M. L.; DeRoos, F. L.; Hoffmann, M. K. *Org. Mass Spectrom.* **1977**, *12*, 258.

(36) However, an interpretation of kinetic energy release data based only on the analysis of transition-state structures without taking into account dynamic effects is not necessarily imperative; for a detailed discussion and further references, see: Donchi, K. F.; Derrick, P. J. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1983; Vol. 24.

(37) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, R. G. *Metastable Ions*; Elsevier: Amsterdam, 1973.

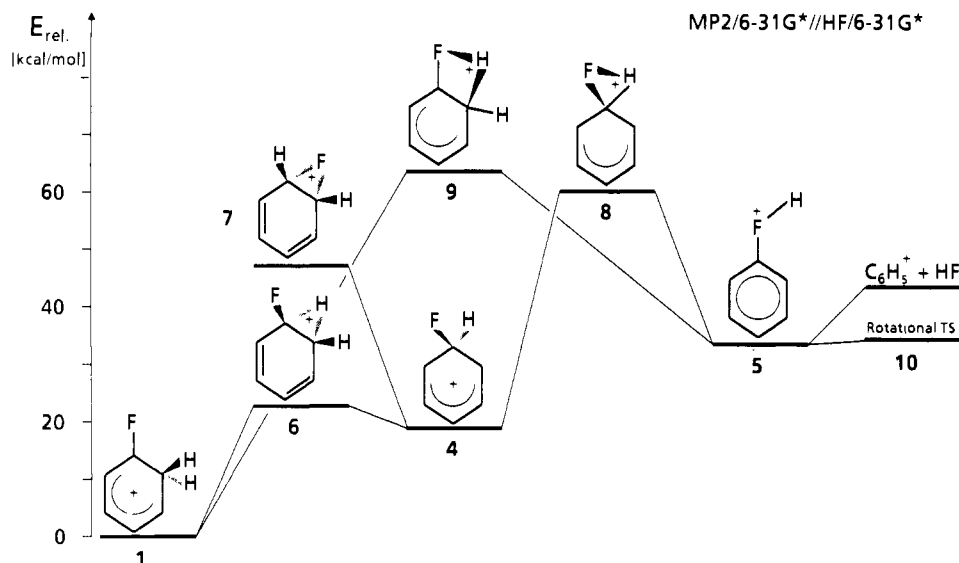


Figure 5. Calculated potential energy surface at the MP2/6-31G\*\*/HF/6-31G\* level of theory.

ination processes, have been located on the PES of  $C_6H_6F^+$ .

The geometry of the transition structure **8** for the 1,1-elimination process is shown in Figure 4. As compared to the corresponding minima **4** and **5** both, the C–H and the F–H bonds are significantly elongated ( $R_{CH} = 1.31 \text{ \AA}$ ;  $R_{HF} = 1.18 \text{ \AA}$ ). The associated C–F–H bond angle is computed to  $57.6^\circ$ , with the CHF plane perpendicular to the benzene ring. The C–F bond is elongated by  $0.14 \text{ \AA}$  to a value of  $R_{CF} = 1.48 \text{ \AA}$  as compared to the ipso-protonated isomer **4**. In the analysis of the hessian matrix, **8** is characterized by an imaginary frequency of  $-2007 \text{ cm}^{-1}$ , being typical for a hydrogen migration; thus, this transition structure can be assigned to the process ( $4 \rightarrow 8 \rightarrow 5$ ). At the HF/3-21G\* level of theory, the energy of **8** is calculated as  $76.3 \text{ kcal/mol}$  relative to **1**; after inclusion of electron correlation this energy difference decreases to  $60.1 \text{ kcal/mol}$  at the MP2/3-21G\*\*//MP2/3-21G\* level and  $60.4 \text{ kcal/mol}$  at MP2/6-31G\*\*//3-21G\* and finally reaches  $60.8 \text{ kcal/mol}$  at MP2/6-31G\*\*/HF/6-31G\*. In view of the good convergence, we believe that a further refining of the computational level will not result in significant changes in the geometry and relative stability of **8**.

Enormous effort was undertaken to localize an additional transition structure which would explain the third component of the composite kinetic energy release for the HF loss from protonated fluorobenzene. In fact, a TS corresponding to a migration of a hydrogen atom from the ortho-position in **1** to the fluorine was found. The geometry of **9**, as shown in Figure 4, can be described as a TS for the 1,2-elimination process with the moving hydrogen atom lying above the plane of the aromatic ring with almost similar distances to both carbon atoms ( $R_{HC-1} = 1.53 \text{ \AA}$ ;  $R_{HC-2} = 1.57 \text{ \AA}$ ) and a relatively long bond to the fluorine ( $R_{HF} = 1.22 \text{ \AA}$ ); the in-plane C–F bond is elongated to  $1.43 \text{ \AA}$ . The imaginary frequency of  $-2280 \text{ cm}^{-1}$  associated with the hydrogen migration to the fluorine atom, accompanied by an in-plane movement of the second hydrogen at C-2, is  $273 \text{ cm}^{-1}$  larger than that for the 1,1-elimination process; this indicates a somewhat stronger binding situation in **9** as compared with **8**. The relative stability of **9**, as calculated at both the UHF/3-21G\* ( $80.4 \text{ kcal/mol}$ ) and the MP2/6-31G\*\*/HF/6-31G\* ( $62.9 \text{ kcal/mol}$ ) levels, is comparable with the energy obtained for **8**. Thus, **8** and **9** may, indeed, serve as the two competing transition structures for the HF loss from initially ring-protonated fluorobenzenes.

## Conclusions

The kinetic energy release of the HF loss from protonated fluorobenzene corresponds to composite signals which we interpret in terms of three reactions. By analysis of labeling experiments and the ab initio calculated PES, the very narrow component (Figure 2) is assigned to a direct protonation of the fluorine atom to generate **5**. This species results from the relatively close PAs

of methane and the fluorine atom in fluorobenzene. On protonation with much stronger acids, e.g.,  $H_3^+$ , the high exothermicity would lead to rapid dissociation of "hot" **5**. For weaker acids, e.g.,  $C_2H_5^+$  or  $H_3O^+$ , either formation of **5** is impossible or the internal energy of **5** is not high enough to bring about unimolecular loss of HF.<sup>38</sup> The remaining two components, having a medium and a large kinetic energy release, are associated with ring-protonated isomers. According to our MO calculations, the degenerate fluorine migration should not affect the kinetic energy release for HF loss. Interestingly, as the energy barrier for fluorine migration (via **7**) is below the transition structures **8** and **9**, this process as well as the conventional "ring walk" via **6** may contribute significantly to the experimentally observed hydrogen equilibration of the ring protons preceding HF loss.

The analysis of the singlet potential energy hypersurface (Figure 5) of protonated fluorobenzene indicates that for the ring-protonated isomers two competing reactions are expected to occur. One of them is associated with a formal 1,1-elimination via transition structure **8**, and the other one corresponds to a formal 1,2-elimination process via **9**. The analysis of the structural features of **8** and **9** as well as the energetics of both fragmentations permit the following conclusions to be drawn. Due to the similar height of the energies of **8** and **9**, both reaction pathways can compete with each other, leading to the same product with different translational energy distributions. In the comparison of the geometries of the transition structures **8** and **9** with their corresponding minima, especially with respect to the C–F bond lengths, the TS **9** for the 1,2-elimination process can be viewed as a late transition state (the C–F bond is similar to that of the ion–dipole complex), whereas the changes TS **8** experiences relative to **4** are not so dramatic, thus pointing to an *early* transition state.<sup>35</sup> Following these arguments, the broad component of the KER in Figure 1 can be associated with the 1,2-elimination process.<sup>36</sup> This interpretation is in line with the general observation that 1,1-elimination processes usually exhibit smaller kinetic energy releases than 1,2-eliminations.<sup>37</sup>

To the best of our knowledge, a situation in which protonation of the same reactant with different Brønsted acids affords identical products via three different channels is unprecedented in gas-phase chemistry.

**Acknowledgment.** The generous support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and helpful comments and suggestions by the reviewers are appreciated.

(38) (a) This point is also well-taken and discussed in ref 9. (b) For related effects operative in the protonation of  $NF_3$ , see: Grandinetti, F.; Hrušák, J.; Schröder, D.; Karrass, S.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 2806.