chromes (100–115 amino acids) exchange electrons slowly (10^2–10^4 M^{-1} s^{-1}) while short cytochromes (80–90 amino acids) do so quickly (10^6–10^7 M^{-1} s^{-1}).[18] As seen in Table I, the model compounds have rate constants only approximately 10-fold larger than those of the short cytochromes. This indicates that other factors serve either to decrease the rate of electron transfer in models or increase the rate in the small proteins. Differences in inner-sphere reorganization energies are presumably small, because neither the bond lengths nor the force constants change appreciably in going from the models to the proteins. Outer-sphere reorganization is important for the models (a contribution of ~2 kcal to $\Delta G^{\ddagger}$); in the proteins it would depend on the amino acid sequence. Electrostatic interactions are not important for the models (the Fe(II) species is uncharged) but may be very important for the proteins. Other contributing factors in the proteins might include differences in complex formation and sequence-specific effects.

We have shown that model hemes transfer electrons only approximately 10 times faster than the small cytochromes. The steric effect found experimentally is substantially smaller than that calculated, arguing that other factors play an important role in determining the rate of electron transfer in cytochromes.

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(18) (a) Heme exposure alone does not account for this wide range. For example, horse heart cytochrome *c*, with 0.6% heme exposure,[4] has an electron self-exchange rate constant of 10^3–10^4 M^{-1} s^{-1} (ref 14 and 15) while *Ps. aeruginosa* cytochrome *c*-551, with 3% heme exposure,[18b] has a rate constant of ~10^7 M^{-1} s^{-1} (ref 17). (b) Stellwagen, E., personal communication.

Neutral Products from Fluoride Abstraction in Gas-Phase Cation–Molecule Reactions[1]

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Ion–molecule reactions corresponding to fluoride abstraction from a neutral molecule by an alkyl cation, reaction 1, have been widely observed.[2] Here we report the first experimental detection of electrically uncharged products of such a reaction. We have

$$R^+ + R'F \rightarrow R'^+ + RF \qquad (1)$$

used a specially designed electron bombardment flow (EBFlow) reactor[3] to collect neutral molecules that are formed by reactions of 2-fluoroisopropyl cation **3** in the gas phase, and we describe the use of NMR for identification and quantitation.

In previously reported examples, fluoride abstraction has been the only thermochemically accessible pathway for the experimentally observed production of R'^+ from the reactants shown in reaction 1. In these cases, mass spectrometric experiments have provided sufficient evidence for inferring the identity of the neutral product as RF. In closely related cases, however, studying the ionic products alone cannot prove that fluoride abstraction takes place. For example, the experimental observation of reaction 2 admits of two interpretations. From the heats of formation of

$$\underset{\substack{1.\ X=H\\2.\ X=D}}{CH_3(CX_3)_2CF} \xrightarrow{\text{electron impact}} \underset{\substack{3.\ X=H\\4.\ X=D}}{CH_3\overset{+}{C}FCX_3} + \underset{5.\ X=D}{(CX_3)_2\overset{+}{C}F} \xrightarrow{CH_3(CX_3)_2CF} \underset{\substack{6.\ X=H\\7.\ X=D}}{CH_3(CX_3)_2C^+} \qquad (2)$$

ΔH_f° −74 kcal/mol 138 kcal/mol 166 kcal/mol

the reactants and the ionic product,[4–6] thermochemical estimates predict that there are two possible exothermic pathways, fluoride abstraction or proton transfer. The first alternative would yield 2,2-difluoropropane ($\Delta H_f^\circ = -130$ kcal/mol[6]). The second alternative would produce hydrogen fluoride ($\Delta H_f^\circ = -65$ kcal/mol[7]) plus 2-fluoropropene ($\Delta H_f^\circ \approx -40$ kcal/mol[8]).

Electron impact on *tert*-butyl fluoride (**1**) forms ion **3** as the predominant ionization fragment (more than half of the total ionization at 70 eV).[9] The ion–molecule reaction of **3** with its parent neutral produce *tert*-butyl cation **6** with a rate constant of 4.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.[10] The ion chemistry gives no clue as to whether **3** abstracts fluoride ($\Delta H^\circ = -28$ kcal/mol) or undergoes proton transfer as represented by reaction 3 ($\Delta H^\circ \approx -3$ kcal/mol). Examination of the deuterium-substituted

$$(CH_3)_3C\text{-}F \quad H\text{-}CH_2C(CH_3)=F^+ \rightarrow (CH_3)_3C^+ + HF + CH_2{=}CFCH_3 \qquad (3)$$

compound **2** using Fourier transform mass spectrometry (FTMS)[11] shows that only ion **7** is formed by the ion–molecule reaction,[12] but this result is consistent with either pathway.

The only way to distinguish which pathway is operating is to analyze the neutral products. We have collected these using our EBFlow reactor and have examined the major products using NMR. General operating characteristics of the EBFlow reactor have been presented elsewhere.[3] Variation of sample pressure in the EBFlow reaction vessel allows us to ascertain which products arise from homogeneous gas-phase ion–molecule reactions, as distinct from non-ionic or heterogeneous reactions. At low pressures, ion–molecule reaction products ought to be recovered

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(12) Compound **2** was prepared from reaction of (diethylamino)sulfur trifluoride (DAST) with the corresponding alcohol, which was prepared by reaction of acetone-d_6 with methylmagnesium iodide. A sulfur dioxide impurity from workup of the DAST reaction could be easily resolved by FTMS or high-resolution mass spectrometry. In the 282-MHz ^{19}F NMR of neutral products from EBFlow radiolysis of **2**, compounds **8** and **9** appear as a broadened quartet and a broadened singlet separated by 0.4 ppm.

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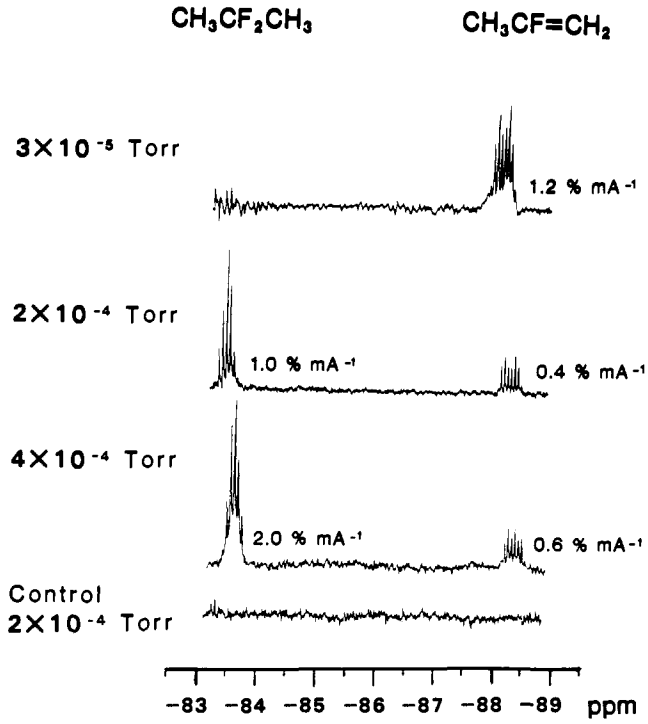


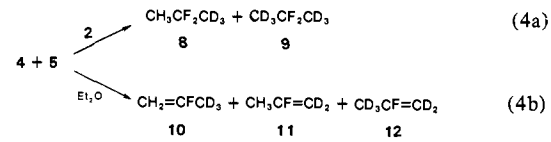
Figure 1. ^{19}F NMR (282-MHz) of neutral products collected from EBFlow radiolysis of *tert*-butyl fluoride at various pressures. Normalized conversions of 2,2-difluoropropane and 2-fluoropropene are expressed as percent of recovered starting material divided by ionizing electron current (% mA^{-1}). Chemical shift relative to $CFCl_3$.

in negligible quantities if the mean free path between reactive collisions is large compared to the dimensions of the reaction vessel. Products that appear only at higher pressures must result from homogeneous gas-phase reactions. Since the mean free path between neutral–neutral collisions is never much shorter than the length of the reaction vessel (even at the highest pressures studied), non-ionic gas-phase reactions can be ruled out.

Neutral products collected in the EBFlow reactor constitute only a small percentage of the recovered starting material. Because of the width of its chemical shift range, its sensitivity, and its dynamic range, ^{19}F NMR was used to examine the recovered material directly, without requiring further purification. As a control experiment, starting material was run through the reaction vessel in a fashion identical with the experimental conditions, but with bias voltages set so that ionizing electrons could not enter the reaction vessel. In this case, ^{19}F NMR showed no substantial products in the recovered starting material.

Figure 1 summarizes our experimental results. EBFlow radiolysis of *tert*-butyl fluoride exhibits a pressure-dependent yield of neutral products. At the lowest pressure, 3×10^{-5} torr, 2-fluoropropene is the predominant product. As pressure is increased, its normalized conversion (percentage relative to unreacted starting material divided by the mean current of ionizing electrons) fluctuates. At the same time, the yield of 2,2-difluoropropane rises markedly and monotonically with pressure. Therefore, ion **3** must be reacting via fluoride abstraction. The production of 2-fluoropropene can be attributed to a combination of non-ionic processes and neutralization of unreacted **3** on surfaces. From the pressure dependence of product yields, we estimate that fluoride abstraction represents >80% of the yield of reaction 2.

EBFlow radiolysis of the deuterated *tert*-butyl fluoride **2** yields neutral products **8** and **9** (reaction 4a) in a ratio of 1.6:1, which is the same as the relative abundances of ions **4** and **5** from 70-eV electron impact on **2**.[13] The ^{19}F NMR resonances of **8** and **9** are



easily resolved, though it is not possible to determine from ^{19}F NMR whether **8** is mixed with $CD_2HCF_2CH_2D$ (as would arise if ion **4** scrambled its hydrogens internally). But 500-MHz proton NMR[14] of recovered **8** shows no evidence of the scrambled product. A separate experiment provides additional confirmation that hydrogen scrambling does not take place in the 2-fluoroisopropyl cation. Brønsted acid–base reaction with diethyl ether yields **10–12**, as reaction 4b depicts. The three deuterated 2-fluoropropenes from **2** are easily resolved by ^{19}F NMR. Trideuterated compound **10** comes from deprotonation of **4**, and it appears as a doublet of doublets (J = 16 and 48 Hz), which can be assigned on the basis of the spin–spin couplings reported for 2-fluoropropene.[15] If ion **4** had undergone hydrogen scrambling prior to its reaction with base, then two geometrical isomers of $CD_2HCF{=}CHD$ should have been recovered from its deprotonation. There is no indication of any additional products aside from **10–12**.

From the EBFlow experiments we conclude that the 2-fluoroisopropyl cation (a) abstracts fluoride from *tert*-butyl fluoride to yield 2,2-difluoropropane, (b) reacts as a Brønsted acid toward diethyl ether to yield 2-fluoropropene; and (c) does not scramble hydrogens internally on the millisecond time scale during its lifetime in the EBFlow reactor. EBFlow techniques offer new methods for assigning ion structures based on NMR analysis of neutral products from ion–molecule reactions. Quenching gaseous ions by fluoride abstraction represents an especially promising approach.

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(13) Spectrum recorded by Dr. Richard Kondrat on the UCR VG-ZAB high-resolution mass spectrometer. Partial funding for this instrument was provided by National Institutes of Health DRR-BRS Shared Instrumentation Grant RR01750-01.

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Twist Form of the Ethylene Radical Cation. ESR Studies

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A number of theoretical studies have predicted a nonplanar, twisted structure of the ethylene radical cation, $C_2H_4^{+\cdot}$.[1] However, the twist angle around the carbon–carbon bond calculated is very sensitive to the method used. For example, ab initio SCF-MO-CI[1c] and MNDO[1j] calculations have predicted an ca. 25° twist, whereas calculations by electronic force theory[1f] and MINDO/3[1g] have resulted in an ca. 45° twist. The twist angle of 25° has been confirmed experimentally by vacuum ultraviolet

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