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Electron detachment reactions of fluorinated carbanions with atomic hydrogen

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Gas phase associative electron detachment reactions were first discovered to be important ionic processes in the mid 1960's when workers at the NOAA laboratories applied the flowing afterglow flow tube technique to the study of reactions of negative ions.[1] Since that time, a number of these reactions have been well characterized, and it has been found that these processes frequently occur rapidly when exothermic.[2] For associative detachment by atomic hydrogen, most such reactions will be exothermic. This is because atomic hydrogen has a gas phase acidity approaching that of a superacid[3] [$\Delta H_{\text{acid}}(\text{H}) = 1318$ kJ mol^{-1} and $\Delta H_{\text{acid}}(\text{H}_2\text{SO}_4) = 1295$ kJ mol^{-1} where ΔH_{acid} is the enthalpy of deprotonation, also referred to as the gas phase acidity].[4] For associative detachment by H to be endothermic would require that the reactant negative ion be the conjugate base of an acid stronger than H, or nearly a superacid. This is shown by the following:

$$\begin{array}{ll} \text{A}^- + \text{H} \rightarrow \text{HA} + e^- & \Delta H_r \\ \text{HA} \rightarrow \text{A}^- + \text{H}^+ & \Delta H_{\text{acid}}(\text{HA}) \\ \hline \text{net:}\quad \text{H} \rightarrow \text{H}^+ + e^- & \Delta H_{\text{acid}}(\text{H}) . \end{array}$$

Thus, $\Delta H_r = \Delta H_{\text{acid}}(\text{H}) - \Delta H_{\text{acid}}(\text{HA})$, and therefore ΔH_r will be positive only if $\Delta H_{\text{acid}}(\text{HA}) < \Delta H_{\text{acid}}(\text{H})$.

In this letter we report rate constants for electron detachment reactions of atomic hydrogen with CF_3^-, C_2F_5^-, and C_3F_3^-. This work is part of our general research program on the ion chemistry of halogenated species;[5–10] relevant applications include plasma processing of microelectronics and other devices. These reactions have not been studied previously. We also report rate constant limits for reactions of these ions with H_2, which is present in the flow tube along with the atomic hydrogen but is unreactive.

The experiments were performed using a selected ion flow tube (SIFT) instrument. The general technique and instrumentation have been fully described in the literature.[11] The following is a brief description of the details specific to the present study. Reactant ions were generated in an electron impact ion source operated at relatively high pressure (0.1–1 Torr). Several different precursor gases were used in the source: C_2F_6, C_2F_4, or c-C_4F_8 for producing CF_3^-; C_2F_4 or c-C_4F_8 for C_2F_5^- and C_3F_3^- (the results were independent of the choice of precursor gas). The ion species of interest was then mass selected in a quadrupole mass spectrometer and injected into a fast flow of He carrier gas in a stainless steel flow tube maintained at ~0.4 Torr. The studied ions, CF_3^-, C_2F_5^-, and C_3F_3^-, were relatively easy to produce in the ion source. Attempts to produce and inject the ions CF^- and CF_2^- were unsuccessful.

The atomic hydrogen reactant neutral was produced from a H_2/He mixture in a microwave discharge located in a glass sidearm which terminates as a Teflon tube inside the flow tube. The amount of atomic hydrogen introduced was varied by changing the amount of H_2 in the mixture. The flow rate of H_2 never exceeded 2% of the flow rate of He in the discharge sidearm. This technique has been used successfully in previous studies,[12,13] and it has been found generally that the degree of dissociation is independent of the flow rate of the diatomic provided that a large excess of carrier gas is maintained. The density of atomic hydrogen was calibrated by studying the reaction of F^- with H, and rate constants were measured relative to the known rate constant for this reaction, 1.5×10^{-9} cm^3 s^{-1},[12] in order to determine the absolute rate constants for the reactions of interest.

The reactant ions were sampled through a 0.2 mm diam orifice in a truncated nose cone, mass analyzed in a second quadrupole mass spectrometer, and detected by a channel particle multiplier. The accuracy of the measured rate constants is estimated to be ±40%, a value higher than usual for SIFT measurements because of the need to calibrate against a known rate constant. The ions studied were essentially unreactive with H_2, and upper limits to the rate constants were determined.

The experimental results are given in Table I and show that the reactions with H are fast, proceeding at 17%–66% of the collisional rates.[14] No ionic products were observed for any of the reactions studied. While the thermochemistry of associative detachment by H is not known quantitatively for C_2F_5^- and C_3F_3^-, these reactions are certainly exothermic since $\text{C}_2\text{F}_5\text{H}$ and $\text{C}_3\text{F}_3\text{H}$ cannot have acidities approaching those of superacids or even strong acids. For CF_3^- and C_2F_5^-, reactive electron detachment forming HF and a second neutral product would also be exothermic. We cannot distinguish between simple associative detachment and reactive detachment forming two neutrals, but the absence of any ionic product shows that some form of electron detachment is occurring.

$$\text{CF}_3^- + \text{H} \rightarrow e^- + \text{CF}_3\text{H} \quad \Delta H = -265 \text{ kJ mol}^{-1}, \tag{1a}$$

$$\rightarrow e^- + \text{CF}_2 + \text{HF} \quad \Delta H = -27.4 \text{ kJ mol}^{-1}, \tag{1b}$$

$$\text{C}_2\text{F}_5^- + \text{H} \rightarrow e^- + \text{C}_2\text{F}_5\text{H} \quad \Delta H = \text{negative}, \tag{2a}$$

$$\rightarrow e^- + \text{C}_2\text{F}_4 + \text{HF} \quad \Delta H = -82.5 \text{ kJ mol}^{-1}, \tag{2b}$$

TABLE I. Rate constants and efficiencies for reactions of $C_mF_n^-$ ions with atomic and molecular hydrogen measured at 298 K. The efficiencies are given as a range of values which reflects the ±40% absolute uncertainty in the rate constants.

Reaction	Rate constant ($cm^3 s^{-1}$)	Reaction efficiency
$CF_3^- + H$	5.3×10^{-10}	17%–39%
$C_2F_5^- + H$	6.0×10^{-10}	19%–44%
$C_3F_3^- + H$	9.0×10^{-10}	28%–66%
$CF_3^- + H_2$	$<4\times10^{-12}$	<0.3%
$C_2F_5^- + H_2$	$<4\times10^{-12}$	<0.3%
$C_3F_3^- + H_2$	$<4\times10^{-12}$	<0.3%

$$C_3F_3^- + H \rightarrow e^- + (C_3F_3H) \quad \Delta H = \text{negative}. \tag{3}$$

The reported thermochemistry is based on the compilation by Lias *et al.*[15] except for the heat of formation of CF_2 (-184.9 kJ mol^{-1}).[16,17]

It is interesting that the reaction efficiencies are high but less than collisional. This may indicate that some simple dynamical principle governs the reactivity. For example, the reaction efficiencies may be controlled by the number of attractive potential curves relative to the number of repulsive ones. Unfortunately, since the neutral products of the reactions are not known, the nature of the potential curves cannot be elucidated. Alternatively, the efficiencies may reflect the relative lifetimes of the complex against autodetachment compared with dissociation back into reactants.

In summary, the reactions of atomic hydrogen with the small fluorinated carbanions CF_3^-, $C_2F_5^-$, and $C_3F_3^-$ proceed rapidly by electron detachment with efficiencies in the ranges 17%–39%, 19%–44%, and 28%–66%, respectively. While associative detachment is exothermic for all three anions, other reactive detachment processes are also possible. These anions were found to be unreactive with H_2.

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