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Electrophilic Fluorination of Methane with "F^+" Equivalent N_2F^+ and NF_4^+ Salts[1]

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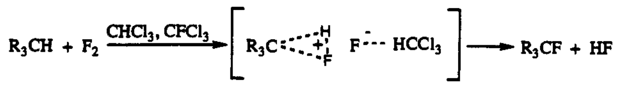
Abstract: The electrophilic fluorination of methane with "F^+" equivalent N_2F^+ and NF_4^+ salts was studied by experiment and theory. Reaction of excess methane with $NF_4^+SbF_6^-$ in pyridinium polyhydrogen fluoride solution gave exclusively methyl fluoride. The reaction of $N_2F^+AsF_6^-$ and $NF_4^+AsF_6^-$ with methane (with 1:2 to 4:1 mole ratio, respectively) in HF solution gave methyl fluoride in 63–92% relative yield with 26–6% methylene fluoride and 2–11% fluoroform with no carbon tetrafluoride formed. In a theoretical study of the $CH_4 + F^+$ model reaction stationary points on the potential energy surface were calculated at the QCISD/6-31G*//QCISD/6-31G* + ZPE level. The mechanistic consequences of these reactions are discussed.

Introduction

The concept of electrophilic fluorination of organic compounds was pioneered by Barton and Hesse in their work with CF_3OF.[2] Adcock and Lagow developed the use of highly diluted fluorine in the polyfluorination of hydrocarbons in a radical reaction.[3] The electrophilic fluorination of aromatics, such as benzene and toluene, was studied with highly diluted F_2 by Cacace and Wolf.[4] Selective electrophilic fluorination of saturated hydrocarbons with F_2 leading to monofluorinated product was demonstrated by Rozen[5] using the $CHCl_3/CFCl_3$ solvent system. They proposed a mechanism involving electrophilic insertion of fluorine into the C–H bond of the alkane in a typical electrophilic fashion with $CHCl_3$ acting as the acceptor of the fluoride ion.



The electrophilic fluorination of methane, the parent alkane, was, however, sofar not investigated. Herein we report direct electrophilic fluorination of methane using $N_2F^+AsF_6^-$ and $NF_4^+AsF_6^-$ (SbF_6^-) salts, as well as related theoretical studies and discuss the results and their mechanistic consequences.

Results and Discussion

Table 1. Fluorination of Alkanes

Mole Ratio of Reagents			% Conversion*	% Product				
CH_4	+	$N_2F^+AsF_6^-$	$\xrightarrow[\text{4 hrs., r.t.}]{\text{HF}}$	CH_3F	+	CH_2F_2	+	CHF_3
1	:	2	87	67	:	24	:	9
1	:	1	81	73	:	22	:	5
2	:	1	64	84	:	12	:	4
4	:	1	68	89	:	8	:	3
CH_4	+	$NF_4^+AsF_6^-$	$\xrightarrow[\text{4 hrs., r.t.}]{\text{HF}}$	CH_3F	+	CH_2F_2	+	CHF_3
1	:	2	60	63	:	26	:	11
1	:	1	70	76	:	18	:	6
2	:	1	24	85	:	15	:	0.5
4	:	1	25	92	:	6	:	2
CH_4	+	$NF_4^+SbF_6^-$	$\xrightarrow[\text{24 hrs., r.t.,30 mL}]{\text{Pyridine-HF}}$	CH_3F	+	CH_2F_2	+	CHF_3
16	:	1		100	:	0	:	0

**based on methane consumption.*

In order to study the electrophilic fluorination of methane and to avoid any possible free radical reactions we have chosen the ionic salts $N_2F^+AsF_6^-$ and $NF_4^+AsF_6^-$ (SbF_6^-) as fluorinating agents. Olah, Christe, et al. investigated[6] previously the fluorination of aromatics with N_2F^+. It is unlikely that even in this system "F^+" can be involved as the *de facto* electrophilic species. An electrophilic mechanism was envisioned with concomitant elimination of nitrogen. N_2F^+ was found to be highly oxidizing in nature resulting also in significant decomposition products. Shack and Christe[7] have studied the reaction of $NF_4^+SbF_6^-$ with toluene and other aromatics. The nature of the ring fluorination products and the lack of side chain substitution seem to imply direct electrophilic fluorination. We have now investigated the fluorination of methane with N_2F^+ and NF_4^+ salts in HF and pyridinium poly(hydrogen fluoride) (PPHF) solvents.

Whereas free "F^+" is unknown in the condensed state, electrophilic fluorination of hydrocarbons is of substantial interest. Barton's pioneering work[2] on low-temperature fluorination with CF_3OF opened up intensive investigations in the field. Others

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Table 2. Calculated Energies (-au), ZPE (kcal/mol), and Relative Energies (kcal/mol) of CH_4F^+

	MP2(FU)6-31G*// MP2(FU)/6-31G*	ZPE[a]	MP4(SDTQ)/6-31G*// MP2(FU)/6-31G*	rel[b]	QCISD/6-31G*// QCISD/6-31G*	rel[c]
1 (C_s)	139.578 26	31.4	139.598 46	0.0	139.594 00	0.0
2 (C_s)	139.522 15	25.5	139.546 54	26.7	139.540 46	27.7
3 (C_s)	139.577 51	31.1[d]	139.584 44	8.5	139.593 32	0.1
4 (C_{4v})	139.503 44	26.9[e]	139.522 96	42.9	139.516 25	44.3
5 (C_{3v})	139.423 88	26.9[e]	139.444 04	92.4	139.436 87	94.1
CH_3F (C_{3v})	139.342 66	25.5	139.360 68		139.355 18	
CH_4 (T_d)	40.195 07	29.1	40.354 79		40.353 37	
F^+	98.730 38		98.750 66		98.769 92	

[a] At MP2(FU)/6-31G*//MP2(FU)/6-31G*. [b] At MP4(SDTQ)/6-31G*//MP2(FU)/6-31G*+ZPE. [c] At QCISD/6-31G*//QCISD/6-31G*+ZPE. [d] NIMAG=1. [e] NIMAG=2.

used CH_3COOF, whereas Rozen[5] pioneered HOF and other reagents.

The electrophilic fluorination of methane with $N_2F^+AsF_6^-$ and $NF_4^+AsF_6^-$ in HF gave high yields of methyl fluoride. With a 2:1 CH_4 to N_2F^+ (or NF_4^+) mole ratio, CH_3F is formed in 67 and 63% relative yield, repectively, with 24–26% CH_2F_2 and 9–11% CHF_3 (no CF_4 was observed). When using a 1:1 CH_4 to N_2F^+ (or NF_4^+) ratio, CH_3F relative yield was around 73–76%, and with a 4:1 mol value 89–92% of CH_3F was obtained with only 6–8% CH_2F_2 and 2–3% CHF_3. When a large excess (16:1) of methane was used with $NF_4^+SbF_6^-$ in pyridinium polyhydrogen fluoride only methyl fluoride was observed. To account for the data, an electrophilic insertion of N_2F^+ and NF_4^+, respectively, into the C–H bond of methane can be envisioned giving methyl fluoride. One of the referees suggested that as the reaction solutions also contain strong superacids, protonation of methane can also occur to give CH_5^+ which may affect the reaction. However, formation of CH_5^+ we believe has no consequence on the experimentally observed direct fluorination reaction. Even if a limited $CH_4 + H^+ \rightleftharpoons CH_5^+$ equilibrium exists due to some superacid present in the system, there must be at any given time a large excess of methane present to react with the strong electrophilic fluorinating reagents.

Since electrophilic fluorination of methane with insertion of FN_2^+ and NF_4^+ is difficult to study by theory we have investigated simplified model, singlet F^+ cation insertion into methane and explored the CH_4F^+ potential energy surface. The related protonation of methyl fluoride was previously investigated experimentally by McMahon and Kebarle in the gas phase.[8] On the basis of the variation of the proton affinities of methyl halides as a function of their valence ionization potential, the authors concluded that 3c–2e bonding occurs upon protonation of a C–H bond in CH_3F. This was based on the fact that the proton affinity of CH_3F does not correlate with its valence ionization potential. This behavior suggested that the CH_4F^+ ions may be structurally different from other CH_3XH^+ ions (hydrido halonium ions) and may possess the 3c–2e bond.[8]

Optimizations on CH_4F^+ isomers were carried out at the MP2(FU)/6–31G* and QCISD/6–31G* levels. At QCISD/6–31G*//QCISD/6–31G*+ZPE structure **1** is 27.7 kcal/mol more stable than structue **2** (Table 2). Structure **1** can be considered as a complex between the CH_3^+ ion and the HF molecule predominantly having hydridofluoronium ion character. Structure **2** is a loosely held complex between CH_2F^+ and H_2 (Figure 1). The structure **1** was also calculated previously at the Hartree-Fock level, and results similar to those reported here were observed.[9] Structure **3** is the transition structure of rotation of **1** around the C–F bond and is only 0.1 kcal/mol less stable than structure **1**, indicating the facile rotation around the C–F bond. The C_{4v} symmetrical structure **4** and the C_{3v} symmetrical structure **5** are not minima as each of them contains two imaginary frequencies in their calculated vibrational spectrum. The dissociation of **1** into CH_3F and H^+ is endothermic by 144.0 kcal/mol (at QCISD/6–31G*//QCISD/6–31G*+ZPE). However, formation of **1** from CH_4 and F^+ is exothermic by as much as 293.1 kcal/mol at the same level. Thus the overall reaction to form CH_3F and H^+ from "F^+" and CH_4 is exothermic by 149.1 kcal/mol.

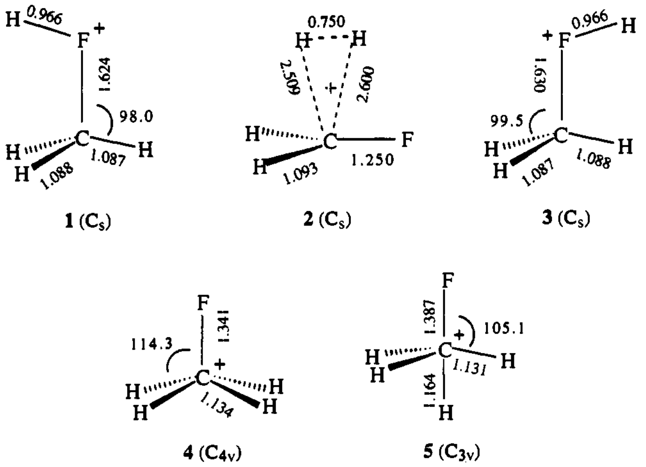
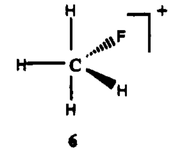


Figure 1. QCISD/6–31G* optimized structures of CH_4F^+. Bond lengths are in angstroms and angles are in degrees.

$$CH_4F^+ \text{ (1)} = CH_3F + H^+ \qquad \Delta H_0 = +144.0 \text{ kcal/mol}$$

$$CH_4 + F^+ = CH_4F^+ \text{ (1)} \qquad \Delta H_0 = -293.1 \text{ kcal/mol}$$

The electrophilic fluorination of methane with N_2F^+ and NF_4^+ in HF solution gives methyl fluoride in 89–92% relative yield with high selectivity. Theoretical studies of the reaction of methane with "F^+" are in accord with insertion of "F^+" into the C–H bond leading to the intermediate CF_3FH^+, **1**. However, attempts to locate the transition state of the reaction CH_4 + "F^+" leading to formation of 3c–2e structure **6** (involving initial "F^+" insertions directly into the C–H bond) failed. This is due to the extremely high reactivity of electrophilic "F^+" reacting with methane practically without any activation energy barrier. Structure **1** was found to be the global minimum on the CH_4F^+ potential energy surface.



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We have also carried out a similar experimental study of the fluorination of ethane with $NF_4^+AsF_6^-$ in HF solution. Whereas the results are more complex, CH_3F and C_2H_5F were formed in a 1.8:1 ratio. Thus NF_4^+ attack takes place in this case in not only the C–H bond of ethane but also the C–C bond. A more

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detailed study of the electrophilic fluorination of ethane and higher alkanes will be reported elsewhere.

Experimental Section

Fluorinating agents ($N_2F^+AsF_6^-$, $NF_4^+AsF_6^-$, and $NF_4^+SbF_6^-$) and pyridinium poly(hydrogen fluoride), PPHF, were prepared according to published procedures.[10] All gaseous chemicals used were purchased either from Matheson Gas Products or PCR Inc. NMR spectra were obtained on a Varian Associate Model VXR-200. GC analyses were carried out on a Varian 3400 gas chromatograph on a DB-1 column. MS analyses were performed on a Hewlett Packard 5971 mass spectrometer (EI). Identity and relative response factors of products were confirmed by comparison with authentic CH_3F, CH_2F_2, and CHF_3 samples. The error margin in the data reported in Table 1 is ±2%. All the fluorinating agents as well as HF and PPHF are exceedingly corrosive and toxic. Therefore, the experiments should be performed in a well-ventilated hood with great caution and precautions are needed for such work.

Typical Fluorination Procedure. (a) Fluorination of Methane with $NF_4^+SbF_6^-$. Methane (500 psi, 150 mmol) was charged to a stirred solution of 3.05 g of $NF_4^+SbF_6^-$ (9.3 mmol) dissolved in 30 mL of pyridinium poly(hydrogen fluoride) (30:70) in a 100-mL monel autoclave. After the reaction mixture was kept at room temperature for 24 h, the gaseous product was passed through a KF trap and collected at −95 °C. GC and MS analysis showed only CH_3F. The identity of CH_3F was further confirmed by its ^1H and ^{19}F NMR spectrum by dissolving the gas in $CDCl_3$.

(b) Fluorination of Methane with $N_2F^+AsF_6^-$ and $NF_4^+AsF_6^-$. The appropiate stoichiometric amounts of fluorinating agents ($N_2F^+AsF_6^-$ and $NF_4^+AsF_6^-$) were placed in 10-mL stainless steel Hoke cylinders under dry nitrogen. Anhydrous HF and methane gas were introduced at −196 °C using a stainless steel Teflon vacuum system (for the ratios, see Table 1). After the samples were kept at room temperature for 4 h, the gaseous products were passed through a KF trap, collected at −196 °C (using liquid nitrogen), and analyzed by GC and MS .

Calculations. All calculations were carried out with the Spartan[11] and Gaussian[12] packages of programs.

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