# Xenon as a Nucleophile in Gas-Phase Displacement Reactions: Formation of the Methyl Xenonium Ion

Abstract. *Xenon undergoes reaction with protonated methyl fluoride in the gas phase to form abundant quantities of the stable methyl xenonium ion, $CH_3Xe^+$. Estimated values for the xenon-carbon and krypton-carbon bond strengths in the rare gas–methyl molecular ions are 43 ± 8 and 21 ± 15 kilocalories per mole, respectively.*

Several groups of investigators have reported the formation by ion-molecule reactions in a mass spectrometer of molecular ions containing rare gas atoms (*1–8*). Such ions have included $ZH^+$ (*1–4*) and small amounts (less than 1 percent of the total ionization) of $ZC_mH_n^+$ ($m = 1$, 2; $n = 0$ to 4) (*1–3, 5, 6*), $ZY^+$ (Y = Cl, Br, I, O) (*5*), $ZC_2N_2^+$ (*7*), $Z_2^+$ (*1, 2, 8, 9*), $ZN_2^+$ (*9*), and $ZCO^+$ (*9*), where Z is a rare gas atom, usually xenon. In a different series of studies the production of rare gas–alkyl ions resulting from the $\beta^-$-decay of the corresponding isoelectronic radioactive alkyl halides has been observed (*10–12*). For example, $^{131}I$-labeled $CH_3I$ undergoes $\beta^-$-decay to produce $CH_3Xe^+$ with the molecular ion remaining intact in 69 percent of the decays (*12*). Obviously, molecular ions containing rare gas atoms have some degree of stability.

We have recently reported the general occurrence of a gas-phase ionic process which has the character of a nucleophilic displacement reaction (*13, 14*). The displacement reaction generalized in reaction 1 occurs, provided that two criteria are met: (i) the reaction is exothermic; and (ii) proton transfer from the substrate, $CH_3M^+$, to the nucleophile, N, is endothermic (*13, 14*)

$$N + CH_3M^+ \rightarrow CH_3N^+ + M \qquad (1)$$

The success achieved when the simple diatomic molecules $N_4$ and CO were used as nucleophilic reagents (*14*) suggested the intriguing possibility that it might be possible to employ rare gas atoms as nucleophilic reagents. We report here the use of xenon as the nucleophile in reaction 1 to generate a rare gas–alkyl molecular ion (*15*).

Examination by ion cyclotron resonance spectroscopy (*16*) at 70 ev of a mixture containing $CH_3F$, Xe, and $H_2$ in the mole ratio 1 : 100 : 400, respectively, leads at a pressure of $\geqq 7 \times 10^{-5}$ torr to the observation of ions at a mass-to-charge ratio *m/e* of 144 to 151, corresponding to the various isotopes of $CH_3Xe^+$. The abundance of $CH_3Xe^+$ increases with pressure, rising to 37 percent of the total ion current at $4 \times 10^{-4}$ torr (Fig. 1). Double resonance experiments indicate that $CH_3Xe^+$ is formed by reaction 2

$$CH_3FH^+ + Xe \rightarrow CH_3Xe^+ + HF \qquad (2)$$

The second-order rate constant associated with reaction 2 is estimated to be $5 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$ ($3 \times 10^9$ $M^{-1}$ $sec^{-1}$), a rather slow nucleophilic displacement reaction (*14*). Investigations at pressures higher than $4 \times 10^{-4}$ torr were prevented by resolution problems resulting from collision-broadening of peak shapes. As in previous studies (*14*), the purpose of $H_2$ in the reaction mixture was to provide an agent capable of forming a protonated substrate, $CH_3FH^+$, without unwanted side reactions.

In contrast to the above results, examination of a mixture containing $CH_3Cl$, Xe, and $H_2$ in the mole ratio 1 : 130 : 33, respectively, did not lead to the formation of any detectable amounts of $CH_3Xe^+$ under conditions such that $CH_3ClH^+$ and $(CH_3)_2Cl^+$ were readily formed. Since the proton affinity of $CH_3Cl$ is greater than that of Xe (*17, 18*), the second of the two criteria given above as requirements for reaction 3 to occur is satisfied. We infer, therefore, that reaction 3 does not occur because it is endothermic

$$CH_3ClH^+ + Xe \not\rightarrow CH_3Xe^+ + HCl \qquad (3)$$

Similarly, a mixture containing $CH_3F$, Kr, and $H_2$ in mole ratios varying from 1 : 50 : 400 to 1 : 1000 : 400, respectively, was examined. Although protonated methyl fluoride was present in abundance no detectable amounts of $CH_3Kr^+$ were observed. Here again, since the proton affinity of $CH_3F$ is greater than that of Kr (*17*), the inference is that reaction 4 does not occur because it is endothermic

$$CH_3FH^+ + Kr \not\rightarrow CH_3Kr^+ + HF \qquad (4)$$

The above results enable us to calculate certain thermochemical quantities. The carbon-xenon bond dissociation energy in $CH_3Xe^+$ is given by the methyl cation affinity (*13*) of xenon, MCA(Xe). The course of reactions 2 and 3 bracket MCA(Xe) as MCA(HCl) = 51 kcal/mole (*13*) > MCA(Xe) > MCA(HF) = 36 kcal/mole (*13*). Thus MCA(Xe) = 43 ± 8 kcal/mole, equivalent to a heat of formation $\Delta H_f(CH_3Xe^+)$ of 217 ± 8 kcal/mole. Similarly, the carbon-krypton bond dissociation energy in $CH_3Kr^+$ is given by MCA(Kr). The course of reaction 4 indicates that MCA(HF) = 36 kcal/mole (*13*) > MCA(Kr), equivalent to $\Delta H_f(CH_3Kr^+) \geqq 224$ kcal/mole. Field *et al.* (*2*) have observed reaction 5, which indicates that $\Delta H_f(CH_3Kr^+) \leqq 253$ kcal/mole (*19*)

$$Kr^+ + CH_4 \rightarrow CH_3Kr^+ + H \qquad (5)$$

Thus, $\Delta H_f(CH_3Kr^+) = 239 \pm 15$ kcal/mole, equivalent to MCA(Kr) = 21 ± 15 kcal/mole. Carlson and White (*10–*

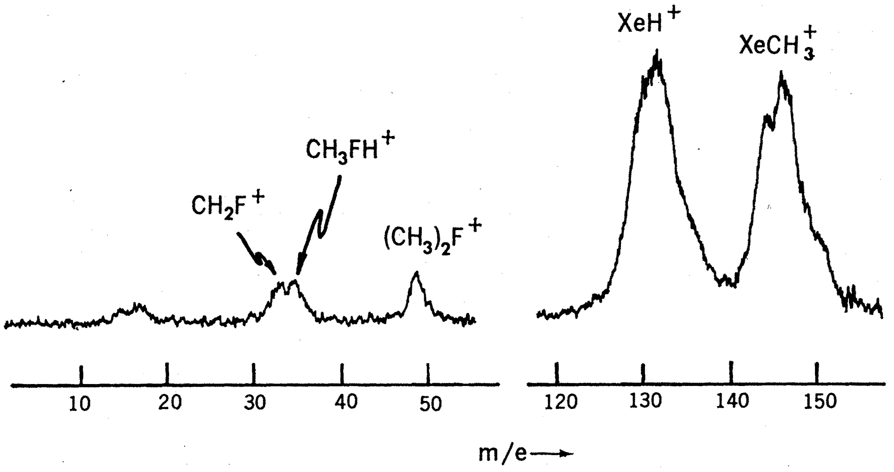

Fig. 1. Single resonance spectrum of a mixture of $H_2$, $CH_3F$, and Xe in the mole ratio 400 : 1 : 100, respectively, at $4 \times 10^{-4}$ torr and 70 ev. The peak labeled $XeH^+$ also contains contributions from $Xe^+$.

*12*) have pointed out the importance of knowing quantitative values of these heats of formation in order to understand the ions resulting from nuclear decay of the radioactive alkyl halides. For example, in 69 percent of the radioactive decays of $^{131}$I-labeled $CH_3I$ the parent ion $CH_3Xe^+$ remains intact; by comparison, in the radioactive decay of $^{82}$Br-labeled $CH_3Br$ only 0.4 percent of the decays produce $CH_3Kr^+$ (*10*). This result is readily interpretable in terms of the carbon–rare gas bond energies estimated above (43 and 21 kcal/mole for xenon and krypton, respectively) and the average excitation energy deposited in the carbon–rare gas bond as a result of the $\beta^-$-decay of the radioactive alkyl halide (5 and 56 kcal/mole for xenon and krypton, respectively) (*10*).

The findings presented here add to a growing body of evidence indicating the generality of gas-phase nucleophilic displacement reactions (*13, 14*). The results also indicate that the nucleophilic displacement process generalized in reaction 1 may be conveniently used in favorable cases for the gas-phase synthesis of rare gas–organic molecular ions of interest.

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### References and Notes

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19. This thermochemical result is based on the assumption that the $^2P_{3/2}$ state of $Kr^+$ undergoes reaction 5. If, instead, only the higher energy $^2P_{1/2}$ state of $Kr^+$ is reactive, then $\Delta H_f(CH_3Kr^+) = 265 \pm 22$ kcal/mole, equivalent to MCA(Kr) = 14 ± 22 kcal/mole.

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# Antiprismatic Coordination about Xenon: The Structure of Nitrosonium Octafluoroxenate(VI)

Abstract. *The structure of nitrosonium octafluoroxenate(VI),* $2NOF \cdot XeF_6$, *has been determined by means of single-crystal x-ray counter methods* (R*-index* = 0.046, *weighted* R*-index* = 0.042). *The space group is* Pnma, *with* a = *8.914(10) angstroms,* b = *5.945(10) angstroms, and* c = *12.83(2) angstroms (the numbers in parentheses are the standard deviations to the least significant digit or digits); the calculated density* (ρ) *is 3.354 grams per cubic centimeter, and there are four formula units per unit cell. The material consists of well-separated* $NO^+$ *and* $(XeF_8)^{2-}$ *ions; the structural formula is thus* $(NO)_2(XeF_8)$. *The anion configuration is that of a slightly distorted Archimedean antiprism. The observed distortion appears incompatible with a lone-pair repulsion model. Xenon-fluorine bond lengths of 1.971(7), 1.946(5), 1.958(7), 2.052(5), and 2.099(5) angstroms were found.*

Several addition compounds of $XeF_6$ with alkali fluorides (*1*) and with nitrosyl fluoride (*2*) have been prepared in the solid state. One of these compounds, $2NOF \cdot XeF_6$, has been prepared by Moody and Selig (*2*) who, on the basis of evidence from infrared and Raman measurements, suggested the formulation $(NO)_2(XeF_8)$ for the solid. The structural investigation reported here

Table 1. Positional and thermal parameters for $(NO)_2(XeF_8)$. The numbers in parentheses are the standard deviations to the least significant digit or digits.

| Atom | Refined coordinates | | | Anisotropic temperature factor* | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| Xe | 0.21834(7) | ¼ | 0.12717(5) | 0.0054(1) | 0.0071(2) | 0.00234(5) | 0 | 0.00039(5) | 0 |
| F(1) | .2650(8) | ¼ | − .0230(5) | .013(1) | .029(3) | .0033(4) | 0 | .0007(5) | 0 |
| F(2) | .0064(7) | ¼ | .1672(6) | .0058(8) | .021(2) | .0070(5) | 0 | .0021(5) | 0 |
| F(3) | .1302(5) | 0.5224(9) | .0695(4) | .0105(7) | .019(2) | .0053(3) | 0.0041(9) | .0006(4) | 0.0035(6) |
| F(4) | .4048(5) | .4641(8) | .1152(3) | .0076(5) | .016(1) | .0046(3) | − .0036(7) | .0003(3) | .0002(6) |
| F(5) | .2131(5) | .4620(8) | .2533(3) | .0120(6) | .015(1) | .0030(2) | − .0010(8) | .0012(3) | − .0017(5) |
| N(1) | − .0016(13) | ¼ | .7319(8) | .010(2) | .008(3) | .0070(9) | 0 | .0032(9) | 0 |
| N(2) | .1143(15) | ¼ | .4667(11) | .015(2) | .023(4) | .0063(10) | 0 | − .0042(11) | 0 |
| O(1) | .0608(10) | ¼ | .7979(7) | .009(1) | .020(3) | .0057(6) | 0 | .0020(8) | 0 |
| O(2) | .2037(15) | ¼ | .4296(8) | .020(2) | .053(6) | .0028(6) | 0 | − .0010(9) | 0 |

* The expression for the anisotropic temperature factor is $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl]$.