Spectroscopic Study on Ion-Ion Recombination and Neutralization Reactions of Kr^+ with $C_6F_6^-$ and SF_6^- in the Flowing Afterglow

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The positive ion-negative ion reactions of $Kr^+(^2P_{1/2,3/2})$ with $C_6F_6^-$ and SF_6^- have been spectroscopically studied in the flowing afterglow. The recombination and neutralization reactions leading to KrF* excimers and Kr* atoms, respectively, were found to compete with each other. The relative formation ratio of KrF*/Kr* in the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ reaction was much smaller than that in the $Kr^+(^2P_{1/2,3/2})/SF_6^-$ reaction.

Although recombination and mutual neutralization reactions between positive and negative ions are significant loss processes of ions in natural and manmade plasmas, little information has been obtained on the internal state distribution of neutral products.[1,2] We have recently succeeded in applying a flowing-afterglow method coupled with an optical detection technique to the study on the internal state distribution of electronically excited products in ion-ion recombination and neutralization reactions: e.g.,[3,4]

$$Kr^+(^2P_{1/2,3/2}) + SF_6^- \rightarrow KrF(B,C,D) + SF_5, \quad (1)$$

$$NO^+(X^1\Sigma^+:v''=0) + SF_6^- \rightarrow NO(A^2\Sigma^+) + SF_6. \quad (2)$$

Although there is a large possibility that recombination and neutralization reactions compete with each other in some reactions, no direct evidence has been obtained. In the present communication, the positive ion-negative ion reactions of $Kr^+(^2P_{1/2,3/2})$ with $C_6F_6^-$ and SF_6^- have been studied in order to study the competition of the recombination and neutralization reactions. Here we report for the first time that ion-ion recombination and neutralization reactions occur simultaneously in the reactions of $Kr^+(^2P_{1/2,3/2})$ with $C_6F_6^-$ and SF_6^-.

The flowing-afterglow apparatus used in this study was the same as that reported previously.[2-4] In brief, the positive $Kr^+(^2P_{1/2,3/2})$ ion was produced by the $He(2^3S)/Kr$ Penning ionization, while the negative $C_6F_6^-$ or SF_6^- ion was formed by a fast nondissociative electron attachment to C_6F_6 or SF_6 10 cm downstream from a Kr gas inlet:

$$He(2^3S) + Kr \rightarrow Kr^+(^2P_{1/2,3/2}) + He + e^-, \quad (3)$$

$$e^- + C_6F_6 \rightarrow C_6F_6^- \ (k_4 = 1.02 \times 10^{-7}\ cm^3s^{-1}\ [Ref.\ 5]), \quad (4)$$

$$e^- + SF_6 \rightarrow SF_6^- \ (k_5 = 3.1 \times 10^{-7}\ cm^3s^{-1}\ [Ref.\ 6]). \quad (5)$$

The partial pressures in the reaction zone were 1.0 Torr for He, 5-40 mTorr for Kr, and 3-5 mTorr for C_6F_6 and SF_6.

The emission spectra, observed around the C_6F_6 or SF_6 gas inlet, were dispersed in the 120-840 nm region with McPherson 218 and Spex 1250M monochromators. Photon signals from a cooled photomultiplier were analyzed with a microcomputer.

Figures 1(a) and 1(b) show emission spectra obtained from the ion-ion reactions of $Kr^+(^2P_{1/2,3/2})$ with $C_6F_6^-$ and SF_6^-, respectively. The strong $Kr(5s[3/2]\text{-}4p^6\ ^1S_0)$ line at 124 nm and weak KrF(B-X,D-X) excimers in the 200-250 nm region are identified in the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ reaction. In contrast,

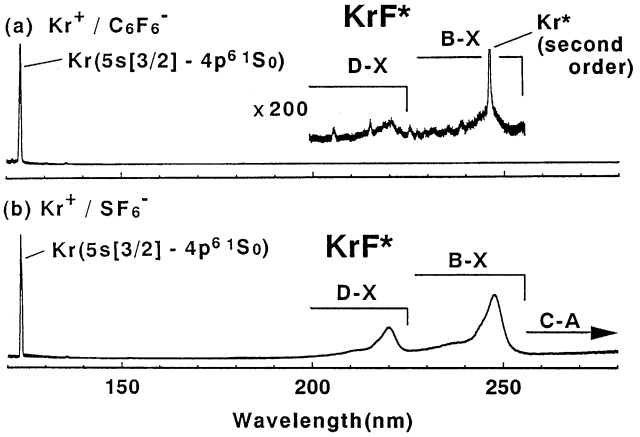

Figure 1. Emission spectra resulting from the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ and $Kr^+(^2P_{1/2,3/2})/SF_6^-$ reactions in the flowing afterglow.

besides the strong KrF(B-X,C-A,D-X) excimers, which have been reported previously,[3] a weak $Kr(5s[3/2]\text{-}4p^6\ ^1S_0)$ line is observed in the $Kr^+(^2P_{1/2,3/2})/SF_6^-$ reaction. When the emission spectrum in the 300-840 nm region was measured, strong Kr(5p[3/2]-5s[3/2]) and Kr(5p[5/2]-5s[3/2]) lines with nearly the same total emission intensity as that of the $Kr(5s[3/2]\text{-}4p^6\ ^1S_0)$ line were found at 760 and 811 nm in the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ reaction. On the other hand, no visible Kr* lines were found in the $Kr^+(^2P_{1/2,3/2})/SF_6^-$ reaction. These results indicate that the Kr(5s[3/2]) level is dominantly formed by radiative cascade from the upper Kr(5p[3/2,5/2]) levels in the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ reaction, while it is directly formed in the $Kr^+(^2P_{1/2,3/2})/SF_6^-$ reaction. On the basis of the energetics, the formation of Kr(5s[3/2],5p[3/2,5/2]) by the predissociation of KrF* excimer can be removed from the possible excitation process of Kr*:

$$Kr^+(^2P_{3/2}) + C_6F_6^- \rightarrow Kr(5p[5/2])) + F + C_6F_5 - 3.24\ eV, \quad (6)$$

$$Kr^+(^2P_{3/2}) + SF_6^- \rightarrow Kr(5s[3/2]) + F + SF_5 - 1.72\ eV. \quad (7)$$

Thus, the observed emissions must result from recombination reactions (8) and (1) and neutralization reactions (9) and (10):

$$Kr^+(^2P_{1/2,3/2}) + C_6F_6^- \rightarrow KrF(B,D) + C_6F_5, \quad (8)$$

$$\rightarrow Kr(5p[3/2,5/2]) + C_6F_6, \quad (9)$$

$$Kr^+(^2P_{1/2,3/2}) + SF_6^- \rightarrow KrF(B,C,D) + SF_5, \quad (1)$$

$$\rightarrow Kr(5s[3/2]) + SF_6. \quad (10)$$

The branching ratios of (8):(9) and (1):(10), which represent relative formation rates of KrF* and Kr* in the two reactions, were evaluated to be 0.001:0.999 and 0.951:0.049, respectively, by comparing the total emission intensities of KrF* and Kr* under the operating condition. The most outstanding difference is a

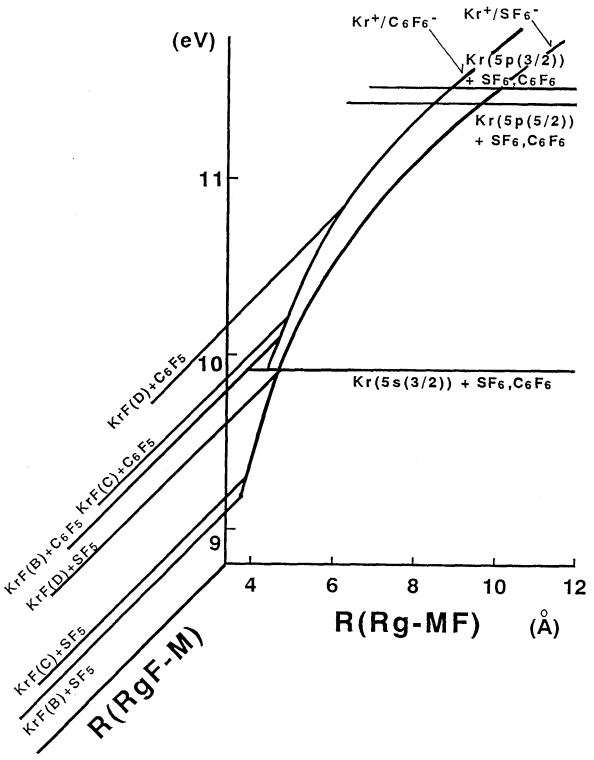

Figure 2. Potential-energy diagram of the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ and $Kr^+(^2P_{1/2,3/2})/SF_6^-$ reactions leading to KrF* excimers and Kr* atoms. The potential energies of $Kr^+(^2P_{3/2})$-$C_6F_6^-$ and $Kr^+(^2P_{3/2})$-SF_6^- ion pairs at infinite intermolecular separation are 13.14 and 12.95 eV, respectively.

much smaller ratio of (8)/(9) than that of (1)/(10).

Figure 2 shows a potential energy diagram of the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ and $Kr^+(^2P_{1/2,3/2})/SF_6^-$ reactions obtained by using known thermochemical and spectroscopic data.[7-12] Strongly attractive entrance ion-pair surfaces cross with flat exit covalent ones. It is clear from the diagram that the Kr(5p[3/2,5/2]) formation in the $Kr^+(^2P_{1/2,3/2})/C_6F_6^-$ reaction occurs at large intermolecular distances, while the KrF(B,C,D) formation in the $Kr^+(^2P_{1/2,3/2})/SF_6^-$ reaction takes place at short intermolecular distances. On the basis of this finding, the magnitude of the crossing point is not a significant factor in accessing the branching ratios of recombination and neutralization channels.

The dissociation energy of SF_5-F^- is smaller than that of C_6F_5-F^-, while an electron affinity of C_6F_6 is smaller than that of SF_6:[8,9,11,12]

$$C_6F_6^- \rightarrow C_6F_5 + F^- - 2.40 \text{ eV}, \quad (11)$$

$$SF_6^- \rightarrow SF_5 + F^- - 1.65 \text{ eV}, \quad (12)$$

$$C_6F_6^- \rightarrow C_6F_6 + e^- - 0.86 \text{ eV}, \quad (13)$$

$$SF_6^- \rightarrow SF_6 + e^- - 1.05 \text{ eV}. \quad (14)$$

On the basis of the above energetics, F^- transfer is more favorable for SF_6^-, while an electron transfer is more favorable for C_6F_6. Since this prediction is consistent with the experimental observation, the dissociation energy leading to F^- and the electron affinity will be important in assessing the branching ratios of recombination and neutralization channels.

According to ab initio calculation of SF_6^-, the highest occupied molecular (HOMO) orbital of SF_6^- is totally symmetric $6a_{1g}$ with S(3s)-F(2pσ*) character.[13] Although Gant and Christophorou[5] have predicted that the HOMO of $C_6F_6^-$ has π* character as in the case of $C_6H_6^-$, later ESR data in the condensed phase demonstrated that it has C-F σ* character.[14] Since ion-ion neutralization reactions occur via an electron transfer, the overlapping between the HOMO orbital with S-F or C-F σ* character and a vacant orbital to which an electron is transferred at the crossing point will be significant for the final state distribution of Kr*.

In summary, the ion-ion recombination and neutralization reactions of $Kr^+(^2P_{1/2,3/2})$ with $C_6F_6^-$ and SF_6^- have been studied by using a flowing-afterglow method. It was found that the recombination channel leading to KrF* excimers and the neutralization channel leading to Kr* atoms compete with each other, though their branching ratios depend strongly upon the negative ion. It was concluded that the energies required for F^- transfer and an electron transfer from negative ions are important factors in accessing the relative importance of the recombination and neutralization channels. We are planning to make a further study on the ion-ion reactions by selecting one spin-orbit state of $Kr^+(^2P_{1/2,3/2})$.

References and Notes

1 M. R. Flannery, in "Adv. Atom. Mol. Opt. Phys.," ed by B. Bederson and A. Dargano, Academic Press, New York (1994), Vol. 32, p. 117.
2 M. Tsuji, in "Trends in Physical Chemistry", Vol. 5, Council of Scientific Information, Trivandrum, India, in press.
3 M. Tsuji, M. Furusawa, and Y. Nishimura, *J. Chem. Phys.*, **92**, 6502 (1990).
4 M. Tsuji, H. Ishimi, M. Nakamura, Y. Nishimura, and H. Obase, *J. Chem. Phys.*, **102**, 2479 (1995).
5 K. S. Gant and L. G. Christophorou, *J. Chem. Phys.*, **65**, 2977 (1976).
6 D. Smith, N. G. Adams, and E. Alge, *J. Phys.*, B **17**, 461 (1984).
7 C. E. Moore, "Atomic Energy Levels," Natl. Bur. Stand. (U.S.) Circ. 467, U.S. GPO, Washington, DC (1949).
8 R. Richter, P. Tosi, and W. Lindinger, *J. Chem. Phys.*, **87**, 4615 (1987).
9 R. C. Weast, M. J. Astle, W. H. Beyer, "CRC. Handbook of Chemistry and Physics," 68th ed, CRC Press, Boca Raton, FL (1987-1988).
10 T. H. Dunning Jr. and P.J. Hay, *J. Chem. Phys.*, **69**, 134 (1978).
11 E. P. Grimsrud, S. Chowdhury, and P. Kebarle, *J. Chem. Phys.*, **83**, 1059 (1985).
12 M. E. C. Chen, E. S. D. Chen, and W. E. Wentworth, *J. Chem. Phys.*, **100**, 6981 (1994).
13 J. A. Tossell, *Chem. Phys.*, **154**, 211 (1991).
14 M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, **98**, 2053 (1976).