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PRELIMINARY

Isolation and Infrared Spectral Identification of the Pentafluorosulfanyl Radical

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The pentafluorosulfanyl radical, $SF_5\cdot$, is thought to be an intermediate in various chemical reactions involving SF_5Cl, SF_5Br, and S_2F_{10} [1-4], though it has not been directly observed in these systems, and the weight of evidence has rested with the formation of products containing the SF_5- moiety. The $SF_5\cdot$ radical has also been proposed, though not directly observed, as an intermediate in certain electron-rich processes involving sulfur hexafluoride, most notably the alkali metal reduction of SF_6 [5], the attack of hydrated electrons on SF_6 [6,7], and the gas-phase interaction of sulfur hexafluoride negative ion (SF_6^-) with electron acceptors in the ionization chamber of a mass spectrometer [8]. The only direct observations of the SF_5 radical are due to Fessenden and Schuler [9], who formed $SF_5\cdot$ by radiolysis of solid SF_6 with 2.8 MeV electrons (though they incorrectly ascribed its ESR spectrum to SF_4^+), and to Morton and Preston [10] who extended the Fessenden study and unambiguously assigned the ESR spectrum to the $SF_5\cdot$ radical.

In this note we wish to report the first matrix isolation and infrared spectral identification of the $SF_5\cdot$ radical as produced both by the vacuum ultraviolet photolysis of sulfur hexafluoride and its derivatives (eq. 1) and by controlled fluorine-atom attack on sulfur tetrafluoride (eq. 2).

$$SF_5X \xrightarrow{h\nu} SF_5\cdot + X\cdot \quad \text{(where X = F, Cl, Br)} \qquad (1)$$

$$SF_4 + F\cdot \longrightarrow SF_5\cdot \qquad (2)$$

For the experiments exemplified by eq. (1), the SF_5X species were deposited in an argon matrix on a CsI window at 8°K while undergoing vacuum-uv photolysis (1048 Å, 1067 Å) from a microwave-excited argon "windowless discharge" lamp [11]. For the experiments of eq. (2), a dilute stream of fluorine atoms from a low-pressure microwave discharge of F_2 (1% in argon) in an alumina tube was directed to the 8°K CsI window during the codeposition of dilute SF_4 in argon at 8°K. In both types of systems, in addition to known secondary products, the $SF_5\cdot$ radical was found as a major new product common to all experiments. Infrared bands at 812 cm^{-1} and 552 cm^{-1} have been assigned to the ν_7 (E) and ν_8 (E) vibrations of an $SF_5\cdot$ radical of approximately C_{4v} symmetry.

In addition to the simple SF_5-X scission indicated by eq. (1), a significant competing process in the photolyses experiments was the molecular photoelimination of the elements of "XF" according to eq. (3),

$$SF_5X \xrightarrow{h\nu} SF_4 + XF \qquad (3)$$

with the relative contribution of (3) increasing with increasing size of "X". Other species of interest observed in the course of this work include the novel intermediates $SF_3\cdot$ and SF_2, both produced by photolysis of SF_4 [12]. A more complete account of this work will be presented in the near future [13].

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