Contribution No. 14969 from the Division of Chemistry,
National Research Council of Canada, Ottawa, Canada

Electron Spin Resonance Spectra of the Halogen Hexafluorides

A. R. Boate,[1] J. R. Morton, and K. F. Preston*

Received June 3, 1975 AIC503881

Interhalogen molecules have a variety of geometries and provide a valuable testing ground for various theories of molecular structure.[2a] Surprisingly few of the known interhalogen species are paramagnetic; in fact, apart from the V_k centers (ClF^-, $BrCl^-$, etc.[2b]), experimental data on interhalogen free radicals are limited to ClF_2[3] and ClF_4, of which only the latter species has been detected[4] by the method of electron spin resonance (ESR). In this paper we report the ESR spectra of chlorine, bromine, and iodine hexafluorides trapped in a sulfur hexafluoride matrix at low temperatures.

Results

At 110 K a γ-irradiated sample of ClF_5 in SF_6 shows, in addition to the spectra of ClF_4 and paramagnetic sulfur fluorides, an intense isotropic spectrum consisting of four 90-G septets. We believe this spectrum to be that of the radical ClF_6 in which the six ^{19}F ($I = 0.5$) nuclei are equivalent and give rise to a 1:6:15:20:15:6:1 hyperfine manifold. At 9019.2 MHz the centers of the components of the ^{35}Cl ($I = 1.5$) quartet were at 1868.5 G ($M_I = 1.5$), 2446.8 G ($M_I = 0.5$), and 4230.1 G ($M_I = -1.5$). The $M_I = -0.5$ transition unfortunately fell in the $g = 2$ region where it was masked by powerful spectra of sulfur fluorides.[5] The best-fit spectral parameters of the new species, which were obtained by exact diagonalization procedures,[6] are summarized in Table I. Although lines attributable to the less abundant isotopic species $^{37}ClF_6$ were observed, they were poorly resolved and no attempt was made to carry out an independent analysis.

The spectrum of BrF_6 was likewise observed in a γ-irradiated sample of BrF_5 in SF_6. Due to the magnitude of the Br ($I = 1.5$) hyperfine interactions in this radical, however, only the highest field ($M_I = -1.5$) transitions of the equally abundant species $^{79}BrF_6$ and $^{81}BrF_6$ were detectable. At 9017.9 MHz, the observed spectrum consisted of overlapping septets of approximately equal intensity centered at 6974.6 G ($^{79}BrF_6$) and 7152.6 G ($^{81}BrF_6$). Each septet had an intensity distribution characteristic of an interaction of the unpaired electron with six equivalent spins 0.5 and a hyperfine splitting of 88.5 G. No other transitions were accessible at the operating microwave frequency (ν) and we were obliged to estimate the bromine hyperfine interaction with the aid of the equation[5]

$$a = (2H - 2)/(2I + 1 - H) \tag{1}$$

where a and H are in units of $\nu/g\beta$; g was assumed to be 2.0181 (as in ClF_6) and $\beta = 1.399611$ MHz/G. The spectral parameters for BrF_6 are given in Table I; the ratio of the hyperfine interactions of the two isotopes ^{81}Br and ^{79}Br (1.0802) is in reasonable agreement with expectation (1.0780).

Attempts to generate a spectrum of IF_6 in a similar fashion were unsuccessful, possibly because of the very low solubility of IF_5 in SF_6. We did, however, detect a spectrum which we attribute to IF_6 upon uv photolysis of a solid solution of IF_7 in SF_6 at 110 K.[7] A single transition was observed, consisting of a binomial septet of lines centered at 11053 G (ν 9019.5 MHz), which is believed to be the $M_I = -2.5$ transition of ^{127}I ($I = 2.5$) in IF_6. The six equivalent ^{19}F hyperfine interactions in IF_6 were 147.7 G and the ^{127}I interaction derived from the above equation for $g = 2.0181$ was 6192 G (Table I).

Table I. ESR Parameters of the Halogen Hexafluorides in an SF_6 Matrix

		Hyperfine interactions, G	
Radical	g	M[a]	^{19}F
$^{35}ClF_6$	2.0181 (9)[b]	775.5 (20)	89.6 (20)
$^{79}BrF_6$	c	4166 (70)[d]	88.5 (10)
$^{81}BrF_6$	c	4501 (70)[d]	88.5 (10)
$^{127}IF_6$	c	6192 (90)[d]	147.7 (10)

[a] Refers to the isotope specified in column 1. [b] Figures in parentheses are errors in the last significant figure. [c] $g = 2.0181$ assumed (see text). [d] This range was obtained from eq 1 with a g value spread of 2.002–2.035.

Discussion

The ESR parameters of the halogen hexafluorides have similar characteristics to those of their isoelectronic counterparts[5] in group 6: SF_6^-, SeF_6^-, and TeF_6^-. ESR spectra of these radicals are evidently characterized by positive g shifts, large central-atom hyperfine interactions, and the equivalence of the six fluorines. We conclude that these species have $^2A_{1g}$ ground states in O_h symmetry. Ground states of lower symmetry, such as that of a pentagonal bipyramid with rapid intramolecular fluorine exchange, cannot be entirely discounted, of course. However, the vibrational spectra of BrF_6^- indicate that the ion possesses high symmetry,[8] D_{3d}, or possibly O_h. It would thus appear that the ns lone pair is stereochemically inactive and therefore that O_h symmetry for the radical BrF_6 is not unreasonable.

Estimates of the central-atom ns contribution to the semioccupied orbital may be obtained by dividing the central-atom hyperfine interaction by the appropriate $A_0 \equiv (8\pi/3)\gamma_e\gamma_M\psi_{ns}^2(0)$. Froese's wave function,[9] widely used for this purpose, yields A_0 values of 1666, 8340, and 7295 G for ^{35}Cl, ^{81}Br, and ^{127}I, respectively. These values imply 47%, 54%, and 85% central-atom ns character in ClF_6, BrF_6, and IF_6, respectively. Although these values are demonstrative of large central-atom ns contributions to the semioccupied orbitals, too much significance should not be attached to them. Other wave functions, for example those of Hermann and Skillman,[10] give somewhat different results. In addition, the empirical correction of Mackey and Wood[11] has to be considered. Applying their correction to the above A_0 values, we obtain for ClF_6, BrF_6, and IF_6 the following percentage ns contributions to the semioccupied orbital: 46, 46, and 54. These figures, which still indicate large central-atom ns contributions, may well be more realistic than uncorrected values.

Experimental Section

ClF_5 was prepared[12] by the fluorination of ClF_3 (Matheson of Canada, Ltd.) over CsF. Liquid BrF_5 and IF_5, obtained from the Allied Chemical and Dye Corp. and from PCR, Inc., respectively, were purified immediately prior to use by bubbling with fluorine gas until they were colorless. Cylinder SF_6 (Matheson) and IF_7 (PCR, Inc.) were used as received.

Thoroughly degassed mixtures of ~5% halogen fluoride in SF_6 were sealed off in quartz ESR tubes, allowed to warm to room temperature to facilitate dissolution in the SF_6, and then cooled to 77 K. The samples were γ irradiated at 77 K for 1 hr in a 9000-Ci ^{60}Co source. ESR spectra were subsequently recorded and measured at 110 K using a Varian E-12 spectrometer and ancillary equipment described elsewhere.[13] Samples in the cavity of the spectrometer could be exposed, when necessary, to the focused light of a Schoeffel 1000-W Xe–Hg arc.[14]

Registry No. $^{35}ClF_6$, 56783-22-3; $^{79}BrF_6$, 56783-23-4; $^{81}BrF_6$, 56783-24-5; $^{127}IF_6$, 56783-25-6.

References and Notes

(1) NRCC Postdoctorate Fellow, 1975.
(2) (a) L. Stein, *Halogen Chem.*, **1**, 133 (1967); (b) C. J. Delbecq, D. Schoemaker, and P. H. Yuster, *Phys. Rev. B*, **7**, 3933 (1973), and references therein.
(3) G. Mamantov, E. J. Vasini, M. C. Moulton, D. G. Vickroy, and T. Maekawa, *J. Chem. Phys.*, **54**, 3419 (1971).
(4) J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 3112 (1973).
(5) J. R. Morton, K. F. Preston, and J. C. Tait, *J. Chem. Phys.* **62**, 2029 (1975).
(6) R. W. Fessenden, *J. Magn. Reson.*, **1**, 277 (1969).
(7) On γ irradiation of this sample the spectrum of IF_7^- was observed ($a_{127} = 6150 \pm 100$ G, $a_{19}(7) = 105 \pm 1$ G); this will be published separately.
(8) R. Bougon, P. Charpin, and J. Soriano, *C. R. Acad. Sci., Ser. C*, **272**, 565 (1971).
(9) C. Froese, *J. Chem. Phys.* **45**, 1417 (1966).
(10) C. M. Hurd and P. Coodin, *J. Phys. Chem. Solids*, **28**, 523 (1967).
(11) J. H. Mackey and D. E. Wood, *J. Chem. Phys.*, **52**, 4914 (1970).
(12) D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, Jr., and V. E. Bedwell, *Inorg. Chem.*, **6**, 1918 (1967).
(13) A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Phys. Chem.*, **79**, 651 (1975).
(14) Since the submission of this article for publication the generation of the radical ClF_6 by the same technique described here has been reported; the ESR parameters derived agreed satisfactorily with ours: K. Nishikida, F. Williams, G. Mamantov, and N. Smyrl, *J. Am. Chem. Soc.*, **97**, 3526 (1975).

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Oxidation of Elemental Mercury with Trifluoromethyl Radicals. Synthesis for Bis(trifluoromethyl)mercury

R. Eujen and R. J. Lagow*[1]

Received June 13, 1975 AIC50421J

We have recently developed in our laboratory a general synthesis for trifluoromethyl organometallic compounds.[2] Trifluoromethyl radicals generated from C_2F_6 in a glow discharge were shown to react with metal halides to produce completely substituted trifluoromethyl organometallic compounds in high yields. The preparation of $Hg(CF_3)_2$ by this method[2] is a facile synthesis which is now operable in our laboratory on a scale of 8 g/4 hr. Haszeldine and Emeleus, in the first preparation of trifluoromethylmercury compounds, established that CF_3I reacts on heating and/or irradiation with mercury metal to yield only CF_3HgI[3] and that the use of amalgams was necessary to produce $(CF_3)_2Hg$.[4] We have found trifluoromethyl radicals generated from C_2F_6 in radiofrequency discharge are capable of oxidizing mercury metal directly to bis(trifluoromethyl)mercury.

A glow discharge is a convenient source of reactive radicals which are likely to be formed in excited electronic vibrational states and rotational states but have little translational energy. The reaction of trifluoromethyl radicals with Hg appears to take place in the gas phase. The elemental mercury is placed on the bottom surface of the plasma reactor and vaporized through the plasma zone. The presence of electronically excited mercury atoms, established by the characteristic lines in the visible spectrum, definitely increases the reaction rate and is probably essential for this reaction. If metallic mercury is placed in a boat or container slightly ahead of the recombination zone of the plasma, no reaction occurs. Gentle heating of the mercury to 45°C increases the concentration of excited mercury atoms in the plasma and markedly increases the overall yield. The use of cadmium amalgam does not influence the reaction.

If a mixture of C_2F_6 (95%) and CF_3I (5%) is used, CF_3HgI and $(CF_3)_2Hg$ are formed in a ratio of about 2:1. With pure CF_3I, nearly quantitative conversion to C_2F_6 and HgI_2 with the formation of only traces of $(CF_3)_2Hg$ is observed. The reaction sequence of eq 1–9 is probable.

$$C_2F_6 \overset{\text{rf}}{\rightleftarrows} 2CF_3\cdot \tag{1}$$

$$CF_3I \overset{\text{rf}}{\rightleftarrows} CF_3\cdot + I\cdot \tag{2}$$

$$Hg + I\cdot \rightarrow \cdot HgI \tag{3}$$

$$Hg^* + CF_3\cdot \rightarrow \cdot HgCF_3 \tag{4}$$

$$\cdot HgCF_3 + I\cdot \rightleftarrows \cdot HgI + CF_3\cdot \tag{5}$$

$$\cdot HgI + CF_3\cdot \rightleftarrows CF_3HgI \tag{6}$$

$$\cdot HgI + I\cdot \rightleftarrows HgI_2 \tag{7}$$

$$\cdot HgCF_3 + I\cdot \rightarrow IHgCF_3 \tag{8}$$

$$\cdot HgCF_3 + CF_3\cdot \rightarrow Hg(CF_3)_2 \tag{9}$$

The results indicate that the high CF_3 radical recombination rate k_{-1} and the abstraction of iodine atoms by mercury and/or Hg–CF_3 compounds are limiting factors for the yields of $(CF_3)_2Hg$ or CF_3HgI. The absence or nearly negligible formation of CF_3HgI in the plasma reactions of CF_3I with Hg or C_2F_6 with HgI_2[2] may be due to its low volatility and therefore long exposure time to the reactive plasma. Pure CF_3Br in a radiofrequency discharge over mercury does not yield trifluoromethylmercury compounds.

These results raise the possibility of the synthesis of other trifluoromethyl organometallic compounds via reactions of trifluoromethyl radicals with metallic substrates.

Experimental Section

In a typical experiment about 30 ml of Hg was placed in a reactor similar to that described previously.[2] The C_2F_6 flow rate was adjusted to 8 mmol/hr; the radiofrequency power level (13.6 MHz, inductive coupling) was adjusted to about 25 W allowing the mercury to warm up to 35–40°C. The operating pressure was approximately 2 mm. Bis(trifluoromethyl)mercury was collected downstream at −78°, dissolved in ether, separated from elementary mercury by filtration, and purified by sublimation. The average yield was 0.25 mmol/hr (80 mg/hr). The products were identified by their characteristic ^{19}F NMR spectra: for $Hg(CF_3)_2$, δ −40.5 ppm, $J_{^{199}HgF} = 1287$ Hz; for $HgCF_3I$; δ −43.5 ppm, $J_{^{199}HgF} = 1760$ Hz (in ether, vs. external TFA). Parent ions in the mass spectrum were at *m/e* 336–342 and 394–400, respectively.

Acknowledgment. We are grateful to the National Science Foundation for support of our work in plasma chemistry.

Registry No. Hg, 7439-97-6; C_2F_6, 76-16-4; $Hg(CF_3)_2$, 371-76-6.

References and Notes

(1) Alfred P. Sloan Fellow.
(2) R. J. Lagow, L. L. Gerchman, R. A. Jacob, and J. A. Morrison, *J. Am. Chem. Soc.*, **97**, 518 (1975).
(3) H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2948 (1949).
(4) H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2953 (1949).
(5) P. B. Ayscough, *J. Chem. Phys.*, **24**, 944 (1956).

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Crystal Structure of β-Zirconium Tribromide

James Kleppinger, Joseph C. Calabrese, and Edwin M. Larsen*

Received June 16, 1975 AIC504279

The structures of zirconium trichloride, tribromide, and triiodide were first deduced from powder data and shown to consist of linear chains of face-sharing ZrX_6 octahedra.[1-3] There was disagreement, however, on the space group assignment and therefore disagreement on whether the metal ions are paired[1] or equally spaced along the chain.[2,3] Sub-