II was isolated by glpc and the ratio of II-d_2 to II determined by mass spectrometric analysis.[10] The analysis was calibrated using weighed and carefully mixed samples of II and II-d_2 (the latter containing 97.2 ± 1.0% dideuterated material as determined by mass spectrometry).[11]

The results of four experiments are given in Table I. Thus factor F is determined experimentally to be 1.80 ± 0.10. This is remarkably similar to the independently determined value required by the theory of eq 2–4. More significantly, the value differs by many times the error of the analysis from the value of unity required if the reactions yielding II and III were independent and the former concerted.

Acknowledgment. We are grateful to the National Science Foundation (NSF GP-7809) for its support.

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[11] Prepared by photolysis of I and I-d_2.[12]

[12] P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Lett.*, 3301 (1965).

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Fluoride Ion Transfer Reactions. Negative Ion–Molecule Reactions of SF_6^-

Sir:

Sulfur hexafluoride is remarkably inert chemically, a fact which appears to be the result of kinetic rather than thermodynamic stability.[1] Compounds containing the PF_6^- and SiF_6^{2-} ions, which are isoelectronic with SF_6, are well known. The formation of SF_6^- in gaseous SF_6 by resonance electron capture[2] of thermal electrons at 0.08 eV is often used to calibrate the electron energy scale in studies of gaseous negative ions produced in the mass spectrometer. However, no compounds containing the SF_6^- ion have been identified in condensed phases.

Recent descriptions[3] of the electronic distribution in SF_6 suggest that a net shift of electron density to the fluorine atoms occurs. A consideration[4] of the distribution of electrons in SF_6^- revealed that the unpaired electron could be incorporated in a molecular orbital where contributions from sulfur atomic orbitals were predominant. These conclusions lend support to the notion that electron density on fluorine is significant.

Demitras and MacDiarmid[5] have reported the reactions of sodium with SF_6 in liquid ammonia and in diphenylethylene glycol–dimethyl ether solutions. It was suggested that SF_6^- was formed in a rate-controlling step by electron transfer from the diphenyl radical ion, and that the reaction of SF_6^- involved elimination of F^- and formation of the SF_5 radical. From these results it appears likely that SF_6^-, which is itself a radical ion, might be reactive in the gas phase under conditions in the mass spectrometer where single collision events could occur. In this communication we wish to report that a reaction process similar to that suggested[5] in the condensed phase has been observed in the gas-phase reaction of SF_6^- with PF_5 and with PF_3.

Negative ions are formed in the mass spectrometer[6] at low electron energies (0–10 eV) by resonance electron capture reactions (reaction 1) or by dissociative electron capture processes (reaction 2). Dissociative ionization reactions or ion-pair processes may occur at electron energies sufficient to produce a positive and a negative ion simultaneously (reaction 3). At electron energies above about 10 eV where positive ions are formed, it is noted[7] that parent negative ions are formed by capture of secondary electrons. In this study, advantage is taken of the fact that at low electron energies the primary ion or ions in the ionization chamber may be controlled by selecting an electron energy where resonance capture reactions occur.

$$AB + e^- \longrightarrow AB^- \tag{1}$$

$$AB + e^- \longrightarrow A + B^- \tag{2}$$

$$AB + e^- \longrightarrow A^+ + B^- + e^- \tag{3}$$

The predominant negative ions formed in SF_6 at low energies are SF_6^- and SF_5^- with maxima in the electron capture ionization efficiency curves at 0.08 and 0.15 eV, respectively.[2] The shapes of the curves for these ions depend on the thermal distribution on the electron beam and on space charge effects which occur at high filament emission currents. In the results reported here, the energy distribution was always measured at low emission currents and low filament currents with SF_6 only in the ionization chamber. No significant changes in the distribution were observed upon addition of the reactant gas PF_5 or PF_3. Furthermore, the position of the maximum in the resonance capture process varied less than about 0.15 eV for the pressure range studied (0.2–2.2 μ).

The reactions were studied by the addition of PF_5 (or PF_3) and SF_6 to the ionization chamber from a dual inlet system. With PF_5 (or PF_3) in the ionization chamber at a known pressure, SF_6 was added and the resonance capture ionization efficiency curves determined for SF_6^-, SF_5^-, and any secondary ions which appeared in the spectrum. The significant ions detected at low energies in these experiments were PF_6^- and PF_4^- from mixtures containing SF_6 and PF_5 or PF_3, respectively. The reverse procedure, addition of PF_5 or PF_3 to SF_6, gave identical results. Neither PF_6^- nor PF_4^- was detected in pure PF_5 or PF_3 at high pressures.

Probable reactions to explain the occurrence of PF_6^- and PF_4^- are (using PF_5 as the example)

$$SF_6^- + PF_5 \longrightarrow PF_6^- + SF_5 \tag{4}$$

$$SF_5^- + PF_5 \longrightarrow PF_6^- + SF_4 \tag{5}$$

$$SF_6^-(SF_5^-) + PF_5 + M \longrightarrow PF_6^- + SF_5(SF_4) + M \tag{6}$$

Reactions 4 and 5 are typical bimolecular processes involving the formation of the secondary negative ion and neutral SF_5 or SF_4, respectively. An alternate explanation of the formation of PF_6^- (or PF_4^-) involves collisional stabilization of the secondary ion by a bath molecule, either SF_6 or PF_5 (PF_3). Reaction 6 is eliminated since a plot of the ratio of secondary to primary ion current varies linearly with pressure.[8] Since PF_6^- (or

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[1] H. L. Roberts, *Quart. Rev.* (London), **15**, 30 (1961).

[2] W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).

[3] D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).

[4] K. A. R. Mitchell, *Chem. Commun.*, 368 (1969).

[5] G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1198 (1964).

[6] R. W. Kiser, "Introduction to Mass Spectrometry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 192.

[7] J. C. J. Thynne, *Chem. Commun.*, 1075 (1968).

[8] F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, **1**, 69 (1961).

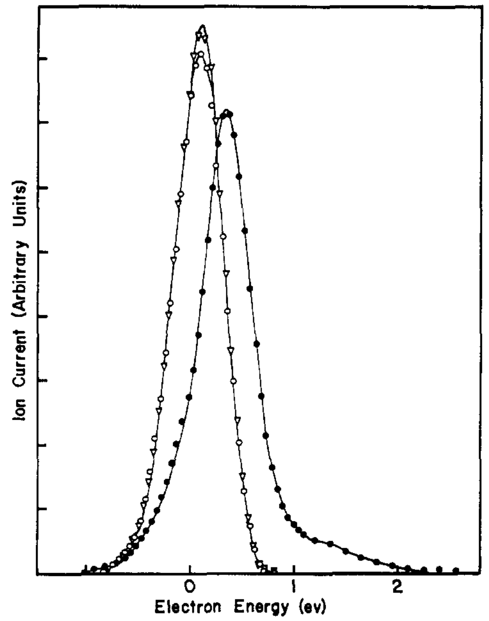

Figure 1. Electron capture ionization efficiency curves ($P(SF_6)$ 0.62 μ, $P(PF_5)$ 0.38 μ): ○, PF_6^- (ion current × 100); ●, SF_5^- (ion current × 33); ▽, SF_6^-.

PF_4^-) can only be detected at electron energies where the primary ion is formed, a comparison of the electron capture ionization efficiency curves for PF_6^- (or PF_4^-) with the curves for SF_6^- and SF_5^- should permit selecting reaction 4 or 5. Typical capture curves for SF_6^-, SF_5^-, and PF_6^- are shown in Figure 1. From this it is clear that reaction 4 is the process leading to the formation of PF_6^- in the ion source. Similar results were obtained for PF_4^-. Thus the general reaction

$$SF_6^- + AF_n \longrightarrow AF_{n+1}^- + SF_6 \qquad (7)$$

indicates the fluoride ion transfer process occurring with SF_6^-.

This study was carried out using an Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer[9] which has been modified for studying ion-molecule reactions. Pressure in the ionization chamber was measured with an MKS Baratron Model 144 capacitance manometer which is attached directly to the ionization chamber by 1 ft of a stainless steel-glass tubing connection apparatus.

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[9] J. G. Dillard, *Inorg. Chem.*, 8, 2148 (1969).

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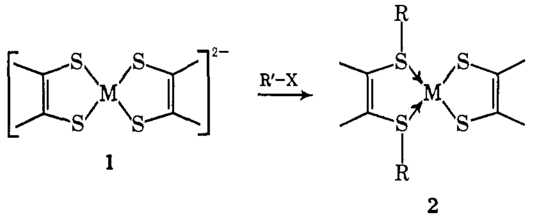
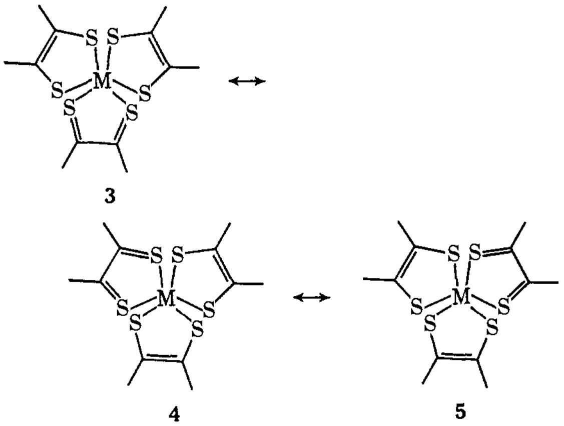
Methyl Derivatives of Tris(*cis*-stilbenedithiolates) of Tungsten and Rhenium[1]

Sir:

The sulfur atoms in the planar d^8 metal bisdithienes[2,3] $MS_4C_4R_4$ with R, *e.g.*, aryl or alkyl, but not with inductively electron-attracting substituents such as CF_3 or CN, become sufficiently nucleophilic on reduction to the dianions $MS_4C_4R_4^{2-}$ to react with alkylating agents according to eq 1.[4] A theoretical analysis of the bonding situation in the neutral group VI metal trisdithienes $MS_6C_6R_6$ revealed the ground-state electronic configuration to be fundamentally related to that of the neutral d^8 metal dithienes, leading to the group theoretically derived set of canonical structures **3**–**5**[5] mainly contributing to the ground state.

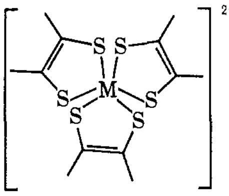


1 **2** (1)



3 **4** **5** (2)

On reduction to the dianions the neutral group VI metal trisdithienes could therefore be expected to become "trisdithiolates" **6**. However, the bonding in the



6

anionic derivatives $MS_6C_6R_6^{-,2-}$ is more complicated than in the planar species $MS_4C_4R_4^{-,2-}$. Depending on the metal and the dithiene substituents the electrons could initially occupy either of the energetically closelying orbitals 5e′ or 2a′$_2$. The former is delocalized over the whole molecule of complex but has significant metal character. The latter is a pure ligand π MO. In addition to this ambiguity, a change in the coordination geometry from trigonal prismatic to octahedral or distorted octahedral is likely to occur as a result of the reduction to the dianion. Although the available evi-

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[2] "Dithienes" are coordination compounds of metals and ligands in a state intermediate between 1,2-dithiodiketones and *cis*-1,2-ethylenedithiolates as, for example, $NiS_4C_4Ph_4$. This nomenclature[3a] is preferred to the indiscriminate naming of all of the chelates as "dithiolenes." [3c]

[3] (a) G. N. Schrauzer, *Accounts Chem. Res.*, 2, 72 (1969); (b) *Transition Metal Chem.*, 4, 299 (1968), and references cited therein; (c) J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).

[4] G. N. Schrauzer and H. N. Rabinowitz, *J. Am. Chem. Soc.*, 90, 4297 (1968).

[5] G. N. Schrauzer and V. P. Mayweg, *ibid.*, 88, 3235 (1966).