

Fluorine Exchange in Complexes of Tungsten Hexafluoride¹

Sir:

Tungsten hexafluoride forms charge transfer² and Lewis acid-base^{3,4} complexes. Both 1:1 and 1:2 complexes of the Lewis acid-base type have been reported on the basis of analytical results for the isolated complexes.^{3,4} In every case only a single magnetically equivalent fluorine species was observed for the complexed tungsten hexafluoride. For protons, however, stereochemical nonequivalence has been observed by magnetic resonance for eight coordinate tungsten tetrahydrides.^{5,6} An intramolecular averaging mechanism has been suggested for the magnetic equivalence of the hydrogens at higher temperature.⁶

We wish to report the identification, by fluorine magnetic resonance, of the simultaneous existence of free tungsten hexafluoride, the 1:1 complex and the 1:2 complex with dimethyl sulfide. At very low temperatures nonequivalent fluorines are observed in the 1:2 complex, which is the predominant species under such conditions.

A sample initially 0.04 M in WF_6 and 0.03 M in $(CH_3)_2S$, in vinyl chloride as solvent, has a single fluorine resonance line down to -40° but yields two lines from free and complexed tungsten hexafluoride at lower temperature, as shown in Figure 1. From the relative areas and chemical shifts of these lines as a function of the ratio of reactants, equilibrium constants for formation of both complexes, and their chemical shifts, may be calculated. At -75° the values determined are 45 ± 5 and 2 ± 1 for the equilibrium constants and -160 ± 2 and -90 ± 1 ppm for the chemical shifts of the 1:1 and 1:2 complexes. For the sample mentioned above this corresponds to an actual ratio for $WF_6:WF_6L:WF_6L_2$ of 63.4:35.5:1.1. Satellites arising from tungsten fluorine spin coupling were observed for free tungsten hexafluoride but not for the complexes.

The 1:1 complex is not appreciably soluble at very low temperature; however, with an excess of dimethyl sulfide primarily the 1:2 complex is present and no precipitation occurs. At about -160° the exchange of nonequivalent fluorines on tungsten in this complex is sufficiently slowed that a quintet is observed at -36.8 ppm and a triplet at -118.4 ppm with a spin coupling constant of 95 Hz. The spectrum is shown in Figure 2. There is no reasonable way for six fluorines to be arranged in an octacoordinated species to give two and four magnetically equivalent fluorine atoms (a hexagonal bipyramid is a geometric possibility). Therefore at least one intramolecular averaging mechanism is still rapid on the nmr time scale. From the temperature and concentration dependence of the exchange rate, it is hoped that information on the mechanism and activation energy for the exchange between the nonequival-

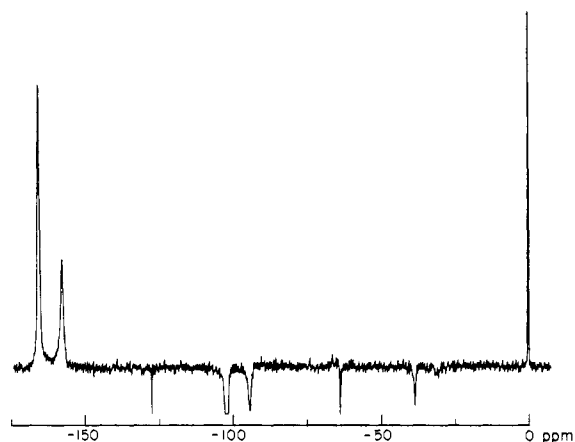


Figure 1. The ^{19}F resonance spectrum of a $WF_6-(CH_3)_2S$ sample (mole ratio 1:0.75) in $CH_2=CHCl$ containing $CFCl_3$ as reference at -75° .

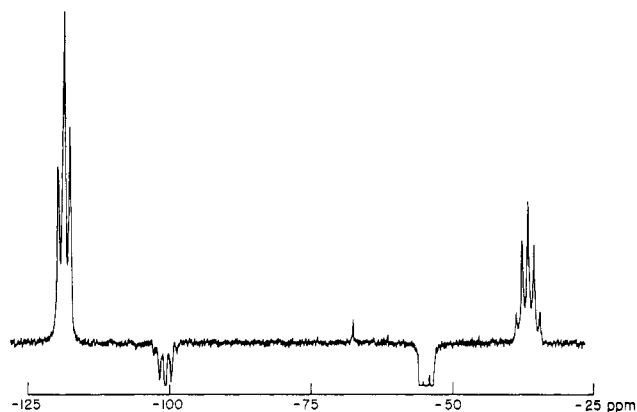


Figure 2. The ^{19}F resonance spectrum of the complex $WF_6 \cdot 2(CH_3)_2S$ at about -160° .

ent fluorines can be obtained. The observation of nonequivalent fluorine atoms in an octacoordinated structure opens up the possibility of studying the stereochemistry of such complexes in solution.

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Gas Phase Benzyl Cations from Toluene Precursors

Sir:

It is known from mass spectrometric¹⁻⁴ and ion photodissociation⁵ results that extensive hydrogen scrambling occurs in the formation and fragmentation of $C_7H_7^+$ from toluene-derived $C_7H_8^+$. Furthermore, those $C_7H_7^+$ ions which subsequently fragment have been shown to undergo loss of carbon positional iden-

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