conceivable that a fundamental change may occur in the esr relaxation mechanism when the trapped electron is divorced[8] from its conjugate 3-MP cation by the act of proton transfer (or charge transfer generally). In this connection it is interesting to note that *strong* esr spectra due to trapped electrons in irradiated organic glasses[9] have been observed hitherto only in cases where the parent cation almost certainly undergoes a change of identity by reaction with the matrix.

[8] By "divorced" we do not mean physical separation in this instance.

[9] D. R. Smith and J. J. Pieroni, *Can. J. Chem.*, **43**, 876 (1965); *J. Phys. Chem.*, **70**, 2379 (1966).

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The Mechanism of Fluorine-19 Exchange in the $TiF_4 \cdot 2$(Donor) Complexes

Sir:

The temperature dependence in the fluorine-19 nmr spectra of solutions of *cis* $TiF_4 \cdot 2$(donor) complexes has been noted.[1] The low-temperature (slow exchange) spectra of these complexes consist of two triplets of equal intensity due to the two F^{19} environments which contain two nuclei each[1,2] (see Figure 1). As a solution is warmed the fine structure of the spectrum is lost; the peaks broaden and then collapse into a single resonance. These observations show that there is a temperature-dependent exchange of fluorine nuclei between the nonequivalent sites. We wish to report evidence that this exchange involves both inter- and intramolecular exchange processes. The data indicate that the exchange mechanism consists of dissociation of a donor molecule followed by anharmonic vibration of a nonrigid intermediate formed by the dissociation.

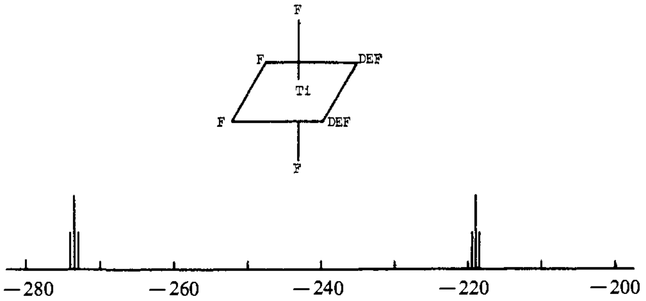

Figure 1. Diagrammatic representation of the F^{19} nmr signals observed for $TiF_4 \cdot 2DEF$ (DEF = N,N-diethylformamide) in acetonitrile at −10°. The chemical shifts are expressed in parts per million displacements from the resonance of external CF_3CO_2H.

The coalescence temperature (T_c) of the spin–spin triplets in the spectrum of $TiF_4 \cdot 2DEF$ (DEF ≡ N,N-diethylformamide) was determined as a function of the concentration of excess amide in acetonitrile solutions. The graph of T_c *vs.* [DEF] (see Figure 2) shows that the addition of excess amide slows the rate of fluorine exchange. Variation of the concentration of $TiF_4 \cdot 2DEF$ in acetonitrile does not change T_c.

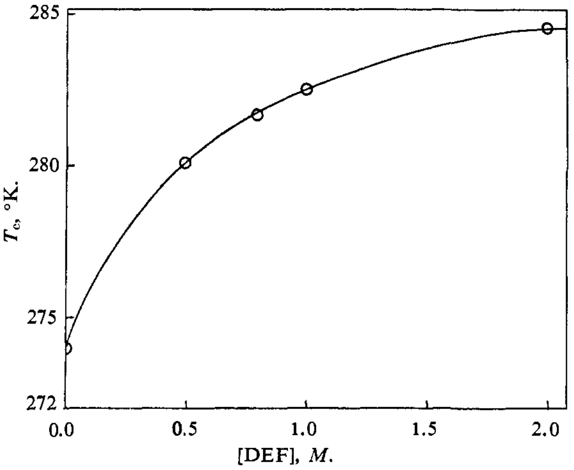

Figure 2. T_c *vs.* [DEF] for 1 *M* $TiF_4 \cdot 2DEF$ solutions in acetonitrile (DEF = N,N-diethylformamide).

Coalescence of a spin–spin multiplet occurs when the exchange rate becomes large enough to satisfy the condition

$$Jt \simeq 1 \tag{1}$$

where J is the spin–spin coupling constant (radians/sec) and t is the average lifetime (sec) of a fluorine-19 spin state. After exchange occurs, the probability that the two F^{19} nuclei in either environment of a $TiF_4 \cdot 2D$ complex will have changed their spin state is $^5/_8$. Therefore, at T_c the pseudo-first-order rate constant,[3] κ, is given by

$$\kappa = \frac{8}{5t} \simeq \frac{8}{5}J$$

Using the value for J (38 cps) obtained from the low-temperature spectrum of $TiF_4 \cdot 2DEF$ gives 370 sec^{-1} for κ.

The loss of fine structure and subsequent collapse of the two peaks were attributed to a rapid base (donor molecule) exchange.[1] It has been shown[4] that donor exchange does occur in these solutions. Since nucleophilic displacement reactions are generally not observed in solutions of transition metal complexes,[5] this exchange would be expected to occur *via* a dissociation mechanism. The rapid equilibrium

$$TiF_4 \cdot 2D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TiF_4 \cdot D + D$$

would be established. However, this equilibrium cannot be sufficient to produce fluorine equivalence because such a mechanism requires that the mean lifetime, τ ($= 1/\kappa$), evaluated from the fluorine-19 nmr spectra[6] be independent of the donor concentration. This is contrary to the experimental data (Figure 2).

The dissociation must, therefore, be followed by a subsequent reaction which scrambles the fluorines. One such reaction could be the formation of a *trans* complex.[7] One would then have

$$TiF_4 \cdot 2D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TiF_4 \cdot D + D$$

$$D + TiF_4 \cdot D \xrightarrow{k_t} D \cdot TiF_4 \cdot D$$

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[1] E. L. Muetterties, *J. Am. Chem. Soc.*, **82**, 1082 (1960).

[2] R. O. Ragsdale and B. B. Stewart, *Inorg. Chem.*, **2**, 1002 (1963).

[3] H. M. McConnell, *J. Chem. Phys.*, **28**, 430 (1958).

[4] D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.*, **6**, 8 (1967).

[5] R. G. Pearson, D. N. Edington, and F. Basolo, *J. Am. Chem. Soc.*, **84**, 3233 (1962).

[6] A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963).

[7] D. S. Dyer and R. O. Ragsdale, *Chem. Commun.*, 601 (1966).

where k_t is a second-order rate constant. Applying the steady-state approximation to $[TiF_4 \cdot D]$ gives[8]

$$\frac{1}{\tau} = \frac{k_1 k_t}{k_{-1} + k_t} \tag{2}$$

Fluorine equivalence could also occur *via* a bridged intermediate

$$TiF_4 \cdot D + TiF_4 \cdot 2D \xrightarrow{k_d} D \cdot F_4Ti\text{–}F\text{–}TiF_3 \cdot 2D$$

For this scheme τ would be given by

$$\frac{1}{\tau} = \frac{k_1 k_d [TiF_4 \cdot 2D]}{k_{-1}[D] + k_d[TiF_4 \cdot 2D]} \tag{3}$$

A third possibility is that upon dissociation a nonrigid five-coordinate species is formed.[9,10] This intermediate would undergo an inversion or series of anharmonic vibrations[11] to scramble the fluorines

$$TiF_4 \cdot D \xrightarrow{k_i} D \cdot TiF_4$$

For this scheme τ is given by

$$\frac{1}{\tau} = \frac{k_1 k_i}{k_{-1}[D] + k_i} \tag{4}$$

The mechanism involving dissociation and inversion is the only one in agreement with the experimental data. Equation 4 requires that excess base will increase the average lifetime of a fluorine-19 spin state, causing the triplets to coalesce at a higher temperature. The concentration of the complex should not effect T_c. The experimental data are compatible with these requirements.

Since the proposed mechanism requires an exchange of donor molecules between the complex and the solution, the proton nmr spectra of $TiF_4 \cdot 2DEF$ solutions were studied at ambient temperature as a function of the concentration of excess N,N-diethylformamide. The resonance of the formyl protons in each of these solutions is a single peak. The chemical shift of this resonance is a weighted average of the formyl proton shifts of the coordinated and uncoordinated donor molecules, showing that a fast donor exchange is occurring. The chemical shift (15 cps at 60 Mc) between the formyl peaks of solutions containing only $TiF_4 \cdot 2DEF$ and those containing only DEF indicates that the rate constant for dissociation, k_1, is larger than $2(15\pi/\sqrt{2})$ ($=67$ sec^{-1}) at ambient temperature.[12] A value for k_1 can be obtained from F^{19} nmr experiments since eq 4 reduces to

$$\frac{1}{\tau} = k_1 \tag{5}$$

as [D] approaches zero. If the equilibrium constant of the dissociation is small, a value of 370 sec^{-1} at 0° is obtained for k_1 from the triplet coalescence of $TiF_4 \cdot 2DEF$ solutions to which no excess donor was added.

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[8] Equation 2 applies to any mechanism in which fluorine equivalence is achieved by attack of the five-coordinate species with a donor molecule.

(9) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

(10) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

(11) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(12) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1957).

Reaction of Carbon Atoms with Benzene

Sir:

While the reactions of atomic carbon with aliphatic hydrocarbons are now quite well outlined,[1] no clear picture has emerged of their interaction with aromatic systems. Most of the literature[2–6] on the subject is restricted to hot carbon atom reactions in the condensed phase and, furthermore, is limited to investigation of only a few products accounting for a relatively small fraction of the total yield. In an attempt to delineate some of the principal features involved, the present communication has a wider scope, including the first reported results of studies of thermal and hot carbon atoms reacting in the gas phase as well as a more complete analysis of products formed in condensed systems.

Free carbon atoms in the form of ^{11}C (20.5 min) were produced by the Yale heavy ion and electron accelerators by nuclear techniques described elsewhere.[7] Such atoms are translationally "hot" species in one of the low-lying (^3P, ^1D, ^1S) electronic states. In certain experiments, they were cooled to thermal energies by the addition of excess neon moderator.

Products were formed on a tracer scale ($\approx 10^8$ molecules), separated by gas chromatography, and radioassayed by flow proportional counting.[8] Both the purity and the identity of the products were confirmed by establishing that they had identical elution properties with known carriers on at least two columns having different separating properties. External monitoring[7] of the number of carbon atoms produced in gas-phase experiments made it possible to establish absolute yields of identified products and provide an estimate of polymeric material.

Eastman Kodak benzene, thiophene free, Fisher Spectrograde benzene, and 99.999% zone-refined benzene (purchased from J. Hinton, Valparaiso, Fla.) were all used without further purification except for meticulous degassing on a vacuum line. All three samples gave similar results within the experimental error. Matheson oxygen and research grade neon were used and were at least 99.5% pure.

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(1) (a) C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965), and references therein; b) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 210 (1964), and references therein.

(2) (a) A. G. Schrodt and W. F. Libby, *J. Am. Chem. Soc.*, **78**, 1267 (1956); (b) J. Sprung, S. Winstein, and W. F. Libby, *ibid.*, **87**, 1812 (1965).

(3) (a) B. Suryanarayana and A. P. Wolf, *J. Phys. Chem.*, **62**, 1369 (1958); (b) A. P. Wolf, *Ann. Rev. Nucl. Sci.*, **10**, 259 (1960); (c) A. P. Wolf, "Chemical Effects of Nuclear Transformations," Vol. II, International Atomic Energy Association, Vienna, 1961, p 3.

(4) A. F. Voigt, Hot Atomic Chemistry Symposium, Purdue University, Lafayette, Ind., April 1-2, 1966.

(5) The reactions of accelerated C^+ ions have been studied by Lemmon and Mullen. See "The Chemical Interactions of Accelerated Carbon-14 Ions with Benzene," by R. T. Mullen, Ph.D. Thesis, University of California, Berkeley, Calif., 1961. Some similarities to the work with nucleogenic carbon atoms were observed.

(6) A. P. Wolf, private communication; *cf.* also ref 3c.

(7) J. Dubrin, C. MacKay, M. Pandow, and R. Wolfgang, *J. Inorg. Nucl. Chem.*, **26**, 2113 (1964).

(8) R. Wolfgang and C. MacKay, *Nucleonics*, **16**, No. 10, 69 (1958); R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).