of the two 1-fluorine atoms are more nearly the same than if only one of the two rotational configurations alone were populated. The environments averaged over the oscillation, however, are not identical. Increased frequency of oscillation with temperature elevation would have no effect on the chemical shift since presumably the frequency is sufficiently high even at the lowest temperature studied to prohibit observation of fluorine resonances characteristic of the two configurations at frequencies of 30 Mc. or less.

Of the four substituted *gem*-difluoroethanes studied, only 1,2-dichloro-1,1-difluoro-2-phenylethane exhibited the temperature dependent spectra discussed above. Spectra for the other ethanes appeared to be temperature independent over their liquid ranges. Of the four substituted ethanes examined, 1,2-dichloro-1,1-difluoro-2-phenylethane with two small chloro substituents rather than with two large bromo substituents would be expected to exhibit the lowest barrier to the 120° torsional oscillation postulated in Fig. 4, and consequently to be most likely to exhibit a temperature dependent spectrum over the accessible temperature range.

WILMINGTON, DEL.

[CONTRIBUTION NO. 394 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Structure of ClF_3 and Exchange Studies on Some Halogen Fluorides by Nuclear Magnetic Resonance[1]

BY E. L. MUETTERTIES AND W. D. PHILLIPS

RECEIVED AUGUST 3, 1956

The high resolution F^{19} magnetic resonance spectra of ClF_3 at 10, 30 and 40 Mc. are presented and interpreted in terms of the structure of C_{2v} symmetry for the molecule. Observed temperature dependencies of the spectra of ClF_3 and IF_5 are interpreted in terms of fluorine exchange. Activation energies for exchange of 4.8 kcal. for ClF_3 and 13 kcal. for IF_5 are estimated from the *n-m-r* temperature-dependence results. It is concluded that fluorine exchange occurs in these halogen fluorides through a dimer intermediate.

Introduction

Electron diffraction[2] and microwave[3] studies of ClF_3 have indicated that the molecule is planar with two long and a short Cl–F bond and exhibits C_{2v} symmetry. Fluorine exchange between HF and ClF_3 and IF_5, and between F_2 and ClF_3 and IF_5 previously has been demonstrated[4] using radioactive F^{18}.

In the present study, the complex F^{19} magnetic resonance spectrum of ClF_3 is analyzed and shown to be consistent with a structure possessing C_{2v} symmetry. An observed dependence of the number, widths and positions of the F^{19} resonances of ClF_3 and IF_5 on temperature is interpreted in terms of fluorine exchange in these molecules. Activation energies for fluorine exchange are estimated for ClF_3 and IF_5 from the temperature dependencies of the F^{19} magnetic resonance spectra.

Experimental

Materials.—The commercial grade of chlorine trifluoride yielded a fluorine *n-m-r* spectrum consisting of a single, broad, relatively temperature-insensitive peak. The fluoride was purified by a series (twelve) of bulb-to-bulb vacuum distillations in quartz equipment that had been previously dried at 400° under high vacuum. It was necessary to exercise extreme precautions in the distillation of the fluoride in order to obtain a pure sample. Samples for analysis were obtained by distilling the fluoride into quartz capillaries (2 mm. i.d.) which were then sealed off. A sample prepared by this method was found to be "stable" (in contact with quartz) indefinitely. The color of the liquid was an extremely pale yellow; the solid melted sharply at −76° (uncor.).

Bromide trifluoride and bromine pentafluoride were purified in the same manner as chlorine trifluoride. Elimination (by purification) of very slow attack of the quartz by bromine trifluoride at 25° was never achieved. The pentafluoride was stable in quartz.

Iodine pentafluoride was treated with silver(I) fluoride to remove elemental iodine and then distilled in a glass-platinum spinning band column.

Method.—The fluorine magnetic resonance spectra were obtained using a Varian high resolution *n-m-r* spectrometer and electromagnet[5] at frequencies of 10, 30 and 40 Mc. and fields of 2,500, 7,500 and 10,000 gauss, respectively. The spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the fluorine resonance of SF_6. Positive frequency displacements indicate resonances occurring at lower fields than the fluorine resonance of SF_6. Calibration was accomplished by superimposing an audiofrequency on the sweep field to produce side band peaks to the SF_6 resonance.[6]

Results and Discussion

1. Spectrum and Structure of ClF_3.—Microwave[3] and electron diffraction[2] studies of ClF_3 concur in assigning the molecule the structure possessing C_{2v} symmetry shown in Fig. 1. On the basis of this structure and to the approximation that the nuclear spin coupling between the two non-equivalent sets of fluorine atoms is much less than the chemical shift separating the two sets,[7] the expected fluorine magnetic resonance spectrum of ClF_3 would consist of a doublet and triplet of relative integrated intensities of 2 and 1, respectively. The doublet would arise from the equiva-

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(1) Presented before the Division of Industrial and Engineering Chemistry, National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956.

(2) R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, **21**, 602 (1953).

(3) D. F. Smith, *ibid.*, **21**, 609 (1953).

(4) M. T. Rogers and J. J. Katz, THIS JOURNAL, **74**, 1375 (1952).

(5) Varian Associates, Palo Alto, California.

(6) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 6108 (1951).

(7) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *ibid.*, **21**, 279 (1953).

lent 1,3-fluorine pair and the triplet from the single 2-fluorine atom. The spacings between the doublet and triplet components would be identical and equal to the nuclear spin coupling between the non-equivalent 1,3- and 2- sets of fluorine nuclei, while the separation between the centers of the triplet and doublet multiplets would be equal to the chemical shift between the 1,3- and 2- sets of nuclei.

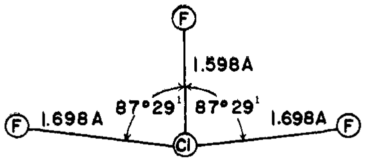

Fig. 1.—Structure of ClF_3.

The fluorine magnetic resonance spectrum of ClF_3 at a frequency of 10 Mc. and a temperature of −60° is that shown in Fig. 2 and consists of not five but eight separate resonances. It is apparent that if the spectrum of ClF_3 is to be interpreted in terms of the model of C_{2v} symmetry, a higher approximation to the nuclear spin–spin coupling must be utilized. Hahn and Maxwell[8] have treated exactly the case of a three-spin system consisting of two non-equivalent sets of nuclei, one set consisting of a single nucleus of spin $= {}^1/_2$ and the other set consisting of two nuclei of total spin = 1.

The allowed transitions for the C_{2v} model of ClF_3 are given by the expressions

$$E_4 - E_3 = \hbar/2[\gamma(2H_0 + 2h_2) - A - B] \quad (1)$$
$$E_6 - E_5 = \hbar/2[\gamma(2H_0 + h_1 + h_2) - J - A] \quad (2)$$
$$E_5 - E_3 = \hbar/2[\gamma(2H_0 + 2h_2) + A - B] \quad (3)$$
$$E_4 - E_2 = \hbar/2[\gamma(2H_0 + 2h_2) - A + B] \quad (4)$$
$$E_2 - E_1 = \hbar/2[\gamma(2H_0 + h_1 + h_2) + J - B] \quad (5)$$
$$E_6 - E_4 = \hbar/2[\gamma(2H_0 + h_1 + h_2) - J + A] \quad (6)$$
$$E_5 - E_2 = \hbar/2[\gamma(2H_0 + 2h_2) + A + B] \quad (7)$$
$$E_8 - E_7 = \hbar/2[\gamma(2H_0 + 2h_1)] \quad (8)$$
$$E_3 - E_1 = \hbar/2[\gamma(2H_0 + h_1 + h_2) + J + B] \quad (9)$$

where γ is the gyromagnetic ratio of fluorine, H_0 is the value of the constant external magnetic field, h_1 and h_2 are the absolute chemical shifts in gauss of the two non-equivalent sets of fluorine nuclei of ClF_3, δ is the chemical shift between the two non-equivalent sets of fluorine atoms of ClF_3,

$$A \equiv (\delta^2 - \delta J + 9J^2/4)^{1/2} \text{ and } B \equiv (\delta^2 + \delta J + 9J^2/4)^{1/2}$$

and J is the nuclear spin coupling between the two non-equivalent sets.

Subtracting equation 6 from equation 2, we obtain

$$[(E_6 - E_4) - (E_6 - E_5)]/\hbar = A \quad (10)$$

Similarly, by subtracting equation 9 from equation 5 we obtain the expression

$$[(E_3 - E_1) - (E_2 - E_1)]/\hbar = B \quad (11)$$

From the definitions of A and B

$$A^2 = \delta^2 - \delta J + 9J^2/4 \quad (12)$$

and

$$B^2 = \delta^2 + \delta J + 9J^2/4 \quad (13)$$

Then

$$B^2 - A^2 = 2\delta J \quad (14)$$

or

$$\delta = (B^2 - A^2)/2J \quad (15)$$

Substituting equations 15 and 14 into equation 12 we obtain

$$A^2 = (B^2 - A^2)^2/4J^2 - (B^2 - A^2)/2 + 9J^2/4 \quad (16)$$

Solving for J^2, we obtain

$$J^2 = (B^2 + A^2)/9 \pm [(B^2 + A^2)^2 - 9(B^2 - A^2)^2]^{1/2}/9 \quad (17)$$

Thus, from experimental values of B and A, values of J may be obtained from equation 17 and values of δ from equation 15.

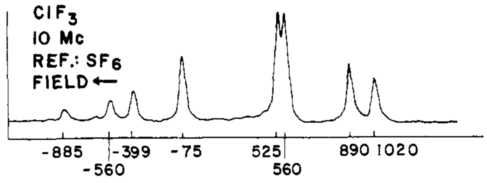

Fig. 2.—F^{19} spectrum of ClF_3 at 10 Mc. and −60°.

The −60° fluorine magnetic resonance spectra of ClF_3 at 40 and 30 Mc. are given in Figs. 3 and 4. It is noteworthy that as the ratio of J to δ reaches

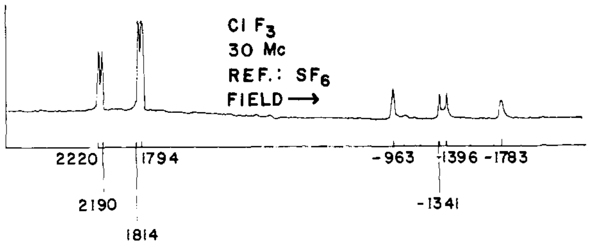

Fig. 3.—F^{19} spectrum of ClF_3 at 30 Mc. and −60°.

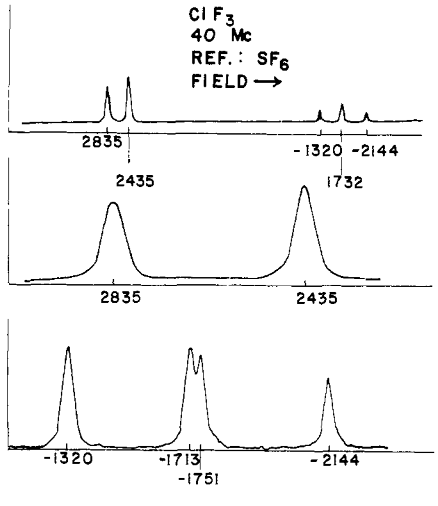

Fig. 4.—F^{19} spectrum of ClF_3 at 40 Mc. and −60°.

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(8) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

a value of ~0.1 at 40 Mc., the spectrum approaches that of a simple doublet and triplet of relative integrated intensities of 2 and 1, respectively. Values of the nuclear spin coupling, *J*, and the chemical shifts, δ, for the three frequencies at which the fluorine magnetic resonance spectrum of ClF_3 was examined are given in Table I.

TABLE I

FREQUENCY DEPENDENCE OF THE CHEMICAL SHIFT AND NUCLEAR SPIN COUPLING PARAMETERS FOR ClF_3

Frequency, Mc.	Chemical shift, δ (c.p.s.)	Spin-spin splitting, *J* (c.p.s.)
10	1114	378
30	3369	395
40	4216	435

As can be seen from Table I, the values of the chemical shift, δ, diverge slightly from a linear frequency dependence, and the values of the nuclear spin coupling constants, *J*, apparently are not independent of frequency. However, in view of the difficulty of precise calibrations as the result of exchange broadening at temperatures above −50° and the fact that values of *J* and δ must be derived from small differences between large numbers, the experimental values for δ and *J* may be taken to reasonably satisfy the field dependence conditions for these two quantities in ClF_3. These nuclear magnetic resonance results confirm the structure of C_{2v} symmetry for ClF_3. The chemical shift and nuclear spin coupling constants between the two non-equivalent sets of fluorine nuclei of ClF_3, the chemical shift being reduced to a resonance frequency of 10 Mc., are assigned the average values of 1097 and 403 c.p.s., respectively.

2. Fluorine Exchange in ClF_3 and BrF_3.—Exchange phenomena of sufficiently high frequency have been shown capable of collapsing a two-line spectrum into a single, concentration-dependent resonance.[9] When the non-equivalent species undergoing exchange are present in equal concentrations, the "fast exchange" single resonance appears at the midpoint of the two "slow exchange" resonances. The average lifetime, τ, in a given electrical (chemical) environment of a nucleus undergoing exchange is given by $\tau = {}^1/_{4}\pi\delta\omega$, where δω is the chemical shift in cycles per second between the exchanging environments.

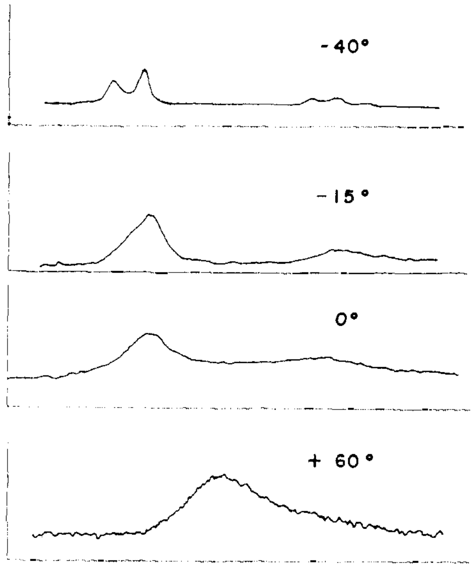

Fig. 5.—Temperature dependence of F^{19} spectrum of ClF_3 at 30 Mc.

The 30 Mc. fluorine magnetic resonance spectra of ClF_3 at temperatures between −40 and 60° are shown in Fig. 5. The resonance absorption of ClF_3 above 60° consists of a broad peak that progressively sharpens with increasing temperature. The spectrum of ClF_3 below 60° consists of two peaks, one displaced to a higher and one to a lower frequency from the "high temperature" resonance. These two peaks sharpen as the temperature is lowered until multiplet structures are revealed at a temperature of about −15°. Thus, the behavior of the magnetic resonance spectrum of ClF_3 as a function of temperature is wholly consistent with that of a molecule undergoing fluorine exchange.

The average lifetimes of fluorine atoms of ClF_3 in a given environment at −15° where the multiplet fine structure of spacing 403 c.p.s. is smeared as the result of exchange are $\tau = {}^1/_{4}\pi(403) = 1.97 \times 10^{-4}$ sec. At 60° the two chemically shifted components merge into a single resonance, and the average lifetime of the chemically exchanging fluorine atoms in a given environment is $\tau = {}^1/_{4}\pi\cdot(3291) = 2.42 \times 10^{-5}$ sec. From these values of the lifetimes of fluorine in a given environment at two temperatures, an average value of about 4.8 kcal. over the temperature range −15° to 60° is calculated for the activation energy of exchange for fluorine atoms in ClF_3.

The room temperature fluorine magnetic resonance spectrum of BrF_3 was examined and found to consist of a single sharp peak. BrF_3 would be expected to exhibit a spectrum similar to that of ClF_3 if it too possessed a structure of C_{2v} symmetry. The absence of structure or breadth in the resonance of BrF_3, assuming the molecule to possess at least two non-equivalent sets of fluorine atoms, indicates that at room temperature the rate of fluorine exchange is so rapid that all spin-spin splittings and chemical shifts have been obliterated. Unfortunately, the high melting point of BrF_3 (8.8°) prevents cooling, thus reducing the rate of fluorine exchange in BrF_3 to the point where the expected fine structure of the F^{19} magnetic resonance spectrum of the molecule appears. Inability to observe slow exchange in BrF_3 through the appearance of structure or at least broadening in the F^{19} spectrum probably can be ascribed to the existence of an activation energy for fluorine exchange in this molecule that is less than that of ClF_3.

3. Fluorine Exchange in IF_5 and BrF_5.—The fluorine magnetic resonance spectrum of IF_5 shown in Fig. 6 is seen to consist of two lines of relative intensities 1 and 4 and multiplet structures of 5 and 2, respectively. The interpretation of the IF_5 *n-m-r* spectrum in terms of a tetragonal pyramid structure[7] confirmed an earlier structure deter-

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(9) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

mination based on analysis of the vibrational spectrum of the molecule.[10]

The spin–spin splitting interaction between the apex and equatorial fluorine atoms of IF_5 amounts to 81 c.p.s. It is evident, therefore, that if exchange is occurring in IF_5 at room temperature, the lifetimes of the apex and equatorial fluorine atoms in a given environment must be greater than $\tau = {}^1/_4\pi(81) = 9.8 \times 10^{-4}$ sec.

The nuclear spin coupling of IF_5 disappears upon heating the sample to 115°, indicating the lifetime of fluorine atoms in a given environment at 115° is 9.8×10^{-4} sec. Further increases of temperature of the IF_5 sample result in progressive broadenings of the two resonances of the compound until at a temperature of 175° the two resonances are barely distinguishable above the background. Because of the accelerated attack of IF_5 on silica at elevated temperatures, spectra were not observed at temperatures above 175°. However, in view of the behavior of the ClF_3 spectrum near the transition temperature, it is estimated that the transition between "slow" and "fast" exchange occurs at ~195° for IF_5. The single "fast" exchange peak was not observed but would be expected to occur at a frequency of −711 c.p.s. On the basis of environmental lifetimes for fluorine of 9.8×10^{-4} sec. at 115° and 5.9×10^{-4} sec. at 195°, an activation energy of about 13 kcal. is estimated for fluorine exchange in IF_5.

As was shown previously,[7] the similarity of structures for IF_5 and BrF_5 is reflected in the fact that the fluorine magnetic resonance of each consists of two peaks of intensities 1 and 4 and multiplet structures of 5 and 2, respectively. The F^{19} spectrum of BrF_5 was observed at elevated temperatures, and there was no significant broadening of the individual lines of the spectrum to temperatures of ~180°. Therefore, it must be concluded that fluorine exchange in BrF_5 proceeds with an activation energy considerably in excess of that for IF_5.

4. Mechanism of Fluorine Exchange in Halogen Fluorides.—The mechanism of fluorine exchange in chlorine trifluoride and iodine pentafluoride is not known. Because of the precautions observed in purifying and preparing the samples and because the samples apparently were stable indefinitely in contact with quartz, impurities are not believed to be responsible for the exchange. There are three plausible mechanisms for exchange: dissociation, association and ionization. Of these three, association appears to be the most probable mechanism.

On the basis of conductivity and chemical studies, Emeleus, *et al.*,[11] have formulated an ionization of halogen acids as

$$2BrF_3 \rightleftarrows BrF_2^+ + BrF_4^-$$

$$2IF_5 \rightleftarrows IF_4^+ + IF_6^-$$

The measured specific conductivities are BrF_3, $8.0 \times 10^{-3}\ \Omega^{-1}$cm.$^{-1}$ at 25°[12]; IF_5, $2.0 \times 10^{-5}\ \Omega^{-1}$cm.$^{-1}$ at 25°[12]; and ClF_3, $3 \times 10^{-9}\ \Omega^{-1}$cm.$^{-1}$ at 25°.[13] If such ionic species are presumed to be responsible for the exchange, and since the rate of exchange would depend upon concentration of ionic species, the observed conductivities indicate that the rate of exchange in IF_5 would be much greater than in ClF_3. The observed rate of fluorine exchange in ClF_3, however, is much greater than that in IF_5. If the mechanism for exchange is the same for these two fluorides, ionization cannot be responsible for the observed exchange.

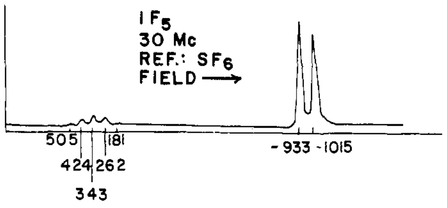


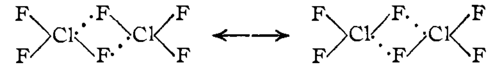
Fig. 6.—F^{19} spectrum of IF_5 at 30 Mc.

Chlorine trifluoride will undergo dissociation at elevated temperatures to chlorine monofluoride and fluorine[14]; Adams, *et al.*,[15] have measured the rate of

$$ClF_3 \rightleftarrows ClF + F_2;\ K_p^{180°} = 0.069 \times 10^{-4}$$

isotope exchange in the system $ClF_3{}^*–F_2$ at 454°K. The exchange was presumed to proceed partly by a dissociative mechanism and partly by a heterogeneous wall reaction (involving a fluoride coating). The observed rate here at 454°K. was much slower than that observed for pure chlorine trifluoride at 223°K. Therefore, a dissociative mechanism cannot account for the observed exchange in pure chlorine trifluoride at or near room temperature nor for iodine pentafluoride which has not been observed to undergo dissociation.

Schmitz and Schumacher[16] found that the deviation of ClF_3 from perfect gas behavior could be explained quantitatively by its association to a dimer. Such a dimer should be present in the liquid and could account for fluorine exchange.



Other data, although less conclusive than the above, have been presented for the existence of association in liquid chlorine trifluoride and iodine pentafluoride.[17,18] These data are based on Trouton and dielectric constants. Similar data were interpreted for BrF_5 in terms of a non-associated liquid.[19]

Dimerization of XF_3 and XF_5 is possible by vir-

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[10] R. C. Lord, M. A. Lynch, Jr., W. C. Schumb and E. J. Slowinski, THIS JOURNAL, **72**, 522 (1950).

[11] J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1954, pp. 44–48.

[12] A. A. Banks, H. J. Emeleus and A. A. Woolf, *J. Chem. Soc.*, 2861 (1949).

[13] J. H. Simons, ref. 11, p. 44.

[14] H. Schmitz and H. J. Schumacher, *Z. Naturforsch.*, **2A**, 362 (1947).

[15] R. M. Adams, R. B. Bernstein and J. J. Katz, *J. Chem. Phys.*, **22**, 13 (1954).

[16] H. Schmitz and H. J. Schumacher, *Z. Naturforsch.*, **2A**, 363 (1947).

[17] M. T. Rogers, H. B. Thompson and J. L. Speirs, THIS JOURNAL, **76**, 4841 (1954).

[18] M. T. Rogers, J. L. Speirs, H. B. Thompson and M. B. Panish, *ibid.*, **76**, 4843 (1954).

[19] M. T. Rogers, R. D. Pruett, H. B. Thompson and J. L. Speirs, *ibid.*, **78**, 44 (1956).

tue of possession of unfilled d orbitals by the X atoms. The stability of bonds involving d orbitals usually increases with increase in the atomic number of X. Likewise, the formation of dimers should be sterically favored by increase in size of X. Therefore, the stability of the dimers should be: $BrF_3 > ClF_3$, $IF_5 > BrF_5$ and $MF_3 > MF_5$. If it is assumed then that dimerization is the mechanism of fluorine exchange in the halogen fluorides, the rates of fluorine exchange might be expected to decrease in the order $BrF_3 > ClF_3 > IF_5 > BrF_5$. The results of the *n–m–r* study of exchange in halogen fluorides confirm this ordering for relative rates of exchange and thus indicate dimerization to be the mechanism for exchange in these systems.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Reactions of Triethylgermanium Hydride with Salts of Transitional Elements and with Organic Haloacids

BY HERBERT H. ANDERSON

RECEIVED JULY 17, 1956

Triethylgermanium hydride reduces salts of certain transitional elements either to a lower oxidation state or sometimes to the free metal. These reductions apparently occur with transitional elements in which the oxidation potential $E°$ for the highest oxidation state present—such as Ti(III) to Ti(IV)—has a value of −0.06 volt or less; as expected, no reduction of $CdCl_2$ occurs. Triethylgermanium hydride yields the corresponding new esters when heated with the strong acids CF_3COOH, C_2F_5COOH and *n*-C_3F_7COOH; the weak acid CH_3COOH does not react at an appreciable rate. Moreover, triethylgermanium hydride reduces certain organic chloroacids, bromoacids or iodoacids. This paper includes new densities and refractive indices for triethylgermanium chloride, bromide, iodide and hydride.

This paper describes the previously unknown reaction of triethylgermanium hydride with salts of the transitional elements, and also with organic haloacids. Triethylgermanium hydride first was prepared by three successive reactions[1]

$$2(C_2H_5)_3GeBr + 2Na \longrightarrow (C_2H_5)_3GeGe(C_2H_5)_3 + 2NaBr$$

$$(C_2H_5)_3GeGe(C_2H_5)_3 + 2Li \longrightarrow 2LiGe(C_2H_5)_3$$

$$LiGe(C_2H_5)_3 + NH_2 \longrightarrow (C_2H_5)_3GeH + LiNH_2$$

The preparation of $C_2H_5SiH_3$[2] from $C_2H_5SiCl_3$ and $LiAlH_4$ and also the preparation of tricyclohexylgermanium hydride[3] from $(C_6H_{11})_3GeCl$ and $LiAlH_4$ suggested the one-step preparation of $(C_2H_5)_3GeH$

$$4(C_2H_5)_3GeCl + LiAlH_4 \longrightarrow 4(C_2H_5)_2GeH + LiCl + AlCl_3$$

which we have demonstrated.

There is little information on the reactions of organogermanium hydrides in the literature. Typically, triphenylgermanium hydride yields $(C_6H_5)_3GeBr$ in reaction with bromine $(C_6H_5)_3GeH + Br_2 \rightarrow (C_6H_5)_3GeBr + HBr$ or with concentrated hydrobromic acid $(C_6H_5)_3GeH + HBr \rightarrow (C_6H_5)_3GeBr + H_2$.[4]

Twenty-one reactions in Table I of the present paper indicate that $(C_2H_5)_3GeH$ is a fairly reactive compound. The corresponding oxide $[(C_2H_5)_3Ge]_2O$ reacts easily with the *weak* acid CH_3COOH to yield $(C_2H_5)_3GeOCOCH_3$,[5] while $(C_2H_5)_3GeH$ and CH_3COOH react very slowly during reflux, if at all. Reflux with *strong* acids such as hydrochloric, sulfuric or trifluoroacetic converts the $(C_2H_5)_3GeH$ into the corresponding halide or ester easily; *weaker* CHF_2COOH in a 2-hour reflux furnishes a 60% yield of ester, while *still-weaker* CH_2FCOOH furnishes a 20% yield of ester at most.

Unlike acetic acid, which contains a much lower concentration of acetate ions, mercuric acetate reacts completely with $(C_2H_5)_3GeH$ in 15 minutes of reflux, with formation of metallic mercury.

In the reaction listed in Table I, there is a reduction of the iodoacetic acid to acetic acid.

$$(C_2H_5)_3GeH + ICH_2COOH \longrightarrow (C_2H_5)_3GeI + CH_3COOH$$

Similar reductions occur in reactions with CCl_3COOH and CBr_3COOH, but none occurs with completely fluorinated CF_3COOH, C_2F_5COOH and *n*-C_3F_7COOH. All this appears consistent with the following bond energies in kcal./mole: C–F, 107; C–H, 87; C–Cl, 67; C–Br, 54; C–I, 46.

A related exchange of Si–H and C–Cl occurs when $AlCl_3$ catalyst is present.[6]

$$(C_2H_5)_3SiH + n\text{-}C_6H_{13}Cl \longrightarrow (C_2H_5)_3SiCl + n\text{-}C_6H_{14}{}^{6}$$

Fourteen reactions of $(C_2H_5)_3GeH$ with salts or halides of transitional elements, listed in Table I, and the previously reported reaction of $(i\text{-}C_3H_7)_2GeH_2$ with $AgOCOCH_3$[7] to yield $(i\text{-}C_3H_7)_2Ge(OCOCH_3)_2$ and silver, suggest the following three conclusions.

1. These reductions apparently occur with transitional elements in which the oxidation potential $E°$ for the next-highest to the highest oxidation state present—such as Ti(III) to Ti(IV)—has a value between approximately −0.06 and −2.0 v. As expected, refluxing $(C_2H_5)_3GeH$ with $CdCl_2$ brings no reduction to Cd, since $E°$ for Cd is +0.40 v. Although there is no available oxidation potential, $E°$, for germanium, the failure of metallic germanium to react with hydrochloric acid

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[1] C. A. Kraus and E. A. Flood, THIS JOURNAL, **54**, 1635 (1932).

[2] A. E. Finholt, *et al.*, *ibid.*, **69**, 2692 (1947).

[3] O. H. Johnson and W. R. Nebergall, *ibid.*, **71**, 1720 (1949).

[4] C. A. Kraus and L. S. Foster, *ibid.*, **49**, 457 (1927).

[5] H. H. Anderson, *ibid.*, **72**, 2089 (1950).

[6] F. C. Whitmore, *et al.*, *ibid.*, **69**, 2108 (1947).

[7] H. H. Anderson, *ibid.*, **78**, 1692 (1956).