[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY]

Six-coördinate Silicon(IV).[1] II. The Hydrolysis and Racemization of the Tris-(acetylacetonato)-silicon(IV) Cation

BY S. K. DHAR, VERA DORON AND STANLEY KIRSCHNER

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The experimental details of the preparation of an asymmetric, octahedral, six-coördinate silicon(IV) complex cation, the formation and resolution of diastereoisomers, and the removal of the resolving anion are described. In addition, the racemization and hydrolysis of the asymmetric tris-(acetylacetonato)-silicon(IV) cation, which were studied by optical rotation techniques in the visible region and optical absorption techniques in the ultraviolet are described. The rates of racemization and hydrolysis were found to be equal to each other in aqueous solution at several different temperatures, which leads to a postulation of the mechanism of racemization of the complex ion. The half-lives and rate constants of the rate process under various conditions are given, as are the heat and entropy of activation.

Introduction

Interest has arisen in the possibility that several cations, which do not ordinarily exhibit six-coördination, may be linked to six atoms by covalent or partially covalent bonds, in certain favorable cases.[2–4] That silicon(IV) falls into this category in the complex tris-(acetylacetonato)-silicon(IV) cation, $[Si(acac)_3]^+$, was presented in a recent communication.[1,5] Support for this viewpoint is given by West,[6] who described the infrared spectra of $[Si(acac)_3]Cl \cdot HCl$ (I) and other β-diketones of silicon(IV), and, from a comparison of these spectra with that of free acetylacetone, concluded that the ligands of I all behave as bidentate chelating agents to silicon.

It is expected, therefore, that silicon(IV) in this complex cation is six-coördinate and has an octahedral configuration,[7,8] and this leads to the conclusion that the cation is asymmetric. The experimental details of the reported resolution[1] of the complex into its enantiomers (which offers conclusive evidence for the existence of six-coördinate silicon(IV) and for its octahedral configuration) are presented below. The possibility of seven-coördination (coördination of the chloride ion) is remote in view of the conductivity of the complex in anhydrous chloroform.

In addition, it was decided to study the racemization and hydrolysis of the cation to determine whether these are in any way related and whether a mechanism of racemization can be formulated. The heat and entropy of activation of the rate process were also studied in an attempt to shed light on the racemization and hydrolysis processes.

Discussion

Hydrolysis Studies.—That slow hydrolysis of $[Si(acac)_3]^+$ occurs was first mentioned by Dilthey[9] and was confirmed recently by West[6] *via* iron(III) chloride tests on aqueous solutions of $[Si(acac)_3]Cl \cdot HCl$ which were allowed to stand for varying periods of time. This was also confirmed by the authors in an experiment in which a diastereoisomer of $[Si(acac)_3]^+$ was precipitated with sodium monohydrogen (−)-dibenzoyl-*d*-tartrate. The quantity of precipitated diastereoisomer decreased if the complex compound was allowed to stand in water before addition of the resolving agent. If the complex was allowed to stand for 6 hr. at room temperature, no precipitate was obtained at all, indicating that essentially complete hydrolysis of the complex ion had occurred.

If $[Si(acac)_3]Cl \cdot HCl$ in aqueous solution is made alkaline by addition of sodium hydroxide (to *p*H 9.2), the associated hydrogen chloride is neutralized instantly, and the slow hydrolysis of the complex cation begins immediately. Figure 1 shows the *p*H decay with time. The initial steep descent of the upper part of the curve probably represents the relatively rapid basic hydrolysis which occurs until the *p*H drops to the region where acid hydrolysis (aquation) can take place. The continued drop in *p*H during acid hydrolysis can be described by the reactions

$$[Si(acac)_3]^+ + 5H_2O \rightleftharpoons Si(OH)_4 + 3Hacac + H_3O^+$$

$$x\ Si(OH)_4 \xrightarrow{H_2O} (SiO_2)_x(H_2O)_{2x-y} + yH_2O$$

In support of this are the absorption spectra given in Fig. 2, which show that the acetylacetonate

TABLE I

HALF-LIVES AND SPECIFIC REACTION RATE CONSTANTS

Temp., °C.	$t_{1/2}$ (min.)	Slope (min.$^{-1}$ × 10^3)	k (sec.$^{-1}$ × 10^4)	*p*H Initial	*p*H Final	Process[a]
19.70	97.5	−3.10	1.19	3.20	2.95	A
19.70	96.5	−3.13	1.20	3.20	2.95	R
21.20	81.5	−3.70	1.42	3.20	2.95	A
22.70	64.3	−4.70	1.80	3.20	2.95	R
22.70	64.3	−4.70	1.80	3.20	2.95	A
23.50	58.9	−5.12	1.96	3.20	2.95	A
23.50	59.9	−5.05	1.97	5.40	5.00	A (1.5 × 10^{-5} mole/l.)
24.65	52.0	−5.80	2.22	3.20	2.95	A
24.65	50.8	−5.95	2.28	4.90	4.48	A (3 × 10^{-5} mole/l.)
24.65	52.0	−5.80	2.22	9.20	3.58	A
24.65	52.0	−5.80	2.22	1.55		A

[a] "A" represents optical absorption study. "R" represents optical racemization study. The concentration of the complex is in the range of 7.5 × 10^{-4} mole/l. except where mentioned in parentheses next to "A."

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(1) For the previous paper in this series see THIS JOURNAL, **80**, 753 (1958).

(2) S. Kirschner, *ibid.*, **78**, 2372 (1956).

(3) F. P. Dwyer and A. M. Sargeson, *J. Proc. Roy. Soc., N. S. Wales*, **90**, 29 (1956).

(4) V. Doron and S. Kirschner, Abstr. of Papers, 132nd Meeting, Am. Chem. Soc., 12N, 1957.

(5) acac = acetylacetonate anion, $C_5H_7O_2^-$. The complex cation is also named tris-(2,4-pentanediono)-silicon(IV).

(6) R. West, THIS JOURNAL, **80**, 3246 (1958).

(7) A. Werner, *Ber.*, **47**, 3087 (1914).

(8) J. C. Bailar, Jr., Ed., "Chemistry of the Coördination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, pp. 274 ff.

(9) W. Dilthey, *Ber.*, **36**, 932, 1595 (1903).

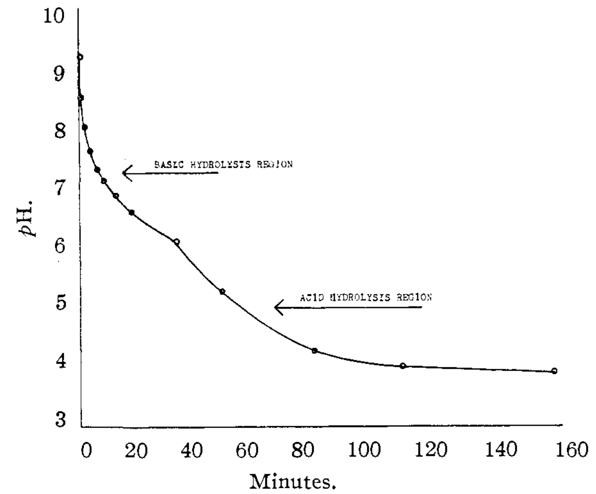

Fig. 1.—*p*H Decay *vs.* time for an aqueous solution of tris-(acetylacetonato)-silicon(IV) chloride hydrochloride (initial *p*H adjusted to 9.2, concn. is 7.5 × 10^{-4} mole/l.).

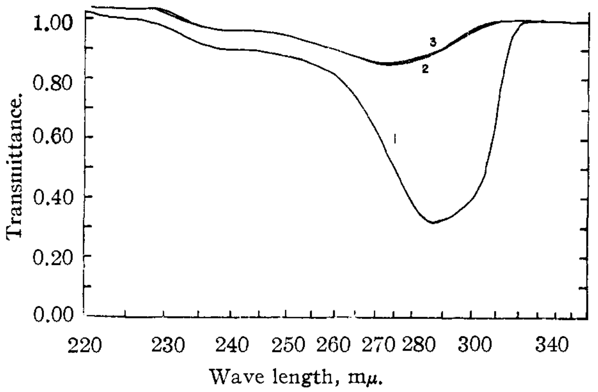

Fig. 2.—Ultraviolet absorption spectra (aqueous solutions): (1) 7.58 × 10^{-4} mole/l. [Si(acac)$_3$]Cl·HCl, freshly prepared; (2) hydrolysis product from (1) (*p*H 3.0); (3) 2.27 × 10^{-3} mole/l. acetylacetone at *p*H 3.0; all the solutions were diluted fifty times before recording the spectra; distilled water blank.

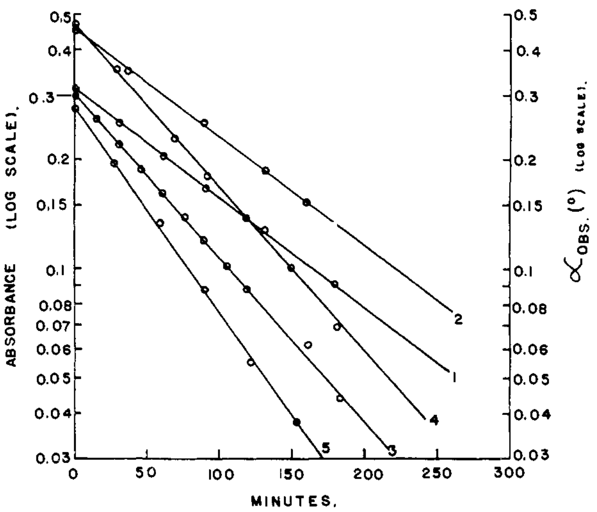

Fig. 3.—First-order kinetics plot: (1) hydrolysis of the complex at 19.7°, optical density against time; (2) racemization at 19.7°, optical rotation against time using 2-decimeter tube; (3) hydrolysis at 22.7°, optical density against time; (4) racemization at 22.7°, optical rotation against time using 2-decimeter tube; (5) hydrolysis at 24.7°, optical density against time.

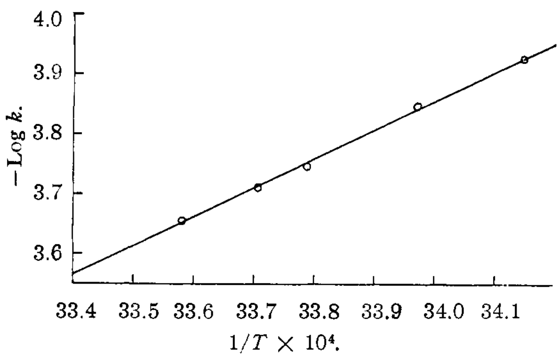

Fig. 4.—Plot of −log *k* against 1/*T* (°K.); "*k*" represents the specific reaction rate constant of the hydrolysis (and racemization).

ligands are liberated as free acetylacetone if [Si(acac)$_3$]$^+$ is allowed to remain in water for an extended period of time. Table I shows that the rate of aquation is independent of the *p*H at a given temperature (at or below *p*H 9.2), which suggests that the first step is the rate-determining one. (Some of the complex is destroyed by rapid basic hydrolysis at alkaline *p*H values.)

Since the ultraviolet absorption curves of [Si(acac)$_3$]Cl·HCl and its hydrolysis products differ, it is possible to follow the rate of hydrolysis of the complex at low concentrations by observation of optical absorption at 305 mμ., where the complex has appreciable absorption and the hydrolysis products essentially no absorption at all. The aquation follows simple first-order (or pseudo-first order) kinetics as evidenced by the linearity of the log plots in Fig. 3. Since the over-all process is irreversible under the conditions operative during the reaction (as shown by the complete disappearance of any optical absorption due to unhydrolyzed [Si(acac)$_3$]$^+$ indicating that an equilibrium has not been established), the reverse rate constants have been neglected.

The temperature dependence of the rate constants is shown in Table I. Figure 4 is a plot of −log *k vs.* 1/*T*(°K.), and ΔH^* and ΔS^* for the hydrolysis were determined from this plot to be 22 kcal./mole/°K. and −0.95 e.u., respectively. These values are based on the assumption of a transmission coefficient of unity.

The inflection points obtained during the titration of [Si(acac)$_3$]Cl·HCl with dilute sodium hydroxide (Fig. 5) show that one mole of base per mole of complex neutralizes the associated hydrogen chloride and that four additional moles of base per mole of complex react liberating three moles of acetylacetonate from the cation and forming [Si(OH)$_4$], which probably undergoes spontaneous dehydration to form hydrated silica. A rapid reaction occurs during the addition of titrant (dilute sodium hydroxide) to an aqueous solution of the complex until a *p*H of about 8 is attained. Thereafter, the process is considerably slower, and the

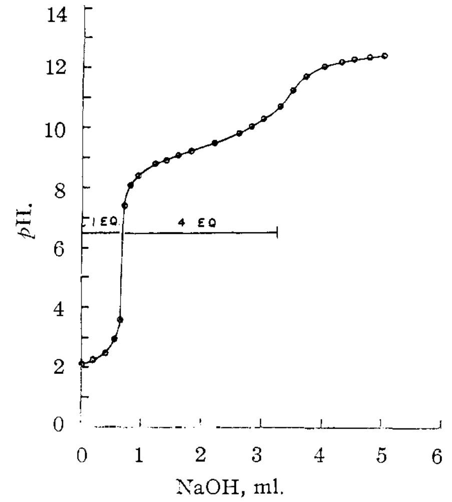

Fig. 5.—Potentiometric titration of 2.56 × 10^{-4} *M* [Si(acac)$_3$]Cl·HCl with 0.395 *M* NaOH.

addition of base above this *p*H probably results in the direct displacement of the acetylacetonate ligands by hydroxyl ions, with the reaction having a measurable rate under these conditions. The titration also results in the formation of a yellow solution between *p*H values of 8 and 9.5. The yellow material, whose color gradually fades if the solution is allowed to stand, is extractable with organic solvents and is currently under study.

Racemization Studies.—After *d,l*-[Si(acac)$_3$]Cl was prepared and resolved into optical enantiomers, the *levo*-isomer was observed polarimetrically until its rotation decayed to zero. If the curve is extrapolated to zero time (the instant at which the resolving anion of the diastereoisomer is replaced by chloride), the specific rotation at that time is −1,300°, which makes polarimetric observation of the racemization relatively easy in this case. Table II gives the optical rotations achieved in the resolution of the complex.

TABLE II

OPTICAL ROTATIONS[a]

Compound	Concn. (%)	$\alpha_{\text{obsd.}}$	$\alpha]_D^{22.7°}$
L-Si(acac)$_3$*d*-(−)-$HC_{18}H_{12}O_8$[b]	0.0088	−0.068°	−773°
L-Si(acac)$_3$Cl·HCl (after 30 min. in aq. soln.)	0.0311	−0.300°	−965°
L-Si(acac)$_3$Cl·HCl (extrapd. to zero time)			−1300°
d-(−)-$C_{18}H_{14}O_8$[c]			−118.5 (20°)

[a] The average deviation of these observed optical rotations in water is ±0.003°. [b] Monohydrogen (−)dibenzoyl-*d*-tartrate is the resolving anion. [c] (−)dibenzoyl-*d*-tartaric acid.

Figure 3 and the data in Table I show that the rates of reaction and hydrolysis are identical under identical conditions. This indicates that the observed racemization of the complex is due to the destruction of the complex by hydrolysis and not to inversion of configuration because of labile Si–O bonds, which suggests that greater stability of the cation toward racemization should hold in solvents where solvolysis is less likely to occur than in water. A study of this possibility is now under way.

Conclusions

Silicon(IV) is six-coördinate in the tris-(acetylacetonato)-silicon(IV) cation, the structure of which is octahedral, as evidenced by its resolution into optical enantiomers and as supported by infrared studies. A comparison of the racemization and hydrolysis rates in aqueous solution indicates that the racemization is due to destruction of the complex by hydrolysis and not to inversion of con-configuration. Both the racemization and hydrolysis are first order (or pseudo first order) processes which is in agreement with the aquation kinetics of other octahedral complexes.[10] The basic hydrolysis (and racemization) of the complex probably occurs by displacement of the acetylacetonate ligands by hydroxyl ions with subsequent dehydration of the silicon(IV) hydroxide to hydrated silica, whereas in acid silution these processes are probably due to initial attack by water molecules as indicated in the mechanism described earlier.

The stability of the complex in water solution is not surprising in view of the existence of silicon(IV) in its maximum coördination state, and in view of the stability of similar metal–1,3-diketone complexes.[11–13]

Experimental

Reagents.—The tetrachlorosilane, acetylacetone and solid chemicals employed were of reagent grade. The solvents were of analytical grade.

Compounds. 1. Tri-(acetylacetonato)-silicon(IV) Chloride Monohydrochloride. [Si($C_5H_7O_2$)$_3$]Cl·HCl.—This was prepared according to the method of Dilthey.[9] It was found to be soluble in water, ethanol and chloroform. The product was recrystallized from chloroform solution by the addition of an excess of diethyl ether. Calcd. for [Si($C_5H_7O_2$)$_3$]Cl·HCl: Si, 7.15; Cl, 17.87. Found: Si, 6.75; Cl, 16.94. The rather low value obtained for chlorine is undoubtedly due to loss of part of the associated hydrogen chloride during vacuum drying of the compound. However, the analysis of the diastereoisomeric salt of the cation (which contains no associated hydrogen chloride) establishes the purity of the product (*vide infra*).

2. (−)-Dibenzoyl-*d*-tartaric Acid, *d*-(−)-$C_{18}H_{14}O_8$.—This was prepared by a modification[14,15] of the method of Zetzsche and Hubacher.[16] Calcd. for $C_{18}H_{14}O_8$; C, 60.34; H, 3.94. Found: C, 60.34; H, 3.90. $[\alpha]^{20}_D$ 118.5° in water. However, the free acid is only slightly soluble in water. The mono- and disodium salts (formed by the addition of sodium hydroxide in water) are both soluble.

Preparation and Resolution of Diastereoisomers.—To 0.36 g. of (−)-dibenzoyl-*d*-tartaric acid (*ca.* 10^{-3} mole) suspended in 30 ml. of water there was added a slight excess over the required quantity of sodium hydroxide (2.1 ml. of approximately 1 *N* NaOH) to convert the acid to the disodium salt.[17] To the resulting solution there was added with stirring 0.80 g. of racemic tri-(acetylacetonato)-silicon(IV) chloride monohydrochloride (*ca.* 2 × 10^{-3} mole) dissolved in 35 ml. of water. The *p*H of this mixture was between 4 and 5 which was optimum for the precipitation. The beaker containing the mixture was placed in an ice-bath for 15

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(12) H. F. Holtzclaw, Jr., A. H. Carlson and J. P. Collman, *ibid.*, **78**, 1838 (1956).

(13) R. M. Isatt, W. C. Fernelius, C. G. Haas, Jr., and B. P. Block, *J. Phys. Chem.*, **59**, 170 (1955).

(14) S. Kirschner, Dissertation, University of Illinois, p. 43, 1954.

(15) C. L. Butler and L. H. Cretcher, THIS JOURNAL, **55**, 2605 (1933).

(16) F. Zetzsche and M. Hubacher, *Helv. Chim. Acta*, **9**, 291 (1926).

(17) Caution must be exercised against adding too large an excess of sodium hydroxide. If the final solution (containing the silicon complex) is alkaline, the diastereoisomer will not precipitate.

minutes, and the resulting precipitate of the diastereoisomer, L-[Si(acac)$_3$]*d*-(−)-$HC_{18}H_{12}O_8$, was filtered quickly, washed with four 2-ml. portions of anhydrous acetone, and dried at room temperature by passing dry air over the product; yield 0.384 g. (56.2%). Calcd. for L-[Si($C_5H_7O_2$)$_3$]*d*-(−)-$HC_{18}H_{12}O_8$: C, 58.11; H, 5.02; Si, 4.12. Found: C, 59.06; H, 5.01; Si, 4.25.

The filtrate (after a fivefold dilution) showed a high positive rotation (α obsd. = 0.650°) which decayed to a constant value of −0.340° after several hours, indicating that not all of the (−)-dibenzoyl-*d*-tartrate had been removed during the precipitation.

Replacement of the Resolving Anion.—The precipitated diastereoisomer, L-[Si(acac)$_3$]*d*-(−)-$HC_{18}H_{12}O_8$ (0.1334 g.), was suspended in water and mixed (with constant stirring) with five grams of Dowex 1-X8 anion-exchange resin in the chloride form (50–100 mesh) for 15 minutes (total volume = 100 ml.). The precipitated diastereoisomer dissolved and the resolving anion exchanged with chloride according to the equation

$$\text{L-}[\mathrm{Si(acac)_3}]d\text{-}(-)\text{-}\mathrm{HC_{18}H_{12}O_8} + 2\mathrm{RCl} \longrightarrow \text{L-}[\mathrm{Si(acac)_3}]\mathrm{Cl} + \mathrm{HCl} + \mathrm{R_2C_{18}H_{12}O_8} \quad (2)$$

where R = the unipositive resin cation. That the hydrogen ion is separated from the resolving anion in the resin procedure is shown by (a) the observed drop in *p*H after the resin treatment, and (b) the appearance of two chloride ions in the filtrate for every silicon, as determined by chloride and silicon analyses on the filtrate containing the enantiomer. That the resin effectively removes all the resolving anion is shown by treating 0.001 mole of sodium monohydrogen (−)-dibenzoyl-*d*-tartrate with resin under the conditions described above. This treatment produces a filtrate without any observable rotation.

The filtrate from the initial precipitation reaction was treated with resin in the manner described above and a 0.209% solution showed $\alpha_{\text{obs.}} = +0.908 \pm 0.003°$; $[\alpha]^{15}\text{D}$ + 435° at 15°. The relatively low value is due to incomplete separation of the *levo*-enantiomer of the complex during the precipitation process. The separation of the *dextro*-isomer from the *levo* is improved if, in the initial precipitation reaction, equimolar quantities of the resolving agent and racemic silicon complex are used. The specific rotation of the *dextro*-isomer prepared in this manner is 680° at 22.7°. The half-life for racemization of the *dextro*-isomer at 22.7° is 64 minutes, which is the same as that for the *levo*-enantiomer.

Hydrolysis Studies.—Ultraviolet absorption spectra were taken of [Si(acac)$_3$]Cl·HCl immediately after dissolving it in water and after it had undergone hydrolysis (6 hr.), as well as of free acetylacetone (see Fig. 2). Since neither the hydrolysis products nor free acetylacetone shows any appreciable absorption at 305 mμ, whereas the complex has appreciable absorption at this wave length, it was chosen as the wave length to study the hydrolysis rate (see Fig. 2). All solutions studied were thermostated to within ±0.1°. In order to obtain measurable transmittance values, it was frequently necessary to dilute aliquots of the solution immediately before transmittance measurements were made. These were usually fifty-fold dilutions resulting in a final concentration of about 1.5×10^{-5} *M* in silicon.

1. **Behavior of the Aqueous Solution of [Si(acac)$_3$]Cl·HCl.**—While the complex was allowed to stand in water, its ultraviolet absorption spectrum changed with time. After 6 hr., there was no further change and the spectrum at that time corresponded exactly to the spectrum of free acetylacetone in water at a concentration of three times the initial molar concentration of the complex. The *p*H values of the untreated solutions of the complex at concentrations of 7.5×10^{-4}, 3.0×10^{-5} and 1.5×10^{-5} mole per liter were 3.2, 4.9, 5.4, respectively. After long standing, these values decayed to 2.95, 4.48 and 5.0, respectively. In order to be better able to observe the decay of *p*H of the aqueous solution of the complex with time, it was decided to add sodium hydroxide to the solution at the instant of dissolution to neutralize the associated hydrochloric acid. This raised the *p*H to about 9, thereby enabling a plot of *p*H *vs.* time of standing to be made (see Fig. 1).

2. **Titration of the Complex.**—This was carried out in the usual fashion using a *p*H meter as the detector and sodium hydroxide as the titrant (see Fig. 5).

Racemization Studies.—These were carried out with the L-[Si(acac)$_3$]Cl isomer obtained from ion-exchange treatment of the diastereoisomer L-[Si(acac)$_3$]*d*-(−)-$HC_{15}H_{12}O_8$.[1] The concentration of the complex was about 7.5×10^{-4} mole per liter. Experiments also were performed where the complex concentration was 3.0×10^{-5} and 1.5×10^{-5} molar. No difference in the kinetic order of the reaction could be observed by these concentration changes.

Instruments.—Ultraviolet spectra were obtained with a Spectracord automatic recording spectrophotometer using 1 cm. quartz cells. The hydrolysis data at 305 mμ were taken with a Beckman model DU spectrophotometer using 1 cm. quartz cells. Determinations of optical rotation were carried out at the sodium-D line on a Rudolph High Precision Visual Polarimeter, Model 80. The *p*H determinations were made with a Leeds and Northrup *p*H Indicator.

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DETROIT, MICHIGAN

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY, CHEMICAL ENGINEERING DIVISION]

Preparation, Properties and Reactions of Bismuth Pentafluoride[1]

BY JACK FISCHER AND EDGARS RUDZITIS

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Bismuth pentafluoride was prepared by synthesis from bismuth and fluorine at 500°. Its crystal structure, density of the solid and liquid, triple point temperature and vapor pressure were determined and the latent heat of vaporization and Trouton constant were calculated. Various chemical reactions of bismuth pentafluoride, such as its reduction with hydrogen and fluorination reactions with various elements and compounds, were studied. Bismuth pentafluoride acts as a strong fluorinating agent.

A literature search revealed little information about bismuth pentafluoride. There have been some unsuccessful attempts to prepare bismuth pentafluoride in aqueous solution.[2,3] The compound was first prepared by von Wartenberg[4] by fluorination of bismuth trifluoride at 550°. Bismuth pentafluoride was found to be extremely reactive and no positive identification was carried out. Gutman and Emeleus[5] next investigated the chemistry of bismuth pentafluoride. They studied

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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[3] Wuorinen, *Suomen Kemistilehti*, **B**, 3 (1940).

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