TABLE I

RATE CONSTANTS FOR THE FORMATION OF MONO-COMPLEXES OF IRON(III) AT 25.0°

L	Fe^{3+} + L k, F^{-1} sec.$^{-1}$	$FeOH^{2+}$ + L k, F^{-1} sec.$^{-1}$	Reference
Cl^-	9.4	1.1×10^4	9
Br^{-a}	20	2.7×10^4	10
SCN^-	1.27×10^2	1.0×10^4	8
SO_4^{2-}	$(6.37 \times 10^3)^b$	3×10^5	12, 13
HSO_4^-	...	$(1.4 \times 10^5)^c$	13
F^-	$(5.0 \times 10^3)^b$	...	11
HF	11.4	$(3.1 \times 10^3)^c$	11
N_3^-	$(1.6 \times 10^5)^b$	...	This work
HN_3	4.0	$(6.8 \times 10^3)^c$	This work

[a] $T = 22 \pm 2°$. [b] Calculated on the assumption that the acid-independent path is $Fe^{3+} + X^- \rightarrow FeX^{2+}$. [c] Calculated on the assumption that the acid-independent path is $FeOH^{2+} + HX \rightarrow FeX^{2+} + H_2O$.

various mono-complexes of iron(III) are presented in Table I. The rate constants for the reactions of $Fe(H_2O)_6^{3+}$ and $(H_2O)_5FeOH^{2+}$ with chloride, bromide, and thiocyanate, respectively, are presented in the second and third columns of the table. A comparison of these columns shows that $(H_2O)_5FeOH^{2+}$ undergoes reaction more rapidly than $Fe(H_2O)_6^{3+}$. Two formulations of the reactants in the acid-independent path involving sulfate, fluoride, and azide are given; the reactants in the first formulation are Fe^{3+} and X^- and in the second $FeOH^{2+}$ and HX.

Eigen[16] and Wendt and Strehlow[12] have adopted the first formulation and consider $Fe(H_2O)_6^{3+}$ and X^- as the reactants in the acid-independent path. It is apparent from the second column of Table I that this interpretation leads, at least formally, to a marked dependence of the rate constants on the nature of the entering ligand. In order to account for this dependence Eigen and Wendt and Strehlow propose that $Fe(H_2O)_6^{3+}$ undergoes hydrolysis in the collision complex formed from the reactants, *i.e.*

$$(H_2O)_5FeH_2O^{3+} + X^- \rightleftharpoons [(H_2O)_5FeOH - HX]^{2+} \rightleftharpoons [*]^{2+} \rightleftharpoons (H_2O)_5FeX^{2+} + H_2O$$

and that the degree of hydrolysis of $Fe(H_2O)_6^{3+}$ increases with the basicity of the entering ligand. In terms of this interpretation, the relatively high rate constants for the acid-independent paths involving sulfate, fluoride, and azide reflect increasing degrees of "inner hydrolysis" of the collision complex.

On the other hand, the second formulation may be adopted and $FeOH^{2+}$ and HX considered as the reactants in the acid-independent path. In this case the rate constants for all the Fe^{3+} + L reactions lie in the range of 4.0 to 127 F^{-1} sec.$^{-1}$ and the rate constants for all the $FeOH^{2+}$ + L reactions lie in the range of 3×10^3 to 3×10^5 F^{-1} sec.$^{-1}$ at 25.0°. Thus not only is the dependence of the rate constants on the nature of the entering ligand reduced in the second formulation, but the dependence of the rate constants on whether $Fe(H_2O)_6^{3+}$ or $(H_2O)_5FeOH^{2+}$ is undergoing substitution is more readily apparent. It should be noted, however, that both formulations are consistent with the kinetic data since the interconversion of the acid and base forms of the reactants is rapid enough to maintain equilibrium between them throughout the reaction; the rate constants in the two formulations are related simply by the appropriate equilibrium constants. Nevertheless, the second formulation does have the advantage of removing the apparent ligand specificity and of emphasizing that the rate constants are primarily determined by whether $Fe(H_2O)_6^{3+}$ or $(H_2O)_5FeOH^{2+}$ is undergoing reaction.

(16) M. Eigen, in "Advances in the Chemistry of the Coördination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 371.

According to Connick and Stover[17] and Connick and Genser,[18] the second order rate constant for water exchange on $Fe(H_2O)_6^{3+}$ is approximately 2.8×10^2 F^{-1} sec.$^{-1}$ at 25°, where any of the coördinated water molecules may be replaced. Connick and Genser also have estimated that the rate constant for water exchange on $(H_2O)_5FeOH^{2+}$ is very roughly 100 times larger than that for water exchange on $Fe(H_2O)_6^{3+}$. The similarity of the rate constants for water exchange and complex formation and the absence of a large ligand specificity lends additional support to the view that the rates are primarily controlled by the elimination of a coördinated water molecule.[17-19]

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Crystalline Lithiomethyl Trimethylsilane and Some of its Properties[1]

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We recently have isolated and characterized lithiomethyl trimethylsilane. Sommer, Murch, and Mitch[2] reported the preparation of this compound in pentane solution and studied its reaction with silicon tetrachloride to form $[(CH_3)_3SiCH_2]_4Si$. These workers, however, did not attempt to isolate the pure compound.

Satisfactory yields (about 60%) of lithiomethyl trimethylsilane can be obtained by the reaction between lithium metal and a solution of chloromethyltrimethylsilane in 2-methylpentane. Vigorous stirring during the entire course of the reaction is essential in order to minimize undesirable coupling of the product lithium

(1) This research was supported in part by the Air Force Office of Scientific Research under contract No. AF 49(638)927 and in part by a National Science Foundation Coöperative Fellowship.
(2) L. H. Sommer, R. M. Murch, and F. A. Mitch, *J. Am. Chem. Soc.*, **76**, 1619 (1954).

alkyl with the starting material, chloromethyl trimethylsilane, while any of the latter remains. When the reaction is complete, generally after approximately 12 hr. of stirring at room temperature, the reaction mixture is filtered to remove the precipitated lithium chloride along with unchanged lithium metal. The solvent then is removed by vacuum distillation from the filtrate to obtain a white solid product. This solid can be sublimed at 100° under a pressure of 10^{-5} mm. and deposits as pure white crystals in the cooler parts of the sublimation apparatus.[3]

The pure crystalline lithiomethyl trimethylsilane thus obtained melts sharply without evident decomposition at 112°. The clear water white liquid is stable below 130° but above this temperature begins to yellow and a slow decomposition into tetramethylsilane and a non-volatile white solid ensues. The apparent stability of the liquid between the temperatures of 112 and 130° is unusual since most of the known solid lithium alkyls melt with appreciable decomposition. The white solid is stable for an indefinitely long period of time at room temperature in the absence of air and moisture. Even in dry air, however, it is extremely pyrophoric.

The compound was characterized by means of its methanolysis wherein a sample weighing 0.0827 g. (0.88 mmole of $LiCH_2Si(CH_3)_3$) reacted rapidly with methanol to produce 0.872 mmole of pure tetramethylsilane.

The apparent molecular weight of resublimed lithiomethyl trimethylsilane in 2-methylpentane solution, obtained by the isopiestic (solvent equilibration) method, was 92, in good agreement with a molecular weight of 94 calculated for the monomer. The behavior of this lithium alkyl in solution thus is in marked contrast to that of the other lithium alkyls so far examined,[4-7] which are extensively associated in solution.

Lithiomethyl trimethylsilane in benzene solution exhibits an n.m.r. spectrum with two proton resonances in a ratio of 4.5 to 1 with an internal shift of −2.16 p.p.m. from the methyl to methylene protons. The methyl proton resonance occurs at −7.07 p.p.m. relative to the benzene proton.

We have been unable to obtain a useful infrared absorption spectrum since the compound reacts readily with fluorolube.

Lithiomethyl trimethylsilane reacts readily with chloromethyl trimethylsilane to form mainly 2,2,5,5-tetramethyl-2,5-disilahexane and tetramethylsilane along with some 2,2,4,4-tetramethyl-2,4-disilahexane and small amounts of less volatile products.

When a heptane solution of the compound is treated with cobaltous chloride, 2,2,5,5-tetramethyl-2,5-disilahexane and tetramethylsilane are the only products.

(3) It occasionally is necessary to repeat this sublimation to obtain samples of lithiomethyl trimethylsilane which are entirely free from coupling side reaction products of low volatility. The presence of these impurities is readily evident since they are liquids at room temperature.

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Preparation of Chlorodifluoroamine, NF_2Cl[1]

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Recently, Petry[2] reported the preparation of chlorodifluoroamine by the reaction of BCl_3 with HNF_2. We wish to report a new preparation *via* reaction between gaseous F_2 and a mixture of NaN_3 and NaCl.

Two products resulted from this reaction: NF_2Cl and ClN_3. By proper temperature control it was possible to suppress the formation of the latter. When the reactor containing the salt mixture was allowed to remain at ambient temperature, it was found to warm slowly during the passage of fluorine from 20° to about 43°. The product gas contained some NF_2Cl, but also a considerable quantity of ClN_3, which was identified from its infrared spectrum (peaks at 4.4 and 4.8 μ). When the reaction was carried out at 0°, NF_2Cl was the main product and the formation of ClN_3 was completely suppressed. NF_2Cl was also the main product at −60°, the lower temperature having the advantage that a higher proportion of NaN_3 could be employed.

The NaN_3:NaCl ratio and the fluorine flow rate affected the vigor of the reaction. If the ratio exceeded 1:4, the reaction was accompanied by frequent explosions within the reactor, and at 1:1 a strong explosion tore the copper reactor apart. If the fluorine rate or concentration exceeded a critical value (dependent on the size of the reactor), the reaction was similarly uncontrollable.

The following reasonable sequence of steps is suggested for the reaction

$$^1/_2F_2 + NaN_3 \longrightarrow NaF + N_3\cdot \qquad (1)$$

$$^1/_2F_2 + NaCl \longrightarrow NaF + Cl\cdot \qquad (2)$$

$$Cl\cdot + N_3\cdot \longrightarrow ClN_3 \qquad (3)$$

$$ClN_3 \longrightarrow ClN + N_2 \qquad (4)$$

$$ClN + F_2 \longrightarrow NF_2Cl \qquad (5)$$

Experimental

The apparatus is shown in Fig. 1. A detailed discussion of equipment and the technique for handling fluorine may be found in a recent paper by Gordon and Holloway.[3] An intimate mixture of 2 g. of NaN_3 and 8 g. of NaCl, prepared by grinding the previously dried constituents together in a mortar and pestle, was added to the copper reactor in a drybox. After being connected to the train, the reactor and the Pyrex trap were immersed in a Dry Ice–chloroform bath at −62°. Nitrogen, which also was used for preliminary flushing, was passed through the system at a rate of about 5 ml./min. during the reaction. The reaction was initiated with a fluorine flow rate of 10 ml./min. After about 15 min., the inception of reaction was indicated by a

(1) This work was supported by the Advanced Research Projects Agency under Contract No. DA-30-069-ORD 2638.

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