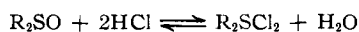
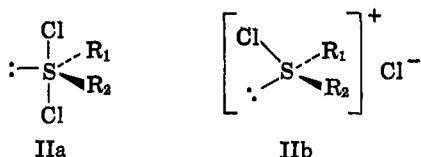


product immediately after racemization. An extension of our method to dialkyl sulfoxides is under investigation.¹¹

It is likely that the mechanism of the hydrogen chloride-catalyzed racemization involves the reversible formation of a sulfur dichloride (R_2SCl_2) intermediate.¹² Such compounds have been previously described,¹³⁻¹⁵ and pertinent equilibria have been postulated.¹³



In support of this conjecture, we find that the rate of exchange of ^{18}O equals the rate of racemization of I in a 2:1 v./v. mixture of dioxane and 12 *M* HCl- $H_2^{18}O$. By analogy with related systems,¹⁶ the structure of the dichloride may be formulated as a slightly distorted trigonal bipyramid with a plane of symmetry (IIa). Alternatively, the dichloride may have two nonequivalent chlorine atoms¹⁷ (IIb), but in this case rapid exchange of the chlorines *via* a transition state (IIa) serves equally well to account for the racemization.



The marked steric effect is in harmony with the increase in coordination number of sulfur in the course of the transformation to the dichloride, whether *via* an intermediate (IIa) or *via* a transition state (IIb).

In the light of our findings, the proposed¹⁸ mechanism of the hydrogen chloride-catalyzed epimerization of menthyl arenesulfonates ($ArSO_2C_{10}H_{19}$) may require modification: the epimerization¹⁸ may be rationalized by the intervention of an intermediate such as IIa or an equilibrium involving IIb, in which $R_1 = Ar$ and $R_2 = OC_{10}H_{19}$.

It has been pointed out¹⁴ that compounds of the type R_2SX_2 and R_3PX_2 are formally analogous. In connection with our mechanistic proposal it is therefore interesting that optically active phosphines add iodine to give racemic diiodides.¹⁹

3362 (1909); H. J. Page and S. Smiles, *J. Chem. Soc.*, **97**, 1112 (1910); E. V. Bell and G. M. Bennett, *ibid.*, 1798 (1927); H. Gilman and J. Eisch, *J. Am. Chem. Soc.*, **77**, 3862 (1955).

(11) In another extension, we have found that *trans*-thianthrene 5,10-dioxides may be smoothly converted into the *cis* forms by our method.

(12) Similarly, Kenyon, *et al.*,⁹ had assumed "reversible replacement of the oxygen atom by bromine."

(13) K. Fries and W. Vogt, *Ann.*, **381**, 337 (1911).

(14) E. Fromm, *ibid.*, **396**, 75 (1913).

(15) K. Issleib and M. Tzschach, *Z. anorg. allgem. Chem.*, **306**, 198 (1960).

(16) SF_4 : W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962); $(C_6H_5)_2SeCl_2$: J. D. McCullough and G. Hamburger, *J. Am. Chem. Soc.*, **64**, 508 (1942).

(17) F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955); H. Böhme and E. Boll, *Z. anorg. allgem. Chem.*, **290**, 17 (1957); G. M. Bennett and F. S. Statham, *J. Chem. Soc.*, 1690 (1931).

(18) H. F. Herbrandson and R. T. Dickerson, Jr., *J. Am. Chem. Soc.*, **81**, 4102 (1959).

(19) L. Horner and H. Winkler, *Tetrahedron Letters*, **No. 9**, 455 (1964). We are grateful to Professor Horner for disclosing these results to us in advance of publication.

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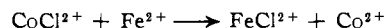
RECEIVED JANUARY 27, 1964

The Oxidation of Iron(II) by Cobalt(III) in the Presence of Chloride Ions¹

Sir:

It is frequently difficult to determine whether electron-transfer reactions proceed by inner- or outer-sphere mechanisms.² Definite evidence for inner-sphere mechanisms has only been obtained in those cases in which the transfer of the bridging group from the oxidizing to the reducing agent results in a substitution-inert species. For example, inner-sphere reactions involving $Cr(H_2O)_6^{2+}$ and $Co(CN)_6^{3-}$ produce $(H_2O)_5CrX^{2+}$ and $Co(CN)_5X^{3-}$, respectively; these products undergo substitution relatively slowly and can be identified by conventional spectrophotometric methods.^{3,4} We have studied an electron-transfer reaction in which both the reactants and both the products are substitution-labile and have established by the application of a flow technique⁵ that this reaction proceeds by an inner-sphere mechanism.

The system studied is the oxidation of iron(II) by cobalt(III) in the presence of chloride ions. The rate constant for this reaction in the absence of chloride ions is $3 \times 10^2 M^{-1} \text{sec.}^{-1}$ in 3.0 *M* $HClO_4$ at 25.0°. The chloride-catalyzed reaction proceeds *via* the path



i.e., $FeCl^{2+}$ is a primary product of the reaction of $CoCl^{2+}$ with Fe^{2+} . The oxidation was investigated at 25.0° in the concentration ranges: $[Co(III)] = 4.8$ to $24 \times 10^{-4} M$, $[Co(II)] = 2.5$ to $15 \times 10^{-3} M$, $[Fe(II)] = 4.6$ to $21 \times 10^{-2} M$, $[Cl^-] = 1.0$ to $2.0 \times 10^{-3} M$, $(HClO_4) = 2.25$ to $2.85 M$, and ionic strength = 3.0 *M*. In a typical series of experiments a solution containing $9.6 \times 10^{-4} M [Co(III)]$, $2.9 \times 10^{-2} M [Co(II)]$, $4.0 \times 10^{-3} M [Cl^-]$, and 3.0 *M* $(HClO_4)$ was mixed with one containing $9.2 \times 10^{-2} M [Fe(II)]$ and 2.7 *M* $(HClO_4)$. Under these conditions the reaction of $CoCl^{2+}$ with Fe^{2+} was complete within 2 to 3 msec. after mixing the two solutions ($k \geq 5 \times 10^3 M^{-1} \text{sec.}^{-1}$) and only the disappearance of the $FeCl^{2+}$ produced in the $CoCl^{2+} + Fe^{2+}$ reaction could be observed ($t_{1/2} = 280$ msec. at the above $Fe(II)$ and $HClO_4$ concentrations). The $FeCl^{2+}$ was identified spectrophotometrically (it has an absorption maximum at 336 $\mu\mu$; the absorption of $CoCl^{2+}$ is negligible at this wave length) and by the fact that its rate of dissociation was identical with that of $FeCl^{2+}$ under comparable conditions. No change in absorbance at 336 $\mu\mu$ was observed when a solution containing $9.6 \times 10^{-4} M [Co(III)]$, $5.0 \times 10^{-3} M [Co(II)]$, and 3.0 *M* $HClO_4$ was mixed with one containing $9.2 \times 10^{-2} M [Fe(II)]$, $4.0 \times 10^{-3} M [Cl^-]$, and 2.7 *M* $(HClO_4)$. At higher cobalt(III) concentrations ($4.8 \times 10^{-3} M$) and with the chloride in only the iron(II), the relatively slow formation of $FeCl^{2+}$ from the reaction $Fe^{3+} + Cl^- \rightarrow FeCl^{2+}$ was observed.⁶ These observations

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) For recent reviews of electron-transfer reactions, see, for example, (a) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959); (b) J. Halpern, *Quart. Rev. (London)*, **15**, 207 (1961); (c) N. Sutin, *Ann. Rev. Nuclear Sci.*, **12**, 285 (1962).

(3) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

(4) J. P. Candlin, J. Halpern, and S. Nakamura, *ibid.*, **85**, 2517 (1963).

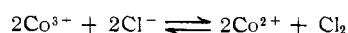
(5) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(6) R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

establish that FeCl^{2+} is produced in the reaction of CoCl^{2+} with Fe^{2+} and that this reaction proceeds *via* an inner-sphere activated complex in which the chloride is bonded directly to both the cobalt and the iron.

It should be noted that the equilibrium constant for the reaction $\text{Co}^{3+} + \text{Cl}^- \rightleftharpoons \text{CoCl}^{2+}$ is about ten times larger than that for the $\text{Fe}^{3+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^{2+}$ reaction.⁷ Consequently, when the chloride is added to only the cobalt(III), the amount of FeCl^{2+} produced in the $\text{CoCl}^{2+} + \text{Fe}^{2+}$ reaction is about forty times its final equilibrium concentration.

In order to minimize the extent of the reaction



the cobalt(III) was generally added to the chloride solution immediately before the runs.⁷ On the other hand, when the cobalt(III) chloride solution was allowed to age for about 15 min. prior to mixing it with the iron(II) solution, a reaction which produces FeCl^{2+} at a rate intermediate between that of the $\text{CoCl}^{2+} + \text{Fe}^{2+}$ and $\text{Fe}^{3+} + \text{Cl}^-$ reactions could be detected. Apparently this reaction is the oxidation of Fe^{2+} by Cl_2 . This was confirmed by mixing a solution of Cl_2 in 3.0 *M* HClO_4 containing 4.0×10^{-3} *M* (Cl^-) with a solution containing 1.0 *M* [Fe(II)] and 3.0 *M* (HClO_4); the formation of FeCl^{2+} ($k \approx 50$ *M*⁻¹ *sec.*⁻¹) and its subsequent dissociation were observed.

(7) T. J. Conocchioli, G. H. Nancollas, and N. Sutin, submitted to *Proc. Chem. Soc.*

(8) Visiting Scientist from the Chemistry Department, The University, Glasgow, W. 2, Scotland.

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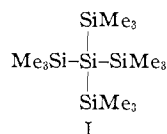
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G. H. NANCOLLAS⁸
N. SUTIN

RECEIVED JANUARY 31, 1964

Tetrakis(trimethylsilyl)silane

Sir:

Since the first reported preparation of a branched chain organopolysilane,¹ several efforts have been made to synthesize tetrasilyl-substituted silanes.^{1,2} Tris(triphenylsilyl)silane (4.4%) was obtained from the reaction of trichlorosilane with triphenylsilyllithium.¹ The attempted synthesis of tetrakis(triphenylsilyl)silane by the reaction of triphenylsilyllithium and silicon tetrachloride only afforded hexaphenyldisilane (72%) and a yellow oil.¹ We now report the preparation of tetrakis(trimethylsilyl)silane (I).



In a typical procedure, 94.18 g. (0.864 mole, 20% molar excess) of chlorotrimethylsilane was dissolved in 200 ml. of sodium-dried tetrahydrofuran, to which 15.13 g. (2.16 g.-atom, 50% g.-atom excess) of lithium wire was added. To this rapidly stirred mixture, 20 ml. of a solution of 30 g. (0.18 mole) of silicon tetrachloride dissolved in 150 ml. of sodium-dried tetrahydrofuran

(1) D. Wittenberg, M. V. George, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 4812 (1959).

(2) G. Schwebke and P. K. Sen, unpublished studies.

was added at room temperature.³ After stirring at room temperature for 4 hr., the reaction mixture became dark brown and heat was evolved. At this stage, dropwise addition of the silicon tetrachloride solution was continued. Upon completed addition, the mixture was stirred overnight at room temperature. Unreacted lithium metal, some salts, and a brown polymer⁴ were separated by filtration of the reaction mixture prior to hydrolysis with 200 ml. of 15% hydrochloric acid. The organic layer was separated, dried over anhydrous sodium sulfate, and the organic solvents were distilled under reduced pressure. To the yellow semisolid residue was added a few milliliters of 95% ethanol. The solids were filtered from the ethanolic solution and purified by sublimation at 75° (0.01 mm.) giving 40.5 g. (70%) of I, m.p. 261–263.⁵ Gas phase chromatography on a Dow Corning silicone grease column at 200° gave a single peak indicative of its purity. *Anal.* Calcd. for $\text{C}_{12}\text{H}_{36}\text{Si}_5$: C, 44.91; H, 11.31; mol. wt., 321. Found: C, 45.76; H, 11.22; mol. wt., 319 (by osmometry in benzene). The infrared spectrum of I showed no peaks indicative of Si–H, Si–OH, or Si–O–Si. N.m.r. exhibits a sharp singlet at τ 9.79, consistent with the highly symmetrical structure. Also, it is of interest that its high melting point⁶ and ease of sublimation are presumably associated with its symmetry. Other related group IVB types are being investigated.

Acknowledgment.—This research was supported by The United States Air Force under Contract AF-33(657)-10288 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. The authors are grateful to G. Schwebke and W. Atwell for helpful suggestions and Dr. Roy King for the n.m.r. spectral determination.

(3) Silicon tetrachloride reacts with refluxing tetrahydrofuran giving a mixture of chlorobutoxysilanes [M. Kratochvil and J. Frejka, *Chem. Listy*, **52**, 151 (1958); *Chem. Abstr.*, **52**, 16, 329e (1958)].

(4) Possibly mixtures of siloxanes.

(5) Melting points were taken in a sealed tube completely immersed in the heating unit of a Mel-Temp melting point apparatus.

(6) With the straight chain analogs of the type $\text{Me}_3\text{Si}(\text{SiMe}_2)_n\text{SiMe}_3$, only $n = 6$, b.p. 194–198° (3 mm.), m.p. 60–61, and $n = 8$, b.p. 244° (3 mm.), m.p. 113–114°, are low melting solids; whereas $n = 0$ through 5 are liquids. [M. Kumada, private communication; also see M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, **1**, 153 (1963)].

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RECEIVED FEBRUARY 7, 1964

Conversion of Hexasubstituted Benzenes to Cyclohexadienones

Sir:

In a recent communication¹ the use of peroxytrifluoroacetic acid in the presence of boron fluoride to effect hydroxylation of aromatic hydrocarbons was reported. For example, mesitylene was converted to mesitol in good yield with efficient use of the peracid. In the oxidation of prehnitene (I) a cyclohexadienone (II) was isolated in small quantities, and its formation was attributed to attack by a positive species (here referred to, for simplicity, as OH^+), followed by methyl

(1) C. A. Buehler and H. Hart, *J. Am. Chem. Soc.*, **85**, 2177 (1963).