

existence of a B₈ hydride. The maximum of 100, also observed by the authors, in the mass spectrum of a B₈ hydride,¹⁰ which was not isolated,¹¹ is apparently an unsafe criterion of the formula B₈H₁₂ inasmuch as the maximum masses observed¹⁰ for B₄H₁₀, B₅H₁₁, and B₉H₁₅ are all less by two mass units than the maximum permitted by each of these compounds.

Besides the hydrides B₂H₆, B₄H₁₀, B₅H₉, B₅H₁₁, B₆H₁₀, and B₁₀H₁₄ discovered by Stock, the known structurally characterized boron hydrides now include² B₈H₁₂, B₉H₁₅, B₁₀H₁₆, B₁₃H₂₂, *i*-B₁₃H₂₂, and B₂₀H₁₆.¹² In addition, the composition of B₆H₁₂ has been reported.¹³

The unexpected lowering of symmetry of B₈H₁₂ from C_{2v} to C_s suggests to us that the theory of boron hydride structures may become applicable to carbonium ion chemistry, where the somewhat smaller size of C, as compared with B, also appears to lead to lowering of symmetry in complex carbonium ions.

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The Hydrogen Chloride-Catalyzed Racemization of Sulfoxides¹

Sir:

We have found that sulfoxides are rapidly and cleanly racemized at room temperature by solutions of hydrogen chloride in organic solvents such as benzene, dioxane, and THF. The presence of water slows the rate of racemization; nevertheless, we have found that for many purposes an effective medium may be prepared most conveniently² by mixing one volume of 12 *M* aqueous hydrochloric acid and two volumes of dioxane. Typically, a colorless solution of 100 mg. of (+)-phenyl *p*-tolyl sulfoxide³ (I) in 5.0 ml. of the above medium was allowed to stand at room temperature under nitrogen for 24 hr. The acid was neutralized with aqueous sodium hydroxide or sodium carbonate (alternatively, with magnesium oxide) and the sulfoxide was extracted with ether; removal of the organic solvents under reduced pressure left a white, crystalline residue of the racemic sulfoxide (100 mg.), m.p. 67–68.5° (lit.⁴ m.p. 69–70°), infrared spectrum identical with that of starting material.

The marked effect of water on the rate of racemization may be illustrated by the following observation: under the above described conditions the half-life

(1) We gratefully acknowledge support by the National Science Foundation (Grant No. GP-757).

(2) We reported on the efficacy of this medium at the Eighteenth National Chemistry Symposium of the American Chemical Society, Columbus, Ohio, June 19, 1963 (Abstracts, p. 81).

(3) K. Mislow, A. L. Ternay, Jr., and J. T. Melillo, *J. Am. Chem. Soc.*, **85**, 2329 (1963).

(4) H. Burton and W. A. Davies, *J. Chem. Soc.*, 528 (1948).

(*t*_{1/2}²⁵) of I is 2.4 hr., whereas in *anhydrous* dioxane, 4.0 *M* in hydrogen chloride, *t*_{1/2}²⁵ is less than 30 sec. Conversely, *t*_{1/2}²⁵ is 27 hr. in a 1:1 v./v. mixture of 9 *M* aqueous hydrochloric acid and dioxane. The rate is also highly dependent on the concentration of the acid.

The specificity of hydrogen chloride as an effective catalyst is remarkable. Thus the rotation on a solution of I in a 2:1 v./v. mixture of dioxane and 48.8% hydrofluoric acid remains unchanged for 11 days at 25°. In a 2:1 or 1:1 v./v. mixture of dioxane and 47% aqueous hydrobromic acid, decomposition (with evolution of bromine) of I is an important side reaction and racemization studies were therefore vitiated.

The rate of racemization is extraordinarily sensitive to the steric requirements of the groups attached to the asymmetric sulfur atom. As seen in Table I, the specific rate constants of racemization of methyl and *t*-butyl *p*-tolyl sulfoxides differ in this medium by a factor of greater than 3.5 × 10⁵.

TABLE I
RATE CONSTANTS OF RACEMIZATION OF *p*-CH₃C₆H₄-SO-R^a

R ^b	<i>k</i> ₁ ²⁵ × 10 ⁵ , sec. ⁻¹	[α] _D (acetone)
Methyl	3700	+145°
Ethyl	957	+188°
Isopropyl	29.3	+177°
(<i>R</i>)-2-Octyl ^c	23.7	+118°
(<i>S</i>)-2-Octyl ^c	22.3	+138°
Phenyl	8.00	+25°
<i>m</i> -Tolyl	7.53	+15°
<i>o</i> -Tolyl	4.53	-89°
Mesityl	0.0418	-284°
<i>t</i> -Butyl	0.0105	+161°

^a In a 2:1 v./v. mixture of dioxane and 12 *M* aqueous HCl.
^b All compounds were prepared from (–)-menthyl (–)-*p*-toluenesulfinate by the Andersen synthesis [K. K. Andersen, *Tetrahedron Letters*, No. 3, 93 (1962)] and gave satisfactory elemental analyses. ^c Rates of mutarotation. The diastereomeric sulfoxides were separated by chromatography and the configurations were established by oxidation to the sulfones. For phenyl 2-octyl sulfoxide of m.p. 21° [(D. J. Cram and S. H. Pine, *J. Am. Chem. Soc.*, **85**, 1096 (1963)] we observe the comparable value of *k*₁²⁵ = 20.8 × 10⁻⁵ sec.⁻¹.

The mildness of the conditions employed and the freedom from side reactions present distinct advantages over previous approaches. Thermal stereomutations^{5,6} are inconvenient since elevated temperatures are required and we find that partial decomposition cannot be easily avoided. Although sulfoxides racemize in 97% sulfuric acid,⁷ the development of a pronounced color in this medium contrasts sharply with the absence of color in our hydrogen chloride solutions.⁸ The action of hydrogen bromide requires further study.⁹

It should be pointed out that some sulfoxides are reported to suffer decomposition in hydrochloric acid^{5,8,10} and it is therefore advisable to isolate the

(5) K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911); *Ann.*, **381**, 312 (1911).

(6) G. Farina, F. Montanari, and A. Negrini, *Gazz. chim. ital.*, **89**, 1548 (1959).

(7) S. Oae, T. Kitao, and Y. Kitaoka, *Chem. Ind. (London)*, 291 (1961).

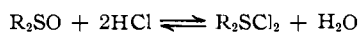
(8) The chemical instability of aromatic sulfoxides in concentrated sulfuric acid has been discussed by H. J. Shine and L. Piette [*J. Am. Chem. Soc.*, **84**, 4798 (1962)], and by R. J. Gillespie and R. C. Passerini [*J. Chem. Soc.*, 3850 (1956)].

(9) We must distinguish between racemization and the mere loss of optical activity (which could be due to decomposition). Thus J. Holloway, J. Kenyon, and H. Phillips [*ibid.*, 3000 (1928)] observed the loss of optical activity of (+)-ethyl *m*-carboxyphenyl sulfoxide in 3.3 *N* hydrobromic acid at 25° (*k*₁ ~ 6 × 10⁻⁷ sec.⁻¹) but the product was not isolated.

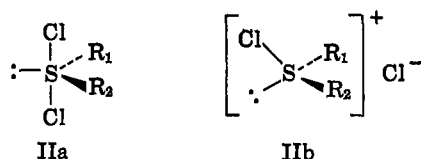
(10) J. A. Smythe, *ibid.*, **95**, 349 (1909); M. Zincke and P. Jörg, *Ber.*, **43**,

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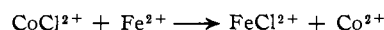
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The Oxidation of Iron(II) by Cobalt(III) in the Presence of Chloride Ions¹

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 $Co(CN)_5^{3-}$ 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).

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