[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Reaction between Ammonia and $SeO_2{\cdot}2HCl$ and $SeO_2{\cdot}2HBr$

BY JULIUS JACKSON[1] AND G. B. L. SMITH

The materials formed when selenium dioxide reacts with hydrogen chloride and bromide have been studied by several investigators.[2] Muehlberger and Lenher[2c] have shown that $SeOCl_2{\cdot}H_2O$ is identical with $SeO_2{\cdot}2HCl$ of Ditte[2a] and that $SeO_2{\cdot}2HCl$ will give selenium oxychloride on dehydration. Latimer and Hildebrand[3] have listed this material as $H_2SeO_2Cl_2$. This paper presents a study of the reaction between ammonia and $SeO_2{\cdot}2HCl$ and $SeO_2{\cdot}2HBr$. The data obtained are in harmony with the postulation that these materials are mixtures of $2H^{++}(SeO_2X_2)^{--}$ and $(SeOXH_2O)^+X^-$.[4]

Experimental

Five g. of either $SeO_2{\cdot}2HCl$ or $SeO_2{\cdot}2HBr$, prepared by treating selenium dioxide with two equivalents of the respective halogen hydride, was dissolved in 100 ml. of the anhydrous solvent and ammonia passed into the solution for a period of two hours. The resulting precipitate was separated by filtration, washed with the solvent, dried in a vacuum desiccator, and analyzed for selenium, ammonia and the respective halogen. The data obtained are summarized in Table I.

TABLE I

DATA FOR THE REACTION BETWEEN $SeO_2{\cdot}2HCl$, $SeO_2{\cdot}2HBr$ AND NH_3 IN ETHER

Reactant	Temp., °C.	Analyses,[a] % Se	Cl or Br	N	Calculated composition $(NH_4)_2$-SeO_2X_2	$(NH_4)_2$-SeO_3	NH_4X	Total
$SeO_2{\cdot}2HCl$[b]	− 4	29.83	30.68	17.17	42.29	30.03	24.71	97.03
$SeO_2{\cdot}2HCl$	−10	29.37	30.08	17.49	38.22	32.21	26.90	97.13
$SeO_2{\cdot}2HCl$[c]	17	28.01	36.11	14.95	71.80	4.12	19.10	95.02
$SeO_2{\cdot}2HCl$[d]	2	10.41	53.49	23.65	14.06	11.00	75.14	100.02
$SeO_2{\cdot}2HCl$	12	25.56	39.43	16.25	64.59	4.49	27.79	96.87
$SeO_2{\cdot}2HBr$	5	27.96	42.20	12.17	62.11	24.81	12.11	99.03
$SeO_2{\cdot}2HBr$	− 5	25.17	47.33	12.31	63.35	18.36	18.04	99.75
$SeO_2{\cdot}2HBr$	−10 to −5	24.88	47.28	10.80	73.94	12.12	10.65	96.71

[a] Analyses represent mean values of two to four determinations. [b] Solvent was anhydrous ethyl acetate. [c] Solvent was anhydrous acetic acid and ammonia added as ammonium acetate. [d] Ammonia added for thirty minutes.

Discussion

Since the analyses indicated that the reaction products were mixtures, the composition of which varied with conditions, a number of arbitrary hypotheses were tested by computing the composition by the method of "indirect analysis." Reasonable material balances were obtained by assuming that the products were ammonium halide, ammonium selenite and ammonium dihalogenoselenite. These conclusions were confirmed by microscopic examination and X-ray diffraction measurements of several of the materials.

The formation of the ammonium salts of dichloroselenious acid and dibromoselenious acid shows that these acids are present in $SeO_2{\cdot}2HCl$ and $SeO_2{\cdot}2HBr$. However, the formation of the ammonium salts of selenious acid and of hydrogen halide indicates that no single structure can be assigned to $SeO_22{\cdot}HCl$ or $SeO_2{\cdot}2HBr$. Accordingly, the authors suggest that these materials comprise an equilibrium (dynamic isomers) mixture as follows

$$H_2SeO_2X_2 \rightleftarrows SeOXH_2O{\cdot}X$$

The water in the $SeOXH_2O{\cdot}X$ is replaced by ammonia forming $SeOXNH_3{\cdot}X$ and this liberated water causes hydrolysis of the $SeO_2X^=_2$ ion yielding HX and H_2SeO_3. Further work is necessary, however, to establish definitely the presence of $SeOXNH_3{\cdot}X$.

Summary

1. The products of the reaction of $SeO_2{\cdot}2HCl$ or $SeO_2{\cdot}2HBr$ with ammonia are ammonium selenite and the corresponding ammonium halide and ammonium di-halogeno-selenite.

2. $SeO_2{\cdot}2HCl$ or $SeO_2{\cdot}2HBr$ comprises an

---

[1] Research Fellow in Selenium Oxychloride Investigations. Presented before the Division of Physical and Inorganic Chemistry at the Baltimore meeting of the American Chemical Society, April, 1939. Original manuscript received June 1, 1939.

[2] (a) Ditte, *Compt. rend.*, **33**, 223 (1876); *Ann. chim. phys.*, (5) **10**, 82 (1877); (b) Lenher, THIS JOURNAL, **42**, 2499 (1920); (c) Muehlberger and Lenher, *ibid.*, **47**, 1842 (1925); (d) Henley and Sugden, *J. Chem. Soc.*, 1058 (1929); (e) Parker and Robinson, *ibid.*, 2853 (1929); 1316 (1931).

[3] Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1933, p. 205.

[4] See Smith, *Chem. Rev.*, **23**, 165 (1938), who regards water dissolved in selenium oxychloride as a base.

equilibrium mixture of dynamic isomers of which the di-halogenoselenious acid is one of the most probable constituents.

BROOKLYN, NEW YORK RECEIVED DECEMBER 15, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Selenium Oxychloro Compounds of Pyridine, Pyridinium Chloride and Related Substances

BY JULIUS JACKSON[1] AND G. B. L. SMITH

Introduction

The basic properties of pyridine and compounds of the same type have been demonstrated not only through the formation of salts, as pyridinium chloride, but also by the formation of series of pyridinates and analogous substances. It is to be expected, therefore, that pyridine and related substances will form definite compounds with selenium oxychloride which may be regarded as bases of the selenium oxychloro system.[2]

This paper presents a summary of the investigations into the nature of the reactions of pyridine, quinoline and isoquinoline in selenium oxychloride. Gordon[3] and Heimerzheim[4] have studied metathetical reactions in selenium oxychloride by conductometric and potentiometric titrations. Solutions of pyridine in selenium oxychloride (base[5]) have been allowed to react with solutions of stannic chloride, ferric chloride, sulfur trioxide and arsenic trichloride in selenium oxychloride (acids). The curves obtained when relative conductances or voltages were plotted against volume of reagent added showed that the acids and bases had reacted in definite stoichiometric ratios. Edgington and Firth[6] have demonstrated the formation of a dipyridinate of selenium oxychloride and found that the compound decomposes to $(C_5H_5N)_2SeCl_4$ and $(C_5H_5N)_2SeCl_2$ at temperatures above 145°.

The present studies have demonstrated the formation of well-defined compounds of selenium oxychloride with pyridine, quinoline and isoquinoline which may be characterized by the general formulas: $RSeOCl_2$; $(R)_2SeOCl_2$. The substances formed are very finely crystalline, or possibly amorphous, white to creamy white solids. The compounds in which two moles of the bases are combined with one mole of selenium oxychloride are not decomposed at 61° in the case of quinoline and isoquinoline but in the case of pyridine this compound loses the base and decomposes to the "monopyridinate" at 61° in 167 hours. Isoquinoline appears to have the greatest tendency to combine in 2-1 ratio and pyridine the least. The compounds of the type $RSeOCl_2$ are all stable at 61°. Attempts to recrystallize these materials from selenium oxychloride yield gelatinous products which cannot be separated from the excess solvent. An attempt to recrystallize the "monopyridinate" $C_5H_5N{\cdot}SeOCl_2$ from glacial acetic acid yielded a substance which gave the atomic ratios 1:3:1 for Se:Cl:N and for which the formula $C_5H_5NH{\cdot}SeOCl_3$ is suggested. Definitely crystalline compounds also were obtained by adding pyridinium, quinolinium and isoquinolinium chlorides to $SeOCl_2$. In the case of pyridinium chloride the product appears as beautiful cubical crystals. They all may be characterized by the general formula $(RHCl){\cdot}(SeOCl_2)_2$, except in the case of isoquinoline which appears to be a mixture of $RHCl{\cdot}SeOCl_2$ and $(RHCl)(SeOCl_2)_2$.

Experimental

Materials.—Commercial carbon tetrachloride was purified by fractionation. C. p. pyridine, quinoline and isoquinoline were dried with potassium hydroxide, distilled and preserved in glass ampules. The corresponding chlorides were prepared by precipitation in benzene solution with hydrogen chloride.

Analyses.—Selenium was weighed as elementary selenium, which was precipitated by sulfurous acid from a solution containing 20% hydrochloric acid. Chlorine was weighed as silver chloride. Pyridine, quinoline and isoquinoline were separated by distilling from a solution containing 25% sodium hydroxide and then were absorbed in an approximately 0.1 N solution of hydrochloric acid,

---

[1] Research Fellow in Selenium Oxychloride Investigations. Presented at the Boston meeting of the American Chemical Society, September, 1939. Original manuscript received July 8, 1939.

[2] Smith, *Chem. Rev.*, **23**, 165 (1938).

[3] Gordon, Thesis, B.S. in Chem., 1937, Polytechnic Institute of Brooklyn.

[4] Heimerzheim, Thesis, M.S. in Chem., 1939, *ibid.*, also ref. (2).

[5] The concept of *acid–base* employed in these studies is that of Gilbert N. Lewis, "Valence and the Structure of Atoms and Molecules," A. C. S. Monograph, Reinhold Publishing Co., N. Y., 1923. See also reference 2, and *J. Franklin Inst.*, **226**, 293 (1938).

[6] Edgington and Firth, *J. Soc. Chem. Ind.*, **55**, 192T (1936).