

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

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## Selenium Oxychloro Compounds of Pyridine, Pyridinium Chloride and Related Substances

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### 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.<sup>2</sup>

This paper presents a summary of the investigations into the nature of the reactions of pyridine, quinoline and isoquinoline in selenium oxychloride. Gordon<sup>3</sup> and Heimerzheim<sup>4</sup> have studied metathetical reactions in selenium oxychloride by conductometric and potentiometric titrations. Solutions of pyridine in selenium oxychloride (base<sup>5</sup>) 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<sup>6</sup> 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  $C_5H_5NH \cdot SeOCl_2$  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.*, **58**, 192T (1939).

TABLE I  
 DETAILS OF EXPERIMENTS ON REACTIONS OF SELENIUM OXYCHLORIDE AND PYRIDINE, PYRIDINIUM CHLORIDE AND RELATED SUBSTANCES

Compound employed	Approx. ratio base/SeOCl <sub>2</sub> taken	Atomic ratios found <sup>a</sup>			Formula of compound formed	Analyses <sup>b</sup>								
		Se	Cl	Base		Se	Cl	Base	Se	Cl	Base			
Pyridine	1-1	1.000	1.986	1.027	C <sub>5</sub> H <sub>5</sub> N·SeOCl <sub>2</sub>	31.81	28.59	32.61	32.24	28.96	32.30			
Pyridine	2-1	1.000	2.013	1.890	(C <sub>5</sub> H <sub>5</sub> N) <sub>2</sub> ·SeOCl <sub>2</sub>	This material decomposed to the "monopyridinate" in 167 hours at 61°								
Quinoline	1-1	1.003	2.001	1.000	C <sub>8</sub> H <sub>7</sub> N·SeOCl <sub>2</sub>	25.55	23.74	43.75	26.77	24.05	43.75			
Quinoline	2-1	1.000	1.981	2.030	(C <sub>8</sub> H <sub>7</sub> N) <sub>2</sub> ·SeOCl <sub>2</sub>	18.05	18.46	60.13	18.62	16.73	60.88			
Isoquinoline	1-1	1.000	1.969	1.070	C <sub>8</sub> H <sub>7</sub> N·SeOCl <sub>2</sub>	23.12	21.90	49.25	26.77	24.05	43.75			
Isoquinoline	2-1	1.000	1.994	2.009	(C <sub>8</sub> H <sub>7</sub> N) <sub>2</sub> ·SeOCl <sub>2</sub>	18.26	16.91	60.47	18.62	16.73	60.88			
Pyridinium chloride	Crystallized from SeOCl <sub>2</sub>	2.054	5.105	1.000	C <sub>5</sub> H <sub>5</sub> NHCl·(SeOCl <sub>2</sub> ) <sub>2</sub>	34.73	38.90	17.35	35.31	38.82	17.31			
Quinolinium chloride	Crystallized from SeOCl <sub>2</sub>	2.100	5.059	1.000		35.87	38.80	17.10						
Quinolinium chloride	Crystallized from SeOCl <sub>2</sub>	2.017	4.986	1.000	C <sub>8</sub> H <sub>7</sub> NHCl·(SeOCl <sub>2</sub> ) <sub>2</sub>	32.07	35.65	26.01	31.75	35.65	25.97			
Isoquinolinium chloride	Crystallized from SeOCl <sub>2</sub>	2.974	7.080	2.000	Probably mixtures of the monosolvate and disolvate	29.39	31.42	32.33	28.63	33.91	32.18	Probably mixtures		
		2.910	7.678	2.000		31.11	31.17	22.78						
		2.235	4.986	1.000										

<sup>a</sup> Atomic ratios are for the moist material for the first six compounds and are for the crystalline material for the chlorides. These values are all based on at least two determinations. <sup>b</sup> Analyses reported are based on two to four determinations.

The excess hydrochloric acid was titrated with standard sodium hydroxide using methyl orange as indicator, followed by a determination of the combined hydrochloric acid using phenolphthalein as indicator.

**Reaction between Selenium Oxychloride and Pyridine Bases.**—A weighed sample of selenium oxychloride was dissolved in 50 ml. of carbon tetrachloride. Either a one or two molar equivalent quantity of pyridine or other base was dissolved in 50 ml. of the same solvent and the two solutions were added dropwise to 50 ml. of carbon tetrachloride contained in a 500-ml. Wolf flask. The white solid which formed was separated by filtration and washed three times with fresh carbon tetrachloride. One portion of the material was analyzed immediately for selenium, chlorine and base. Another portion was freed of carbon tetrachloride by drying in an Abderhalden oven at 61° and 17 mm. pressure. The experimental details and analytical data obtained are presented in Table I.

**Reaction between Selenium Oxychloride and the Chlorides of Pyridine Bases.**—Ten ml. of selenium oxychloride was saturated with the respective chloride at a temperature of 70–80° and the resulting solution chilled to 0° or slightly lower and allowed to remain at this temperature for one hour. The resulting crystals were separated by filtration after adding 25 ml. of carbon tetrachloride, washed with the same liquid and dried in a vacuum desiccator. Table I presents the analytical data obtained.

### Discussion

The experimental findings presented in this paper are in agreement with the thesis that selenium oxychloride is the parent solvent of a system of compounds.<sup>2</sup> The formation of C<sub>5</sub>H<sub>5</sub>N·SeOCl<sub>2</sub> and (C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>·SeOCl<sub>2</sub> and the analogous compounds of quinoline and isoquinoline is suggestive of ammonium hydroxide and ammonium oxide. It is suggested that the pyridine type compounds act as bases, "electron pair donors" toward the solvent cation, SeOCl<sup>+</sup>. This is a

verification of the postulation that pyridine when dissolved in selenium oxychloride forms selenium oxychloro-pyridinium cation, C<sub>5</sub>H<sub>5</sub>NSeOCl<sup>+</sup>, and chloride ion.

The isolation of definite selenium oxychloro compounds of pyridinium chloride and the other two chlorides, which we may term "solvates," indicates something about the solvation of the chloride ion in selenium oxychloride. Julien<sup>7</sup> found that hydrogen chloride is soluble in selenium oxychloride and that the resulting solution has a high electrical conductivity. Wise<sup>8</sup> isolated the mono-solvates of potassium chloride and believed that rubidium and cesium chlorides also formed "mono-solvates." Since potassium, rubidium and cesium ions are not likely to be solvated, it is probable that the molecule of selenium oxychloride is associated with the chloride ion and KCl·SeOCl<sub>2</sub> is potassium trichloroselenite, K<sup>+</sup>(SeOCl<sub>3</sub>)<sup>-</sup>. The data presented in this paper, however, for pyridinium chloride and related chlorides are indicative of a disolvated chloride ion, *i. e.*, Se<sub>2</sub>O<sub>2</sub>Cl<sub>5</sub><sup>-</sup>. In each case selenium would have a covalent number of four.

### Summary

1. Selenium oxychloride forms two series of compounds with pyridine, quinoline, and isoquinoline in which one and two moles of the base are combined with one mole of selenium oxychloride. These facts substantiate the view that pyridine and related substances act as bases in selenium oxychloride.

(7) Julien, *THIS JOURNAL*, **47**, 1799 (1925).

(8) Wise, *ibid.*, **45**, 1233 (1923).

2. Pyridinium chloride and quinolinium chloride crystallize from solutions in selenium oxychloride with two molecules of the solvent. Isoquinolinium chloride probably forms a mixture

of the mono-solvate and the di-solvate. These facts indicate the possibility of disolvation of the chloride ion in selenium oxychloride.

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## Chlorogermanic Acid and the Chlorogermanates. Properties and Crystal Structure of Cesium Hexachlorogermanate

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The tendency of the elements of Group IV, exclusive of carbon and thorium, to form complex ions with the halogens is well recognized. Germanium is known<sup>1</sup> to form hexafluogermanates but no other halogen complexes of germanium have been studied. Pauling<sup>2</sup> has shown that it is possible to predict the type of aggregate which two ions can form by considering the ratio of the ionic radii. Using his values for the radii, the ratios of the univalent ionic radius of germanium to those of fluorine, chlorine, bromine, and iodine are 0.54, 0.42, 0.39, and 0.35, respectively. Since 0.41 is the minimum radius ratio which will permit hexacoördination it is evident that germanium should form hexahalogen complex ions with fluorine and chlorine but can only have a coördination number of four toward bromine or iodine. Because the ratio in the case of chlorine is so close to the limit between hexa- and tetra-coördination, it is to be anticipated that the hexachlorogermanate ion will not form except under the most favorable conditions.

In the present investigation the formation of chlorogermanic acid and its salts has been studied.

### Experimental

**Formation of Chlorogermanic Acid.**—Germanium tetrachloride is slightly soluble in concentrated hydrochloric acid.<sup>3</sup> This indicates that chlorogermanic acid may be formed, but that it is not very stable in solution since its formation to any great extent would give rise to high solubility of the tetrachloride.

Chlorostannic acid crystallizes as the hexahydrate when a solution of stannic chloride in concentrated hydrochloric acid is chilled. A similar procedure was tried in an effort to isolate chlorogermanic acid. Germanium tetrachloride was added to an equal volume of 12 *N* hydrochloric acid to give a two liquid layer system and the mixture was

chilled to  $-49^{\circ}$ . No crystals appeared. When gaseous hydrogen chloride was bubbled through cold anhydrous germanium tetrachloride no solid formed above  $-49^{\circ}$ , the freezing point of germanium tetrachloride. If chlorogermanic acid is formed under such conditions it is present in such small amounts that it will not crystallize out.

Migration studies of solutions of various concentrations of germanium tetrachloride in 6 *N* hydrochloric acid gave evidence that the small amount of germanium in solution is present in complex ions. The solutions were electrolyzed in a migration cell which had a capacity of 60 cc. The concentration of germanium in anolyte and catholyte was determined before and after electrolysis with a given current for a definite period of time. These experiments are summarized in Table I.

TABLE I  
MIGRATION OF GERMANIUM DURING ELECTROLYSIS OF SOLUTIONS OF  $\text{GeCl}_4$  IN 6 *N* HCl

Expt.	Time, min.	Current, m. amp.	Grams Ge per 1000 g. solution		
			Original	Anolyte finally	Catholyte finally
1	70	86	2.001	2.072	1.903
2	60	87	4.681	4.734	4.627

Both of these experiments show a small but significant migration of germanium toward the anode, indicating the presence of an anion of this element, presumably  $\text{GeCl}_6^-$ . The solutions contained such large concentrations of other ions that the concentration of chlorogermanate ions could not be calculated from the data.

**Formation of Chlorogermanates.**—The direct addition of ammonia to 12 *N* hydrochloric acid saturated with germanium tetrachloride gave only a precipitate of ammonium chloride with no evidence of chlorogermanate formation.

The reactions of the alkali chlorides with germanium tetrachloride were studied under a variety of conditions.

Anhydrous germanium tetrachloride was refluxed with a weighed amount of sodium chloride for several days, the mixture being protected from atmospheric moisture. No evidence of any reaction could be observed. Similarly the chlorides of lithium, potassium, cesium and calcium did not react when refluxed with anhydrous germanium tetrachloride.

The low solubility of germanium tetrachloride in concentrated hydrochloric acid makes it impossible to achieve any large concentration of germanium tetrachloride in an

(1) Winkler, *J. prakt. Chem.*, **36**, 177 (1887); Müller, *Proc. Am. Phil. Soc.*, **65**, 44 (1926); Dennis and Staneslow, *THIS JOURNAL*, **55**, 4392 (1933).

(2) Pauling, *THIS JOURNAL*, **49**, 765 (1927).

(3) Allison and Müller, *THIS JOURNAL*, **54**, 2833 (1932).