TABLE II

SODIUM IODIDE, ACETONE AND WATER AT 25°

Solid phase	NaI, % by wt.	*Ac*, % by wt.	H_2O, % by wt.	Density (Fig. 2)	Point
$NaI.3(CH_3)_2CO$	28.5	71.5	00.0	1.062	*a*
$NaI.3(CH_3)_2CO + NaI$	..	..	..	...	*b*
NaI	29.4	70.6	00.0	1.067	*a'*
	34.7	62.9	2.4	1.144	
	37.7	58.0	4.3	1.192	
	40.5	53.4	6.1	1.240	
$NaI + NaI.2H_2O$	44.5	46.1	9.4	1.320	*c*
$NaI.2H_2O$	46.3	40.3	13.4	1.358	
	49.9	30.1	20.0	1.450	
	54.3	19.4	26.3	1.565	
	60.2	8.2	31.6	1.753	
	64.7	0.0	35.3	1.927	*d*

is that in equilibrium with pure sodium iodide; it is easily obtained and may be kept a long time without depositing crystals of the double compound. The solubility of sodium iodide in acetone is considerably increased by the presence of small amounts of water, as shown by the steep rise of Curve *bc*. The solubility of the dihydrate is represented by Curve *cd*.

Summary

Because of the use of sodium iodide in purifying acetone, the solubility of the salt in acetone has been measured from —34° to the boiling point of the saturated solution, 59.8°. The composition of the compound which is formed has been confirmed as being $NaI.3CH_3COCH_3$. At 25.7° it melts incongruently to sodium iodide. The solubility of the double compound decreases with decrease in temperature, while that of pure sodium iodide decreases with increase in temperature. The 25° isotherm of the system sodium iodide-water-acetone has also been determined.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

SOME PROPERTIES OF SELENIUM MONOCHLORIDE

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Selenium monochloride prepared according to the method of Lenher and Kao[1] is a red-brown liquid which cannot be distilled without decomposition. It begins to boil at 127° (733 mm.) but decomposition commences as soon as the vapor phase appears. Distillation in the vapor of hydrogen chloride or carbon dioxide does not prevent this decomposition, nor is it possible to avoid decomposition by boiling under greatly diminished pressure.

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[1] Lenher and Kao, THIS JOURNAL, **47**, 772 (1925).

The substance can be purified by dissolving it in fuming sulfuric acid, reprecipitating by hydrogen chloride and washing with sulfuric acid. The last traces of this acid can be removed by treatment with anhydrous barium chloride.

Divers and Shimosé[2] have suggested the use of potassium chloride, but in as much as potassium and sodium sulfates are slightly soluble in selenium monochloride, barium chloride, which forms the insoluble sulfate and is itself insoluble, is more satisfactory.

The specific gravity of selenium monochloride has been reported by Divers and Shimosé to be 2.906. This value is probably due to their preparation containing an excess of selenium which is readily soluble in the monochloride. Highly purified selenium monochloride freed from dissolved selenium and alkaline salts has a specific gravity of 2.7741 at 25°/4°.

The melting point has been found to be —85°. Its specific conductance is 5.12×10^{-7} reciprocal ohms and the index of refraction at 25° is 1.59617.

Solubility of Sulfur in Selenium Monochloride.—Enough sulfur will dissolve in selenium monochloride to form a very viscous solution. Its solubility at 25° has been determined to be 48.81 in 100 parts of solution.

Replacement of Sulfur in Sulfur Monochloride by Selenium.—Rathke[3] has shown that replacement of the sulfur in sulfur monochloride can be accomplished by selenium but the reaction has not been studied in detail. By treatment of the resulting selenium monochloride solution with carbon tetrachloride and by hydrolysis of the selenium monochloride, the reaction has been established quantitatively to be $S_2Cl_2 + 2Se \longrightarrow Se_2Cl_2 + 2S$.

Solubility of Selenium in Selenium Monochloride.—Ramsay and Evans[4] state that when selenium is treated with the tetrachloride the resulting liquid contains 80% of selenium, which is more than the amount of selenium in the monochloride. The rate of solution of selenium in the monochloride in the cold is very slow, while in the hot liquid it forms a saturated solution from which, on cooling, black selenium crystallizes. It has been found that a warm saturated solution must be shaken in a thermostat at 25° for a very long time in order to reach equilibrium. Analysis of such a solution by two different methods showed that 100 parts of selenium monochloride dissolve 9.73 parts of selenium at 25°, and that the liquid contains 71.85% of selenium.

Dry sulfur dioxide does not react with selenium monochloride even at 130°, the boiling point of the latter substance.

Sulfur trioxide forms a green solution with selenium monochloride which, according to Divers and Shimosé,[1] corresponds to the formula

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[2] Divers and Shimosé, *J. Chem. Soc.*, **45**, 198 (1884).

[3] Rathke, *Ann.*, **152**, 181 (1869).

[4] Ramsay and Evans, *J. Chem. Soc.*, **45**, 62 (1884).

$Se_2Cl_2SO_3$. With this substance hydrochloric acid gives Se_2Cl_2, SO_3HCl and H_2SO_3.

Oxidizing Agents.—Potassium dichromate, chromate, permanganate and perchlorate do not react even when hot. Halogens are liberated and selenium dioxide is produced with excess of iodic acid, potassium iodate, chlorate or bromate.

Hydrogen has no action.

Hydrogen sulfide acts slowly with evolution of heat, giving hydrogen chloride, sulfur and selenium.

Reaction with Selenium Dioxide.—It has been indicated by Lenher[5] that selenium oxychloride dissolves selenium. Further study has shown that the reaction, $2Se_2Cl_2 + SeO_2 \rightleftharpoons 2SeOCl_2 + 3Se$, is reversible and the products of the reaction can be separated by carbon tetrachloride.

Elementary tellurium and tellurium dichloride are both converted into the tetrachloride of tellurium when treated with selenium monochloride. In each case elementary selenium is set free.

Tellurium dioxide gives the tetrachloride of tellurium, selenium oxychloride and elementary selenium.

Phosphorus.—The white variety of phosphorus explodes with selenium monochloride while the red variety reacts slowly. Baudrimont[6] has identified phosphorus trichloride in the product. We have studied the reaction in detail in order to ascertain whether any phosphorus pentachloride is formed, and we can state that the reaction gives only the trichloride. When phosphorus pentachloride is treated with selenium, the reaction products are phosphorus trichloride and selenium monochloride additional evidence that the reaction forms only phosphorus trichloride lies in the fact that selenium is formed when the monochloride acts on elementary phosphorus. On long standing with excess of phosphorus pentachloride, the product $SeCl_4.PCl_5$, a red solid, separates.

Silicon with selenium monochloride is slowly attacked giving silicon tetrachloride and elementary selenium.

Iodine dissolves in large quantities in selenium monochloride to form a very dark, nearly black solution having a specific gravity at 25° of 3.1597. The amount of iodine in solution has been determined by two different methods to be 25.48% and 25.47%.

The Action of Selenium Monochloride on the Metals and Metallic Selenides

Sodium reacts slowly in the cold to form sodium chloride and selenium but the reaction soon stops due to the formation of insoluble sodium chloride. When heated the action proceeds with the evolution of light and heat.

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[5] Lenher, THIS JOURNAL, 43, 29 (1921).

[6] Baudrimont, *Ann. Chim. Phys.*, [4] **2,** 5 (1864).

When potassium is added to selenium monochloride the mixture explodes violently at ordinary temperatures forming potassium chloride and selenium. Potassium chloride is slightly soluble in selenium monochloride.

Copper gives copper selenide and cupric chloride when the copper is in excess. When the selenium monochloride is in excess, only cupric chloride and free selenium are separated. Both cupric and cuprous selenides react with excess of selenium monochloride to form cupric chloride. Cuprous chloride is also oxidized to cupric chloride by selenium monochloride.

Silver gives the chloride and selenide when it is in excess. When selenium monochloride is in an excess, silver chloride and selenium are formed.

Silver selenide is attacked giving silver chloride and selenium.

Magnesium forms the chloride and selenium. Magnesium chloride has a great tendency to hold monochloride in the same manner that it retains oxychloride.[7] When metallic magnesium is in excess, a small amount of magnesium selenide is formed.

Zinc, cadmium and chromium are only tarnished on the surface when heated with selenium monochloride for five months. Zinc dust, however, on account of its content of zinc oxide, takes fire when introduced into selenium monochloride. The products of the reaction are zinc chloride, zinc selenide, selenium oxychloride, and selenium when the metal is in excess, but no selenide is formed when the monochloride is in excess.

Zinc selenide gives zinc chloride and selenium.

Mercury, when warm, shows a vigorous reaction giving mercury selenide and mercuric chloride if the metal is in excess; when the monochloride is in excess, mercuric chloride and selenium are produced.

Mercuric selenide is attacked at once by selenium monochloride forming mercuric chloride and selenium.

Manganese and lead are attacked only very slowly. Lead required four months to give sufficient chloride for analysis and identification, while manganese required even longer.

Aluminum is not attacked in the cold but at 80° the reaction is vigorous and the metal burns brilliantly. When the metal is in excess aluminum chloride and selenide are formed. When the monochloride is in excess aluminum chloride and selenium are produced. When the two are heated together for 12 hours the product $2AlCl_3.SeCl_4$, which has been described by Weber,[8] is obtained. This shows that, in this instance, the monochloride is decomposed into tetrachloride and selenium.

Aluminum selenide is transformed into aluminum chloride and selenium.

Arsenic reacts in the cold forming arsenious chloride and yielding selenium. The selenide of arsenic also gives these reaction products.

Antimony yields the pentachloride and selenium with the intermediate

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[7] Wise, This Journal, **45**, 1236 (1923).

[8] Weber, *Pogg. Ann.*, **104**, 427 (1858).

formation of the selenide. Antimony trichloride is oxidized when warmed with selenium monochloride, to the pentachloride which subsequently reacts with more monochloride yielding $2SbCl_5.SeCl_4$. This reaction is another example of selenium monochloride acting as a mixture of the tetrachloride and selenium.

Bismuth gives bismuth trichloride and selenium. Bismuth selenide also gives these reaction products. Tin and stannic selenide both yield stannic chloride and selenium. Stannous chloride is oxidized to stannic chloride. Iron reacts to form ferric chloride and selenium. Iron selenide and ferrous chloride both give ferric chloride and selenium. Nickel and cobalt are not attacked at 100° in five months, and at the end of this time they are not even tarnished. Their selenides are only very slowly converted into chlorides.

The sulfides of the metals are in general attacked giving the corresponding chlorides with the separation of selenium and sulfur. The sulfides of Cu, Ag, Cd, Zn and Al react readily. Those of Hg, Mg, As, Bi, Sb, Sn and Fe are acted on at 100° The sulfides of lead and nickel are acted on but slowly by warm selenium monochloride while calcium and barium sulfides are attacked only slightly when heated with selenium monochloride for a week.

Action of Selenium Monochloride on Some Oxidized Compounds

Sodium peroxide reacts violently with evolution of light and heat producing sodium chloride, selenite, selenate and free selenium.

Potassium tetroxide acts more violently than sodium peroxide, forming the same order of products.

Lithium oxide gives lithium selenite and chloride and selenium.

The oxides of copper and silver give cupric and silver chlorides with the liberation of selenium and, when the monochloride is in excess, selenium oxychloride is also formed.

The oxides of beryllium and magnesium yield selenium oxychloride, selenium and anhydrous chlorides, which are contaminated by occlusion of selenium monochloride.

The oxides of calcium, strontium and barium are very slowly converted to chlorides, with production of selenium oxychloride and selenium.

The oxides of zinc and mercury react giving the chlorides, selenium dioxide and elementary selenium when the oxides are in excess and the chlorides, selenium oxychloride and selenium when the monochloride is in excess.

Cadmium oxide is only partially attacked in months.

The oxides of arsenic, antimony and bismuth yield the respective trichlorides with production of selenium oxychloride and selenium.

Lead monoxide and lead dioxide are converted to lead chloride with production of selenium oxychloride and selenium. Lead dioxide acts readily while lead monoxide acts very slowly.

Ferric oxide gives ferric chloride, selenium oxychloride and selenium.

The oxides of nickel and cobalt are acted on only very slowly. They give the chlorides.

Sodium and potassium carbonate, when freshly fused, are readily attacked forming the respective chlorides, selenium oxychloride, carbon dioxide, and selenium as do dry lithium carbonate and silver carbonate.

Basic copper carbonate gives cupric chloride.

Magnesium basic carbonate is not attacked in the cold but when heated to 130° in the vapor of selenium monochloride it is attacked, giving carbon dioxide.

The carbonates of calcium, strontium and barium give no carbon dioxide in 24 hours in the cold, but when moistened with water they give the calculated yield of carbon dioxide in a few minutes.

Zinc carbonate gives the chloride and carbon dioxide. Cadmium carbonate is not attacked.

The carbonates of lead and manganese are not attacked in the cold.

The mineral siderite ($FeCO_3$) is not attacked.

The basic carbonates of nickel and cobalt are only very slowly attacked even when heated.

Action on the Hydrocarbons

Selenium monochloride is immiscible with pentane, hexane and heptane and is miscible with such aromatic hydrocarbons as benzene, toluene and the xylenes. Its action on the aliphatic hydrocarbons has been carefully studied[9] and resembles that of sulfur monochloride. The action on benzene in the presence of metallic iron as a catalyst has been studied by Chabrie.[10]

Separations of the hydrocarbons by selenium monochloride are not possible.

Such carbohydrate- and protein-containing substances as hair, silk, wool or leather are not readily attacked. Gliadin from wheat, and elastin, as well as albumen are undissolved. Cellulose is not appreciably acted on.

Vegetable and fish oils react much as with sulfur monochloride, precipitating selenium and forming a rubber-like substance.

Rubber, both pure and vulcanized, is acted on slowly in the cold, the reaction being accelerated by heat.

Bakelite is soluble in warm selenium monochloride.

Coal of the bituminous type when dried at 160° shows little action.

[9] THIS JOURNAL, **44**, 395 (1922); *J. Ind. Eng. Chem.*, **12**, 1100 (1920); *J. Chem. Soc.*, **117**, 1453 (1920).

[10] Chabrie, *Ann. chim. phys.*, [6] **20**, 256 (1890).

Summary

A systematic study is herewith presented of the physical and chemical properties of selenium monochloride.

Its properties in general are those of a typical acid chloride and a strong chlorinating agent.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL ACTION OF GASEOUS IONS PRODUCED BY ALPHA PARTICLES

VII. UNSATURATED CARBON COMPOUNDS

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Following the work in Part VI on the oxides of carbon[1] an investigation of hydrocarbons was begun. Complications which were encountered in the kinetics of the saturated members owing to simultaneous reactions have delayed completion of the study. The unsaturated carbon compounds, however, behave more simply. Although the oxidation and hydrogenation of the unsaturated compounds also involve simultaneous reactions, they have not proved to be too complex to resolve fairly well. The present is an account of the polymerization, condensation (slight except for ethylene), oxidation and hydrogenation (omitting hydrogen cyanide) of acetylene, cyanogen, hydrogen cyanide and ethylene. They were chosen as representative of the simpler unsaturated organic gases. The same experimental procedure was employed as in Part VI.

Preparation of Gases

Hydrogen and oxygen were prepared as described in Part VI.

For the preparation of acetylene we were fortunate in having at our disposal some very pure calcium carbide, which was made by Mr. Herbert Krase of this Laboratory, by fusing pure precipitated calcium oxide and Acheson graphite and which was proved to contain no phosphorus. The acetylene was purified by washing with a solution of potassium dichromate in concd. sulfuric acid and then with potassium hydroxide solution. It was dried with phosphorus pentoxide and condensed in a liquid-air bath for the removal of any permanent gases by pumping.

Cyanogen was prepared by heating mercuric cyanide. It was dried by phosphorus pentoxide and fractionated at —90° to remove carbon dioxide.[2] The sample of gas used for radiating cyanogen alone contained about 0.5% of carbon dioxide (see later). That used for mixtures of cyanogen with oxygen and with hydrogen was further purified until it contained no carbon dioxide.

The hydrogen cyanide used was prepared by Dr. Perry and Mr. Porter.[3] A sample

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[1] THIS JOURNAL, **47,** 2675 (1925).

[2] Compare Perry and Bardwell, *ibid.*, **47,** 2629 (1925).

[3] Perry and Porter, *ibid.*, **48,** 299 (1926).