copper gauze catalyst, and by a continuous process. The product has been reduced and fractionated, yielding twelve definite chemical individuals, the characteristics of which are reported.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA]

Iodine Monochloride. II. Reactions with Salts

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In an earlier publication[1] Cornog and Karges report that potassium nitrate is converted quantitatively to potassium chloride if a mixture of potassium nitrate with iodine monochloride in excess is evaporated to dryness. This observation raises a question as to what becomes of both the iodine and the nitrate in this particular reaction, also the more general question, "What are the reactions between salts and iodine monochloride?" These questions have prompted the exploratory investigation here reported.

1. **Chlorides.**—Chloride salts, in excess quantity, were placed in iodine monochloride at 50°, the resulting mixtures were kept in a thermostat at 40° for two or more hours, the material remaining undissolved was removed by filtration, the excess iodine monochloride was removed by evaporation, and the residue was weighed and identified.

From such experiments we learned that the residue products thus obtained from 100 g. of iodine monochloride solution were always chlorides and weighed less than 0.6 g. This statement includes the chlorides of sodium, lithium, silver, cupric, and barium. The residues obtained from the chlorides of potassium, ammonium, rubidium, and cesium merit special mention. Data concerning them are shown in Table I.

TABLE I

Chloride	Salt diss. by 100 g. ICl	Residue	
		Formula	Stability, °C.
KCl	5.80	$KCl \cdot ICl$	0
NH_4Cl	6.27	$NH_4Cl \cdot ICl$	25
$RbCl$	14.10	$RbCl \cdot ICl$	110
$CsCl$	19.9	$CsCl \cdot ICl$	180

The residues indicated in Column 3, Table I, are all bright golden yellow crystalline powders. These compounds also may be formed with iodine monochloride vapor by placing the corresponding chlorides within a desiccator which also contains iodine monochloride in a separate beaker. While the method of preparation differs, the general properties of these compounds resemble the compounds of similar formulas reported by Wells[2] and co-workers. Wells states that the compound represented by $KCl \cdot ICl$ decomposes at 215° while we noted slow decomposition of this compound even at 0°.

These data indicate that the chloride salts investigated are sparingly soluble in iodine monochloride, with the exception of the chlorides of potassium, ammonium, rubidium, and cesium.

2. **Nitrates and Sulfates.**—The nitrates and sulfates of sodium and potassium are completely converted to the corresponding chlorides, if portions of these salts are submerged in excess iodine monochloride and the resulting mixtures are evaporated to dryness. However, if these nitrate and sulfate salts are submitted to the treatment described for chlorides, the residues obtained by evaporation of the filtrate weigh less than 0.1 g. per 100 g. of iodine monochloride used. These residues are pure chlorides.

3. **Cyanides, Cyanates, and Thiocyanates.**—Qualitative experiments showed that these salts react vigorously with iodine monochloride. The final products obtained from such reactions are easily separated and identified. See illustrative equations, 1, 2, and 3.

$$NH_4CN + ICl = NH_4Cl + ICN \qquad (1)$$

$$3KCNO + 3ICl + 3KCl + I(CNO)_3 + I_2 \qquad (2)$$

$$3KCNS + 3ICl = 3KCl + I(CNS)_3 + I_2 \qquad (3)$$

Iodine tricyanate and iodine trithiocyanate appear to be new compounds; further, all of the reactions between iodine monochloride and cyanide, cyanate, and thiocyanate salts appear to be new reactions. Both the new compounds and new reactions are described in the following text.

The quantitative experiments with cyanide, cyanate, and thiocyanate salts were executed in

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[1] I, Cornog and Karges, THIS JOURNAL, 54, 1882 (1932).

[2] Wells, *Z. anorg. Chem.*, 1, 85 (1892).

TABLE II

Formulas and quantities of end-products. "(f)" indicates quantity experimentally gotten. "(t)" indicates" quantity theoretically required.

Formula and quantity of salt mixed with equiv. quantity of ICl	End-products I			II			III		
a. Cyanides: Typical reaction $NH_4CN + ICl = NH_4Cl + ICN$									
NH_4CN	NH_4CN	0.6297 g.	(f)	ICN	1.7826 g.	(f)			
0.5203 g.		.6425	(t)		1.8077	(t)			
CsCN	CsCl	.1213	(f)	ICN	0.1116	(f)			
0.1217		.1257	(t)		.1137	(t)			
KCN	KCl	.4110	(f)	ICN	.9057	(f)			
0.3709		.4238	(t)		.8828	(t)			
$Cd(CN)_2$	$CdCl_2$	.3627	(f)	ICN	.6026	(f)			
0.3206		.3624	(t)		.5985	(t)			
CuCN	$CuCl_2$	.3011	(f)	ICN	.3515	(f)	I_2	0.2765 g.	(f)
0.1989		.2982	(t)		.3391	(t)		.2839	(t)
$Pb(CN)_2$	$PbCl_2$	.7745	(f)	ICN	.8408	(f)			
0.6948		.7962	(t)		.8200	(t)			
AgCN	AgCl	.4925	(f)	ICN	.5227	(f)			
0.4614		.4918	(t)		.5280	(t)			
b. Cyanates: Typical reaction $3KCNO + 3ICl = 3KCl + I(CNO)_3 + I_2$									
KCNO	KCl	0.2776	(f)	$I(CNO)_3$	0.3087 g.	(f)	I_2	0.3204	(f)
0.3044		.2795	(t)		.3165	(t)		.3169	(t)
$Pb(CNO)_2$	$PbCl_2$	.3468	(f)	$I(CNO)_3$	.2050	(f)	I_2	.2193	(f)
0.3602		.3492	(t)		.2086	(t)		.2094	(t)
c. Thiocyanates: Typical reaction $3NH_4CNS + 3ICl = 3NH_4Cl + I(CNS)_3 + I_2$									
NH_4CNS	NH_4Cl	0.1956	(f)	$I(CNS)_3$	0.3637	(f)	I_2	0.2840	(f)
0.2767		.1945	(t)		.3704	(t)		.3076	(t)
KCNS	KCl	.2757	(f)	$I(CNS)_3$	.3831	(f)	I_2	.3177	(f)
0.3639		.2793	(t)		.3937	(t)		.3169	(t)
$Pb(CNS)_2$	$PbCl_2$	.2498	(f)	$I(CNS)_3$	.1849	(f)	I_2	.1489	(f)
0.2885		.2475	(t)		.1786	(t)	I_2	.1515	(t)
AgCNS	AgCl	(lost)		$I(CNS)_3$	.2321	(f)	I_2	.1948	(f)
0.3873		...			.2142	(t)	I_2	.1984	(t)

the following manner. In each case a weighed equivalent quantity of the salt was added to a weighed quantity of iodine monochloride contained in a glass stoppered flask cooled by an ice-water bath. After the mixture had remained at zero temperature for several hours, water was added to the mixture. Extraction with carbon tetrachloride followed, which removed free iodine, if present. Filtration of the water layer removed iodine tricyanate or iodine trithiocyanate if these substances were present. Ether extraction of the water layer removed iodine cyanide when that substance was present. After the filtration and extractions only chloride salt remains in the water layer. In the order mentioned the end-products were estimated as follows. Iodine in the carbon tetrachloride layer was titrated with sodium thiosulfate. Iodine tricyanate or trithiocyanate on the filter was dried and weighed. Iodine cyanide in the ether layer was weighed after the removal of ether by evaporation. Iodine cyanide also was determined by the method of Chattaway and Wadman.[3] The salt remaining after the water layer finally obtained had been evaporated to dryness was usually weighed though methods of precipitation or titration were used at times. The data thus obtained are shown in Table II.

Iodine tricyanate was analyzed for iodine by fusion with metallic sodium, followed by hydrogen peroxide treatment to liberate iodine, and titration with sodium thiosulfate. The Kjeldahl method was used to determine nitrogen. Oxygen and carbon were not determined.

	I, %	N, %
Experimental	49.81	16.43
Computed from formula $I(CNO)_3$	50.18	16.50

Iodine tricyanate is a dark brown powder that is sparingly soluble in water or alcohol. It does not melt or sublime when heated but chars at temperatures above 160°.

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[3] Chattaway and Wadman, *J. Chem. Soc.*, 81, 191 (1902).

Iodine trithiocyanate was analyzed for iodine by digestion in hot concentrated potassium hydroxide solution, followed by treatment with hydrogen peroxide and titration with sodium thiosulfate. Nitrogen was determined by the Kjeldahl method. Sulfur was determined by digesting a sample with fuming nitric acid and later precipitating as barium sulfate. Carbon was not determined.

	I, %	N, %	S, %
Experimental	43.62	13.27	32.11
Computed from the formula $I(CNS)_3$	43.17	13.95	31.90

Iodine trithiocyanate is a yellow brown powder that is sparingly soluble in water and most organic solvents. It is dissolved by concentrated sulfuric acid without visible signs of reaction. Iodine trithiocyanate does not melt or sublime when heated but chars at temperatures above 260°.

This portion of the text describes two new compounds and thirteen new reactions.

4. **Sulfides.**—Qualitative experiments showed that mixtures of the sulfide salts, here reported, and fused iodine monochloride react vigorously. In these reactions the metal of the sulfide salt was changed to the corresponding iodide, while sulfur monochloride and free sulfur also were found as end-products. These are believed to be new reactions. In the quantitative experiments only the metallic iodide was determined. Both experimental difficulty and time limitations precluded analysis of the mixtures of sulfur, sulfur monochloride and perhaps other sulfur chlorides. Hence equations representing this group of reactions are balanced only with respect to the initial products and the metallic iodide. Table III contains data obtained from study of these reactions.

TABLE III

Typical reaction $CdS + 2\ ICl = CdI_2 + S_2Cl_2 + S$

Formula and quantity of salt mixed with equiv. quantity ICl.	Formulas and quantities of end-products. "(f)" indicates quantity experimentally gotten. "(t)" indicates quantity theoretically required. "Qual" indicates qualitative determination of indicated product.				
	End-products I			II	III
CdS	CdI_2	1.2716 g.	(f)	S_2Cl_2 (qual.)	S (qual.)
0.5037 g.		1.2780	(t)		
ZnS	ZnI_2	1.2248	(f)	S_2Cl_2 (qual.)	S (qual.)
0.3642		1.1970	(t)		
PbS	PbI_2	0.7612	(f)	S_2Cl_2 (qual.)	S (qual.)
0.4084		.7874	(t)		
Ag_2S	$^1/_2$ AgI	.2414	(f)	S_2Cl_2 (qual.)	S (qual.)
0.2498		.2374	(t)		

5. **Reactions in Acetic Acid.**—Iodine monochloride was both a solvent and a reactant in the previously described reactions. A study of reactions in acetic acid was undertaken with the thought of observing reactions in which iodine monochloride was a reactant but not a solvent. Though acetic acid dissolves iodine monochloride freely without decomposition, its utility is limited by the fact that many salts are sparingly soluble or else are decomposed. Cyanides and thiocyanates were the only salts studied from which conclusive data were obtained. Cyanates were decomposed while other salts yielded inconclusive results.

a. **Cyanides and Thiocyanates.**—Alkali cyanides and thiocyanates and iodine monochloride in acetic acid solution react just as they do in the absence of acetic acid.

$$KCN + ICl = KCl + ICN$$

$$3KCNS + 3ICl = 3KCl + I(CNS)_3 + I_2$$

The analytical data supporting these statements are similar to those previously given. In making these analyses the iodine trithiocyanate–iodine mixtures were freed from acetic acid by placing them in a desiccator over dry potassium acetate. This is a little known and convenient method for freeing materials from acetic acid without heating them.

b. **Heavy Metal Acetate and Iodine Monochloride in Acetic Acid.**—A number of acetate salts of heavy metals are appreciably soluble in acetic acid which in turn visibly react with iodine monochloride dissolved in acetic acid. Efforts toward quantitatively studying such reactions were not successful. From these unsuccessful efforts we definitely obtained three compounds not previously recorded. The compositions of these compounds are represented, respectively, by the formulas $Pb_2(C_2H_3O_2)_2 \cdot ICl$, $Cd_3(C_2H_3O_2)_2 \cdot 2ICl$, and $Cu_2(C_2H_3O_2)_2 \cdot ICl$. These formulas are intended to represent composition and not any implications as to structure.

The first of these compounds is obtained by joining solutions of acetic acid containing, respectively, equivalent quantities of lead acetate and iodine monochloride. Immediately a precipitate, lead chloride, forms and is removed by filtration. About half the lead originally present is thus removed. Long yellow prism-like crystals form in the filtrate after a few days. These crystals were recrystallized from acetic acid and analyzed.

	Pb, %	I, %	Cl, %	Acetate, %
Experimental	59.36	18.46	5.20	16.26
Computed from formula $Pb_2(C_2H_3O_2)_2 \cdot ICl$	59.49	18.29	5.09	16.98

The preparation of the cadmium compound was like that of the lead compound. The crystals are yellow cubes, and were analyzed.

	Cd, %	I, %	Cl, %	Acetate, %
Experimental	43.06	32.26	9.08	14.35
Computed from formula $Cd_3(C_2H_3O_2)_2 \cdot 2ICl$	43.24	32.54	9.20	15.13

The copper compound is formed by joining solutions containing equivalent quantities of cupric acetate and iodine monochloride. No precipitate forms. The mixture is evaporated to dryness under reduced pressure. The residue consists of a mixture of pale blue plate-like crystals of the copper compound and brown-yellow cupric chloride. These two compounds were separated by ether extraction, the new compound being much more soluble than cupric chloride.

	Cu, %	I, %	Cl, %	Acetate, %
Experimental	31.44	28.64	8.46	30.84
Computed from the formula $Cu_2(C_2H_3O_2)_2 \cdot ICl$	31.42	28.96	8.69	31.15

All three of these compounds are well-formed crystalline substance with a high solubility in water.

We offer the following speculation as to the possible nature of these compounds. When lead chromate is boiled in alkaline solutions compounds are formed which are sometimes represented by formulas such as $PbCrO_4 \cdot PbO$, $PbCrO_4 \cdot 2PbO$, and so forth. In acetic acid solution lead acetate would be the analog of lead hydroxide or oxide in water solution. The existence of lead iodochloride, PbClI does not seem unreasonable. Hence our thought would be that the new lead compound may be an acetic acid system basic salt which might be represented correctly by the formula $PbICl \cdot Pb(C_2H_3O_2)_2$. The other two compounds would be represented, respectively, by the formulas $CuICl \cdot Cu(C_2H_3O_2)_2$ and $2CdICl \cdot Cd(C_2H_3O_2)_2$ or $CdCl_2 \cdot CdI_2 \cdot Cd(C_2H_3O_2)_2$.

Summary

1. The chlorides of lithium, sodium, silver, copper, and barium do not react with iodine monochloride and have solubilities of less than 0.6 g./100 g. of iodine monochloride. The chlorides of ammonium, potassium, rubidium, and cesium form addition compounds of the type $MCl \cdot ICl$.

2. The nitrates and sulfates of sodium and potassium are converted to the corresponding chlorides when mixed with iodine monochloride and the mixture is evaporated to dryness.

3. Iodine monochloride reacts with the cyanides studied as is indicated by the type equation $ICl + MCN = ICN + MCl$.

4. Iodine monochloride reacts with the cyanates and thiocyanates studied as is indicated by the type equations $3MCNO + 3ICl = 3MCl + I(CNO)_3 + I_2$; $3MCNS + 3ICl = 3MCl + I(CNS)_3 + I_2$. Iodine tricyanate, $I(CNO)_3$, and iodine trithiocyanate, $I(CNS)_3$, are believed to be new compounds.

5. The metallic sulfides studied react with iodine monochloride as is indicated in the unbalanced type equation $MS + ICl = MI_2 + S_2Cl_2 + S$.

6. In acetic acid cyanides and thiocyanates, but not cyanates, react with iodine monochloride, just as indicated by the type equations in items 3 and 4 of this summary.

7. Reactions between heavy metal acetates and iodine monochloride in acetic acid yielded indeterminate results. From these experiments three new compounds were obtained which are represented by the formulas $Pb_2(C_2H_3O_2)_2 \cdot ICl$, $Cd_3(C_2H_3O_2)_2 \cdot 2ICl$ and $Cu_2(C_2H_3O_2)_2 \cdot ICl$.

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