4. Arc spectrum analysis indicated the probable presence of element number 72 in the potassium double sulfate residues from the yttrium group.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# REACTIONS IN LIQUID HYDROGEN SULFIDE. III THIOHYDROLYSIS OF CHLORIDES[1]

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In the two previous papers from this Laboratory concerning liquid hydrogen sulfide as a reaction medium[2,3] it has been shown that while liquid hydrogen sulfide has, in many ways, more the properties of an organic solvent than water has, nevertheless there are some reactions that bring out its close relationship with water. One of these is its reaction with chlorides, especially those of the elements of the fifth group in the periodic table. This reaction, which corresponds to hydrolysis in water systems and ammonolysis in ammonia systems, has been designated as thiohydrolysis. While the above mentioned chlorides are the most reactive, other chlorides have been studied in order to make the series complete.

Most of the truly metallic chlorides, except $AlCl_3$, $FeCl_3$, $HgCl_2$ and $ZnCl_2$, are quite insoluble and non-reactive, but the more non-metallic chlorides are not only very soluble but many of them are quite reactive. An attempt has been made to bring about these reactions and to examine the products formed to show how complete is the thiohydrolysis.

## Experimental

The liquid hydrogen sulfide was prepared in an apparatus very similar to that used by Quam.[2] The chlorides, after careful purification, were placed in heavy-walled, well-annealed glass tubes of about 10cc. capacity which had been dried by washing with alcohol and ether and then heating in an oven while passing a current of dry air through them. The liquid hydrogen sulfide was transferred directly from the generator to these after they had been cooled in a freezing mixture of ether and solid carbon dioxide contained in Dewar bulbs.

The reactions were allowed to take place at that temperature (about $-77°$) and at the same time other tubes were sealed at this temperature and then permitted to come to room temperature at which they were kept for a week or more, if necessary, for any slow reaction to take place. After the reaction had taken place at either temperature the excess of liquid hydrogen sulfide and any volatile substances were permitted to evaporate

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[1] This paper is from a portion of the work presented by A. W. Ralston in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Iowa State College.

[2] Quam, THIS JOURNAL, **47**, 103 (1925).

[3] Quam and Wilkinson, *ibid.*, **47**, 989 (1925).

and the residue was examined by analysis to find whether any reaction had taken place and if so what products had been formed.

The samples for analysis were weighed in small glass capsules which were broken beneath the surface of a concentrated solution of potassium hydroxide contained in a stoppered vessel. This prevented any loss of hydrogen sulfide. This solution was used for analyses.

## Data

The chlorides of the alkali metals and of the alkali earth metals, $CuCl_2$, $CdCl_2$, $MnCl_2$, $CoCl_2$, $FeCl_2$ and $CrCl_3$ (both the green and violet forms) are insoluble and non-reactive in liquid hydrogen sulfide both at low temperature and at room temperature. Cuprous chloride and silver chloride react with liquid hydrogen sulfide, the former blackening immediately and the latter reacting more slowly to form a flocculent, yellow solid which turns black on exposure to the air. Hydrogen chloride is liberated, showing that some thiohydrolysis has taken place.

Zinc chloride is slightly soluble at the low temperature and more soluble at room temperature, although it is non-reactive at all temperatures. The halides of mercury where the valence is two are soluble but non-reactive at the low temperature, the iodide being the most soluble and the chloride the least. The solubility increases with rise of temperature and at room temperature the chloride is thiohydrolyzed to the black sulfide, which later turns to the red form. The iodide is not thiohydrolyzed but on the evaporation of the liquid hydrogen sulfide the iodide crystallizes out as the yellow form which later turns to the stable red form.

Mercurous chloride is insoluble in liquid hydrogen sulfide but reacts even at the low temperature to form a brown, flocculent, gelatinous mass which on analysis was found to contain 85.81% of Hg and 13.65% of S, which is very close to the composition of HgSH (85.85% of Hg and 13.72% of S). It cannot be mercurous sulfide (92.6% of Hg and 7.4% of S) and it is unlikely that it is a mixture of mercuric sulfide and mercury, not only from the brown color but also because hydrogen sulfide is shown to be a strong reducing agent with other elements such as titanium, selenium and tellurium and so it would hardly be expected to permit the oxidation of the HgSH to mercuric sulfide.

Boron trichloride and aluminum chloride are both quite soluble in liquid hydrogen sulfide. The former reacts very vigorously, even at the temperature of the ether and solid carbon dioxide mixture, forming a white, crystalline compound. As the temperature is raised, this compound melts to a clear liquid at −47° from which the crystals again separate on cooling. Due to its low melting point and to its instability it was impossible to get a weighed sample for analysis to find the per cent. and the formula. However, by adding an unweighed quantity of the crystals to a solution of potassium hydroxide and analyzing aliquot portions of this for the weights of boron, chlorine and sulfur, the formula of the solid may be calculated. The chlorine was determined by the Volhard titration with silver nitrate and ammonium thiocyanate and the sulfur by distilling, after acidifying with hydrochloric acid, into ammoniacal cadmium chloride and titrating with standard iodine solution. The boron was determined by distilling it as methyl borate, saponifying with lime and weighing as boron trioxide. Two hundred cc. of such a solution showed 0.0344 g. of boron trioxide and other 200cc. portions required 48.4 and 48.32 cc. of silver nitrate solution, one cc. of which is equivalent to 0.00217 g. of chlorine. Twenty-five-cc. portions were used to determine the sulfur and they required 29.57 cc. and 29.68 cc. of an iodine solution, one cc. of which is equivalent to 0.001585 g. of sulfur. This shows that there was present in the unweighed sample 0.0344 g. of boron trioxide or 0.01069 g. of boron, 0.10503 and 0.10485 g. of chlorine and 0.37495 and 0.37632 g. of sulfur. Calculating the formula from these results shows quite clearly that the formula for the compound is $BCl_3.12H_2O$.

This calculation is made by dividing the weight of each element by its respective atomic weight and finding the ratios of these quotients which will give the relative number of atoms that are present in the compound.

Aluminum chloride shows solubility but no thiohydrolysis, and no thiohydrates were found to crystallize out on evaporation although Biltz[4] has shown the existence of thiohydrates of aluminum choride by vapor pressure measurements. Quam reported aluminum choride as insoluble and non-reactive but there is definite evidence of the fact that it dissolves as shown in the conductance of the solution, which will be discussed later.

In the fourth group of the periodic table where the elements become more non-metallic the solubility of the chlorides in liquid hydrogen sulfide becomes quite marked. Carbon tetrachloride and silicon tetrachloride are miscible with liquid hydrogen sulfide in all proportions and show practically no thiohydrolysis. However, when silicon tetrachloride was kept at room temperature with hydrogen sulfide for several weeks a small amount of brown silicon disulfide was formed. Stannic chloride, which freezes at $-33°$ is insoluble and non-reactive at the low temperatures but at room temperature the two liquids are miscible. After standing for two weeks at this temperature a small amount of yellow stannic sulfide was formed. Biltz[4] has shown that plumbic chloride is reduced to plumbous chloride. This group of chlorides which are so easily hydrolyzed in water are very inert in liquid hydrogen sulfide. It should, therefore, be an excellent medium in which to study the reactions of these compounds.

Titanium tetrachloride at very low temperatures forms a yellow crystalline body, the composition of which is shown by analysis to be $2TiCl_4.H_2S$.

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[4] Biltz, *Z. anorg. allgem. Chem.*, **147**, 171 (1925).

This compound is very unstable and decomposes into titanium tetrachloride and hydrogen sulfide as the temperature is slowly raised. If it is rapidly warmed to room temperature the decomposition takes place almost explosively. It is therefore impossible to get a weighed portion of this addition product, due to its instability. By allowing the excess of hydrogen sulfide to evaporate off at −77° and taking an unweighed portion of the residue and dissolving in potassium hydroxide solution, as was done with the boron compound, the formula may be determined. The following values were obtained.

*Titanium.* 0.0378 g. of $TiO_2$ = 0.0378/80.1 = 0.000472 atom = 2 × 0.000233.
*Chlorine.* 0.2674 g. of AgCl = 0.2674/143.3 = 0.001866 atom = 8 × 0.000233.
*Sulfur.* 0.0544 g. of $BaSO_4$ = 0.0544/233.4 = 0.000233 atom = 1 × 0.000233.

This shows that the formula for the compound is $2TiCl_4.H_2S$.

Biltz[4] reported only two thiohydrates of $TiCl_4$, $TiCl_4.2H_2S$ and $TiCl_4.H_2S$.

At room temperature the reaction between liquid hydrogen sulfide and titanium tetrachloride is very vigorous. A brown solid is first formed which is soluble in the liquid hydrogen sulfide giving a red solution. Later a layer of black solid mixed with a yellow one forms. When this mass is extracted for a long time with carbon disulfide, the yellow dissolves and is found to be sulfur, showing that some reduction has taken place. The black residue was analyzed and found to be titanous chloride. The brown solid which is first formed is soluble in alcohol, giving a solution with a decided mercaptan odor. Pfordten[5] prepared similar compounds by the action of dry hydrogen sulfide gas on titanium tetrachloride. Titanium tetrachloride seems to be one of few chlorides studied where it is possible that the thiohydrolysis first gives an SH body corresponding to the OH in hydrolysis. Further work is being done on the reaction between hydrogen sulfide and titanium tetrachloride.

Phosphorus trichloride is partly miscible but non-reactive at low temperatures with liquid hydrogen sulfide but $P_2S_3$ is formed immediately on mixing at room temperature. Phosphorus pentachloride immediately forms the insoluble $PSCl_3$ at all temperatures. This resembles the similar reaction with water except that there the hydrolysis is completed forming the soluble hydroxide or acid.

Arsenic trichloride gives the sulfide, $As_2S_3$, immediately at all temperatures. This also differs from the similar reaction in water where the soluble hydroxide or acid is formed. Antimony trichloride shows that the element is more metallic than arsenic in that it does not dissolve or react with the hydrogen sulfide at low temperature as does arsenic trichloride. It is very soluble but non-reactive at room temperature. In either case, however, when the liquid hydrogen sulfide is evaporated off, the antimony

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[5] Pfordten, *Ann.*, **234**, 257 (1886).

trichloride reacts with the vapor of hydrogen sulfide to form lemon-yellow crystals and hydrogen chloride is evolved. These crystals were analyzed and found to be $SbSCl.7SbCl_3$. The data obtained are as follows.

*Anal.* Calcd.: Sb, 54.21; Cl, 43.98; S, 1.81. Found: Sb, 54.12; Cl, 43.86; Cl, 1.87.

This same compound has been prepared by Schneider[6] by the action of dry hydrogen sulfide gas on dry antimony trichloride at reduced temperatures.

Antimony pentachloride reacts similarly to phosphorus in hydrogen sulfide forming the $SbSCl_3$. It is more thiohydrolyzed in hydrogen sulfide than it is hydrolyzed in water since the antimony chloride is hydrolyzed only in warm water. Bismuth trichloride reacts immediately, even at low temperatures, with liquid hydrogen sulfide forming an orange-red solid. This solid slowly gave off hydrogen chloride but after standing in a desiccator over sulfuric acid for several days it arrived at constant weight and an analysis showed it to be $Bi_2SCl_4$ or $BiSCl.BiCl_3$.

*Anal.* Calcd. for $Bi_2SCl_4$: Bi, 70.62; Cl, 23.96; S, 5.42. Found: Bi, 70.49; Cl, 23.91; Cl, 5.52.

It seems therefore that an addition product or thiohydrate is first formed which slowly loses hydrogen chloride in the air, forming the basic salt. This corresponds to the action of hydrogen sulfide on titanium tetrachloride except that in the case of bismuth trichloride the addition product is more stable. The formation of the insoluble addition product accounts for the fact that Quam and Wilkinson[3] found that a mixture of bismuth trichloride and hydrogen sulfide did not conduct an electric current in spite of the fact that a visible reaction had taken place. The same body is formed with bismuth trichloride at room temperature.

Selenium tetrachloride at low temperatures reacts slowly with liquid hydrogen sulfide until all of it has disappeared. After boiling off the excess of hydrogen sulfide, a yellow solid remains. When the temperature is raised, this solid melts to a red-brown liquid which has sulfur suspended in it. An analysis of this liquid showed it to be $Se_2Cl_2$. At room temperature selenium tetrachloride reacts rapidly with hydrogen sulfide and is reduced to red selenium. This can be separated from the sulfur mixed with it by means of the greater solubility of the selenium in carbon disulfide compared to the sulfur.

Tellurium tetrachloride in the cold is reduced immediately to tellurium dichloride and sulfur, the former being insoluble in carbon disulfide while the latter dissolves slowly. At room temperature the tellurium tetrachloride, like selenium tetrachloride, is completely reduced to the element.

Chromium trichloride, either the green or violet form, is insoluble and does not react with hydrogen sulfide at any temperature. This is a little

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[6] Schneider, *Pogg. Ann. phys. Chem.*, **108**, 407 (1859).

unusual considering that the trivalent chlorides, aluminum chloride and ferric chloride, are both soluble. Manganous chloride and cobalt chloride are insoluble and non-reactive at low temperature although cobalt chloride will turn black on long standing at room temperature.

Ferric chloride dissolves to a yellow liquid from which, at low temperatures, a white precipitate of ferrous chloride slowly separates. At room temperature the same reaction takes place very rapidly.

## Conductance of Chloride Solutions in Liquid Hydrogen Sulfide

In order to check the conclusions as to whether or not the chlorides dissolved in the liquid hydrogen sulfide, the conductances of the solutions were determined after they had stood until equilibrium had been reached. The cells used were similar to those described by Quam and Wilkinson[3] and the conductance was measured at the temperature of the mixture of ether and solid carbon dioxide.

Potassium, strontium, barium, cadmium, chromic (green and violet forms), manganous and cobalt chlorides all showed non-conductance.[7] Silver, cuprous and mercurous chlorides all show some conductance after standing, due to the hydrogen chloride liberated by the thiohydrolysis. The specific conductances for solutions of the other chlorides are given in the following table.

TABLE I

CONDUCTANCES OF SATURATED SOLUTIONS OF CHLORIDES IN LIQUID HYDROGEN SULFIDE

| Pure $H_2S$, $\lambda = (1 \times 10^{-11})$ | | Pure $H_2S$, $\lambda = (1 \times 10^{-11})$ | |
|---|---|---|---|
| Salt | $\lambda \times 10^6$ | Salt | $\lambda \times 10^6$ |
| $HgCl_2$ | 0.031 | $AlCl_3$ | 2.092 |
| $SnCl_4$ | .106 | $HgBr_2$ | 5.16 |
| $SiCl_4$ | .129 | $HgI_2$ | 9.99 |
| $ZnCl_2$ | .634 | $FeCl_3$ | 209.9 |
| HCl | .881 | $SbCl_3$ | 424 |
| $AsCl_3$ | 1.15 | | |

## Conclusions

A study of the chlorides in different parts of the periodic table shows that the chlorides of the metallic elements are mostly insoluble in liquid hydrogen sulfide except zinc, mercuric, aluminum and ferric chlorides. The univalent chlorides of silver, copper and mercury are insoluble but thiohydrolyze to insoluble hydrosulfides or sulfides.

The chlorides of the non-metallic elements which are easily hydrolyzed in water forming the hydroxides are, in many cases, soluble in liquid hydrogen sulfide in all proportions and show no thiohydrolysis. In other cases they form thiohydrates, addition products and sulfides but there

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[7] In the paper by Quam and Wilkinson (ref. 3) the statement is made that the specific conductance of pure liquid hydrogen sulfide is half that of water. This is obviously an error as the figures which are given show that it is one hundred thousandth as much.

is little evidence that any of them form a thio-acid such as $H_3AsS_3$, except possibly $TiCl_4$.

The reducing action of hydrogen sulfide accounts for many of the differences encountered in comparing these reactions with similar ones in water, for example, with $TeCl_4$, $SeCl_4$, $TiCl_4$ and $FeCl_3$.

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# THE POSITION OF THE ELEMENTS OF THE RARE EARTHS IN THE PERIODIC SYSTEM

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From the time when Mendeléeff enunciated the principles of the periodic system, many attempts have been made to include the elements of the rare earths in the classification. Previous to 1870 the rare earth elements were regarded as divalent, chiefly because of the strongly basic character of their oxides. Mendeléeff, finding difficulty in placing the then known elements of the rare earths in Group II of his system, contended that the metals are tervalent. He, therefore, assigned to yttrium, didymium and erbium positions in Group III and to cerium and lanthanum positions in Group IV. The work done on the rare earths since 1870 has confirmed Mendeléeff's view of the tervalency of these elements and at the same time it has increased their number from five to seventeen. There are included in this remarkable series of elements, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, illinium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium. The order given above is that of ascending atomic number.

The element illinium (atomic number 61) has recently been recognized by Lapp, Rogers and Hopkins[1] by means of x-ray analysis of rare earth fractions, and thus a complete series of elements of atomic numbers 57 to 71 is made up. In order of atomic number lanthanum (57) follows barium (56) and hafnium (72) follows lutecium (71). Consequently it may be taken that the series of rare earths is complete.

Since the time of Mendeléeff many attempts have been made to arrange these elements either in Mendeléeff's system, in modifications of Mendeléeff's system or in geometrical systems by Brauner, R. J. Meyer, Retgers, Benedicks, Soddy, Stefan Meyer, Steele, Werner, Vogel, Rydberg, Aston, Bohr and others. The arrangements in Mendeléeff's system have failed because of an apparent lack of accommodation and because valencies have been assigned to certain of the elements which could not be sub-

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[1] Lapp, Rogers and Hopkins, *Phys. Rev.*, **25**, 106 (1925).