

## Decomposition of Hydroxyamidosulphates by Copper Sulphate.

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When copper sulphate is added to a solution of a hydroxyamidosulphate and the mixture heated, the acid of the salt is quickly decomposed into water, sulphur dioxide, sulphuric acid, amidosulphuric acid and nitrous oxide, with possibly a little nitrogen. By itself, a heated solution of an alkali hydroxyamidosulphate is in a state of very unstable equilibrium, generally hydrolysing into a solution of hydroxylamine acid sulphate, and always doing so in presence of a trace of acid, whilst in presence of even a trace of alkali it slowly passes into sulphite and hyponitrite (this Journ, 3, 219). In the cold with alkali and copper salt, the hydroxyamidosulphate becomes oxidised at once to sulphite, sulphate, nitrous oxide, and water with reduction of the cupric hydroxide (*op. cit.*, 225), and when heated with cupric chloride it reduces the latter to cuprous

chloride, becoming itself converted into sulphur dioxide, sulphate, nitrous oxide, and water. Mercuric nitrate oxidises hydroxyamid sulphate more completely, but ferric chloride seems to act like copper sulphate, and liberates sulphur dioxide.

An alkali hydroximidosulphate is also decomposed by copper sulphate, but not so easily, for it can be heated with it at 100° for a short time without change, and only decomposes (but then suddenly) some degrees above that temperature, yielding the products which a hydroxyamid sulphate gives, together with sulphuric acid from its hydrolysis into that salt.

Although the presence of much sulphuric acid prevents the action of copper sulphate on a hydroxyamid sulphate, the acid in moderate excess has but little effect.

Sodium hydroximidosulphate, if kept with care, decomposes only very slowly in a way which has hitherto been obscure (this Journ, 7, 45), but if considered in connection with the action of copper sulphate it may be regarded as essentially the same as that brought about by heating it in solution with that salt. For, the decomposed hydroximidosulphate contains, besides acid sulphate and hydroxyamid sulphate, both a little gas (nitrous oxide or nitrogen) shut up in its pores which escapes when the mass is dissolved in water, and also a little amid sulphate, which can be separated from the other salts by precipitation with mercuric nitrate (this Journ., 9, 242, also 229, 230).

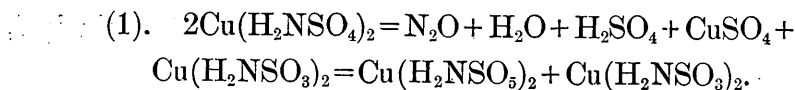
The decomposition of hydroxyamid sulphates by copper sulphate is also in evident relation with the gradual decomposition of impure hydroxylamine hydrochloride, particularly when ferric chloride is among the impurities, water, nitrous oxide and

ammonia (in place of amidosulphuric acid) being the principal, if not the sole, products.

There is a very marked difference in the proportions of the products of decomposition between a hydroxyamidosulphate and a hydroximidosulphate, but this seems to be owing merely to the fact that the temperature of the decomposition is different, for according as hydroxyamidosulphate is heated slowly or rapidly the proportions of the products of decomposition deviate from or approach those which obtain when a hydroximidosulphate is decomposed, this only taking place at a temperature above 100°.

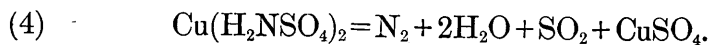
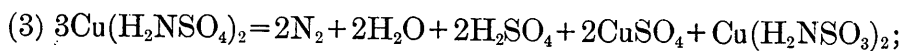
As little as one-tenth of an equivalent of copper sulphate has been found to suffice for the complete decomposition of an alkali hydroxyamidosulphate, the copper sulphate not being consumed in the change it effects; this allows of the decomposition being to a great extent carried out at the boiling temperature, when again the result approaches that observed where hydroximidosulphate is the salt decomposed. Even much less than the amount above named will effect an almost complete decomposition but that the quantity of the catalytic agent cannot be very greatly reduced seems to be due in part to the simple hydrolysis of some of the hydroxyamidosulphuric acid set free by the copper sulphate during the prolonged heating here necessary.

Since the cupric salt suffers no reduction, it will be seen that one part of the hydroxyamidosulphate becomes reduced to amidosulphate by yielding oxygen for the oxidation of the other part to water, sulphate and nitrous oxide. The following equation shows that the hydroxyamidosulphate may change by cumulative resolution, half into a reduced product (amidosulphate), and half into oxidised products together equivalent to the non-existent dihydroxyamidosulphate:



Such an equation expresses much of what happens in the decomposition of a hydroxyamidodisulphate at a lower temperature, but even in this case, and much more in the decomposition of a hydroximidosulphate by copper sulphate, where the temperature is higher, a third molecule decomposes in another way. The result is that the free sulphuric acid shown in the above equation gets neutralised, and the third molecule of hydroxyamidodisulphuric acid yields neither sulphate nor amidodisulphate, all its sulphur being eliminated as dioxide, its nitrogen as nitrous oxide, and its hydrogen as water thus reverting to sulphurous and hyponitrous acids; just as it does under the influence of an alkali (p 497) adding to equation (1) that of  $\text{Cu}(\text{H}_2\text{NSO}_4)_2 = \text{N}_2\text{O} + 2\text{H}_2\text{O} + 2\text{SO}_2 + \text{CuO}$ , we get (2),  $3\text{Cu}(\text{H}_2\text{NSO}_4)_2 = 2\text{N}_2\text{O} + 4\text{H}_2\text{O} + 2\text{SO}_2 + 2\text{CuSO}_4 + \text{Cu}(\text{H}_2\text{NSO}_3)_2$ , with products free from acid.

It is possible to express the decomposition of hydroxyamidodisulphate differently, by making nitrogen one of the products in place of nitrous oxide, thus :



In (3) sulphur dioxide is not a product whilst in (4) it is. Whether, however, nitrogen is formed, even in small quantity, is doubtful. Along with the nitrous oxide soluble in alcohol, we found a little insoluble gas—about 4 per cent. by volume of the whole gas,—but we are not prepared to assert that this was not due to air in spite of the precautions we took to expel all air from the apparatus by carbon dioxide before the decomposition. It will be seen from the equations that, with nitrous oxide as a product of the decomposition, the sulphur appearing as sulphate

equals that as amidosulphate, whereas, with nitrogen as a product, the sulphur as sulphate is double that as amidosulphate in (3), whilst in (4) there is none as amidosulphate. Now, in the observed decompositions of hydroxyamidosulphate the sulphur as sulphate has been found equal, on the average, to that as amidosulphate, a result showing that within the limits of accuracy of the somewhat complex analytical work, no nitrogen is generated.

Although, when using copper sulphate or copper hydroxyamidosulphate, no change to cuprous salt is observable, the reduction of cupric chloride to cuprous chloride points clearly to the activity of the copper salt as a 'carrier of oxygen' from one molecule of the hydroxyamidosulphate to another.

#### *Results and Method of the Quantitative Experiments.*

The results of the experiments are given, not in the order in which they were obtained but in that of the growth in quantity of the sulphur dioxide produced.

In an experiment in which copper hydroxyamidosulphate was heated very slowly, so as to carry out the decomposition at as low a temperature as possible (boiling the solution only at the end in order to expel the last portions of sulphur dioxide), results were obtained which agree sufficiently well with those calculated on the assumption that 3.7 per cent. of the salt gives all its sulphur as dioxide, its hydrogen as water, and its nitrogen as nitrous oxide, whilst the rest of the salt decomposes according to equation (1):

Sulphur as dioxide; as trioxide and amidosulphate.

|               |      |
|---------------|------|
| Found.....3.5 | 96.2 |
| Calc. ....3.7 | 96.3 |

An experiment with sodium hydroxyamidosulphate and its equivalent of copper sulphate, gave results indicating that about 5.3 per cent yielded all its sulphur as dioxide, the rest of the salt giving sulphur trioxide (sulphuric acid) and amidosulphate (equation 1):

Sulphur as dioxide; as trioxide; as amidosulphate; as acidity.

|               |      |      |      |
|---------------|------|------|------|
| Found.....5.5 | 46.0 | 48.0 | 21.6 |
| Calc. ....5.3 | 47.4 | 47.4 | 21.0 |

Copper hydroxyamidosulphate in four experiments gave results agreeing nearly with the assumption that 13.2 per cent. of the salt gave sulphur dioxide, the rest decomposing according to equation (1):

Sulphur as dioxide; as trioxide; as amidosulphate; as acidity.

|                |      |      |      |
|----------------|------|------|------|
| Found.....13.0 | 43.0 | 43.6 | 11.1 |
| „ .....13.0    | 43.3 | 43.2 |      |
| „ .....13.1    |      | 86.6 |      |
| „ .....13.3    |      | 86.5 |      |
| Calc. ....13.2 | 43.4 | 43.4 | 15.1 |

In another experiment copper hydroxyamidosulphate gave the following results, as against calculation for 15.4 per cent. to decompose so as to yield its sulphur as dioxide:

Sulphur as dioxide; as trioxide; as amidosulphate; as acidity.

|                |      |      |      |
|----------------|------|------|------|
| Found.....15.1 | 42.9 | 41.6 | 10.7 |
| Calc. ....15.4 | 42.3 | 42.3 | 13.5 |

In one more trial, copper hydroxyamidosulphate decomposed nearly as if 16.6 per cent. of it yielded all of its sulphur as dioxide:

| Sulphur as dioxide ; as trioxide and amidosulphate ; as acidity. |      |      |      |
|--|------|------|------|
| Found.....   | 16.3 | 83.3 | 9.3  |
| Calc. ....   | 16.6 | 83.4 | 12.5 |

A solution of potassium hydroximidosulphate heated with very little more than its equivalent of copper sulphate, gave results showing that 25 per cent. of the salt yielded all the sulphur of the hydroxyamidosulphate coming from it by hydrolysis, as sulphur dioxide :

| Sulphur as dioxide ; as trioxide ; as amidosulphate ; as acidity. |      |      |      |
|---|------|------|------|
| Found.....  | 25.2 | 37.3 | 37.0 |
| Calc. ....  | 25.0 | 37.5 | 6.25 |

A solution containing sodium hydroximidosulphate and copper sulphate decomposed in two experimentis, in such a way that about 28 per cent. of the hydroxyamidosulphate sulphur became dioxide :

| Sulphur as dioxide ; as trioxide ; as amidosulphate ; as acidity |      |      |      |
|--|------|------|------|
| Found.....   | 27.6 | 36.9 | 35.0 |
| „ .....  | 28.0 | 36.2 | 35.8 |
| Calc. ....   | 28.0 | 36.0 | 36.0 |

The numbers in the above table stand for parts per hundred of the sulphur of the total hydroxyamidosulphate decomposed, and not of the sulphur of the hydroximidosulphate even when such a salt has been that experimented with. The 'acidity' sulphur is calculated as if the acidity is due to sulphuric acid, not amidosulphuric acid. The 'trioxide' sulphur is that of the sulphuric acid and copper sulphate yielded by the decomposition. The differences between the calculated quantities and those found must be largely attributed to imperfect estimation ; they cannot be due to error in theory, because no other explanation of the change than that adopted is possible. In a copper-salt

solution mixed with much barium sulphate, it was not easy to titrate acid with lacmoid paper as indicator. The separation of sulphate and amidosulphate is not a simple process, especially when much sulphate is present derived from sources other than the reaction to be dealt with.

The salt employed in the experiments was either copper hydroxyamidosulphate, or sodium hydroxyamidosulphate with copper sulphate, or one of the alkali hydroximidosulphates with copper sulphate.

1. A solution of the copper salt, containing only a very little copper sulphate was prepared from normal barium hydroxyamidosulphate and copper sulphate, the barium salt (this Journ., 3, 213, 216) had to be prepared as wanted, because of the instability of the hydroxyamidosulphates. The strength of the solution was determined by a barium estimation (hydrolysis in sealed tube and weighing of the barium sulphate). Copper sulphate in slight excess and carefully weighed was added to the weighed solution of the barium salt, and the copper hydroxyamidosulphate at once used without filtering off the barium sulphate.

2. Sodium hydroxyamidosulphate solution was prepared just before use by hydrolysing a centigram-molecule of the hydroximidosulphate by adding to its solution a minute and known quantity of sulphuric acid (this Journ., II, 3) and to it was added after neutralisation with sodium hydroxide half a centigram-molecule of copper sulphate.

3. Potassium or sodium hydroximidosulphate in the quantity of a centigram-molecule was dissolved and directly heated with a half molecule in centigrams of copper sulphate.

The solution (either 1, 2, or 3) being in a small flask



connected with a tube receiver holding bromine water kept cold, was heated, sometimes quickly, sometimes slowly, either by a spirit lamp or in a bath of sulphuric acid, the solution being finally boiled for some minutes, so as to drive all sulphur dioxide into the bromine water. Before heating, air was removed from the apparatus by a current of carbon dioxide. In one experiment the apparatus was made entirely of glass. The oxidised sulphur, dioxide was weighed as barium sulphate.

The boiled-out copper solution was titrated with N/10 soda (free from sulphate), using lacmoid paper as indicator. The imperfection of this operation was proved beyond doubt on calculating out the nature of the changes which had occurred, but it was serviceable and the best available under the circumstances.

To the boiling hot solution and precipitate of barium sulphate, barium chloride was added in excess, the total precipitate collected, well washed, and transferred to a pressure tube in which it was heated with hydrochloric acid for three hours at 150°. The barium sulphate was again washed on the filter, then ignited and weighed. The second filtrate and washings contained sulphuric acid, the quantity of which was estimated as barium salt. To make this part of the analytical process intelligible, it must be explained that barium amidosulphate, although itself quite soluble in water, is partially precipitated along with barium sulphate, even in presence of hydrochloric acid (this Journ., 9, 283). At 150°, the precipitated amidosulphate hydrolyses, yielding barium sulphate and ammonium sulphate in molecular proportions.

The copper filtrate from the crude barium precipitate was evaporated to a small volume, heated with hydrochloric acid for some hours at 150°, and mixed with barium chloride. The precipitated barium sulphate represented the principal quantity

of amidosulphate sulphur, the full amount of which was ascertained by adding to it twice the quantity of that in the ammonium sulphate extracted by hydrolysis from the crude barium precipitate. The sulphur from the hydroxyamidosulphate, obtained as sulphate, was found by subtracting from the total the sum of the quantities of sulphur present as (a) copper sulphate taken; (b) barium sulphate from the hydrolysed barium amidosulphate which had been precipitated along with the barium sulphate by barium chloride; (c) sulphuric acid added for hydrolysing the hydroximidosulphate, when that salt had been started with; and (d) in the same case, sulphuric acid resulting from the hydrolysis of the hydroximidosulphate to hydroxyamidosulphate.

Hardly any attempt was made to estimate the amount of nitrous oxide liberated. To do so would only have been useful as a check on the accuracy of the determinations of the amidosulphate, and for that purpose the two substances would have had to be estimated in the products of one experiment. This, it did not seem possible to do. An experiment in which hydroxyamidosulphate was decomposed gave 55.3 per cent. of the nitrogen as nitrous oxide, as against 56.6 calculated from the equation most in accordance with amidosulphate and other sulphur determinations. The method of measuring the nitrous oxide and nitrogen was to expel air from the apparatus by a current of carbon dioxide continued for some time, and then heat the copper salt and boil out the gases which were collected over mercury and potassium hydroxide and measured. The alkali was then replaced by absolute alcohol to dissolve the nitrous oxide, and the residual gas measured.

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