Chemistry. — The oxidation products of thio-urea. The dioxide as derivative of sulphonylic acid ($H_2SO_2$). By J. Böseken.

(Communicated at the meeting of May 23, 1936).

Concerning the oxidation of thio-urea a great deal is known, yet the direct oxidation products, either containing oxygen or not, were thus far hardly studied. By an investigation of thio-urea and its derivatives as anti-yellowing material in the reproduction technique, which in the main is due to the strongly reducing properties of these important substances, I became acquainted with the oxidation products and the manner in which they were formed.

Already long ago ¹) it was found that with potassium permanganate or with hydrogen peroxide in acid solution thio-urea behaves as the isothio compound, consequently as a mercaptan and that then in accordance with this a dithio compound is formed. Since this compound possesses basic properties, it forms a salt with the added acid which is fairly proof against further oxidation.

With halogens and even with iodine these salts are formed ²) directly and consequently the reaction seems to obtain the character of an addition:

$$2H_2NCNHSH + I_2 \rightarrow [H_2NCNHS]_2 [HI]_2$$

The capacity of thio-urea to change into the isothio compound stamps this substance as a very powerful reductive; this appears, besides from the above-mentioned properties, also from its behaviour towards cupri-salts, such as cuprichloride, which in the cold is reduced to cuprochloride.

$$2SC(NH)_2 + 2CuCl_2 \rightarrow Cu_2Cl_2 + [H_2NCNHS]_2 [HCl]_2$$

These salts of dithioformamidine may be most simply prepared by dissolving thio-urea with a little more than the calculated amount of acid in as little as possible of 50% alcohol and under ice-cooling oxidizing it with the calculated amount ($\frac{1}{2}$ mol) of $H_2O_2$. In this way I prepared the sulphate, oxalate, hydrochloric salt, and tartrate. The sulphate and oxalate have no water of crystallization, the hydrochloric salt five molecules (titrimetrically determined), the tartrate is unstable.

The free basis, dithioformamidine, however, is very unstable, since it

¹) STORCH. M. 11, 452 (1890).
²) CLAUS. Am. 179, 135 (1875).
decomposes into sulphocyanic acid, sulphur and cyanamide. For this reason it did not seem right to start from this compound for the study of the further course of oxidation.

It was found by E. du Barry Bartlett 1) that thio-urea in neutral solution changes with hydrogen peroxide into the dioxide, the composition of which was established by analysis and determination of the molecular weight. He supposes this substance to be formamidine sulphinic acid, HNCNH₂SO₂H, because of a weak acid reaction and the absence of reducing properties. In reality this substance is neutral towards litmus and Congo red and in ammoniacal solution it is one of the most powerful reductives we know; in acid solution also it has a strongly reducing action. This may be apparent from the following phenomena:

On heating an ammoniacal solution of Cd(OH)₂ quickly with an excess of the dioxide, metallic cadmium is precipitated, partly in the form of grey powder, partly as a mirror. As far as I know, this is the only substance capable of this; with Na₂S₂O₄ there is a precipitate of CdS, but not of metal (see below). It stands to reason that all other, less electro-positive, metals are separated by this agent as such, often, as is the case with cadmium, mixed with the sulphide. Lead, for example, is precipitated in the form of a spongy metal, tin from a stannous solution as a mirror; in the same way copper, nickel and cobalt from their ammoniacal solutions, the yet more electro-negative metals bismuth, silver, platinum and palladium as black powders; antimony is also obtained from alkaline solutions as a black powder, arsenic from an arsenite solution as a reddish brown precipitate.

If the reagent is added to an ammoniacal chromate solution, the colour becomes first beautifully red-violet; on heating this turns into blue-mauve; sometimes a greyish blue precipitate is formed of chromoxide hydrate. An alkaline chromate solution becomes slowly red-violet, then blue-violet, finally green. An alkaline KMnO₄ solution is immediately discoloured under formation of manganese peroxide; this precipitate is then completely discoloured [Mn(OH)₂].

Ferrihydroxide turns black, since by the side of Fe(OH)₂ ferrous sulphide is precipitated; in any case no metallic iron is formed, not even by boiling.

Attention may be drawn to the fact that the metals Cd, Pb and Ni are only precipitated on heating the ammoniacal solutions with excess of the reagent; cobalt is formed slowly also in the cold. The behaviour towards an ammoniacal nickel solution is interesting. This blue solution turns into a bright yellow. If this is shaken with air, the blue colour returns. This may be repeated as long as there is dioxide left. Evidently the nickel is brought to a lower degree of oxidation. This solution may be used to determine the oxygen or take it away.

1) Soc. 97, 63 (1910).
The beautiful purple solution of cobalt salts in excess of ammonia first turns reddish brown, then metallic cobalt is slowly precipitated.

To the nature of these powerful reduction-reactions I shall refer later on.

In acid solution the dioxide likewise has a strongly reductive action. KMnO₄ is discoloured at once; at first no sulphuric acid is formed. In a hydrochloric solution (with BaCl₂) BaSO₄ is not immediately deposited (see below).

Ferric-chloride in the presence of HCl and BaCl₂ is slowly reduced, without BaSO₄ being precipitated at first; it is not formed until the reaction has proceeded for some time.

That the reduction sets in immediately, may be demonstrated with potassium ferricyanide: almost immediately Prussian blue is formed.

The velocity of this reaction may be traced iodometrically since the dioxide does not react on KI and very slowly on I₂.

A solution of cupricchloride is reduced at room-temperature exceedingly slowly, similarly a nitric-acid solution of silver nitrate.

With peracetic acid the dioxide is rapidly oxidized to trioxide; not a trace of sulphuric acid being formed. On addition of 1 mol. of this oxidant dissolved in pure acetic acid and evaporization at room-temperature (with an electric drier) of the solvent, this trioxide, formamidine sulphonlic acid remains in beautiful lozenge-shaped plates.

The latter compound is not attacked in the cold by KMnO₄ in acid solution; the oxidations of the dioxide with KMnO₄, chromic acid and ferric-salts, at first no sulphuric acid being formed, consequently take place via the trioxide.

The oxidation of thio-urea in neutral solution with H₂O₂ and subsequently with peracetic acid may, therefore, be represented by:

\[
\begin{align*}
\text{C(NH}_2\text{)}_2\text{S} + 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{C(NH}_2\text{)}_2\text{SO}_2. \\
\text{C(NH}_2\text{)}_2\text{SO}_2 + \text{CH}_3\text{CO}_3\text{H} \rightarrow \text{CH}_3\text{COOH} + \text{C(NH}_2\text{)}_2\text{SO}_3.
\end{align*}
\]

This trioxide shows a very simple splitting-reaction with baryta. On gently heating the solution with two equivalents of this basis, BaSO₃ is precipitated (the precipitate is soluble in acids under formation of SO₂ and it uses an atom of oxygen with KMnO₄). After filtrating from this salt, an ammoniacal silver solution yields the characteristic yellow precipitate of silver cyanamide. The splitting-reaction is therefore:

\[
\text{C(NH}_2\text{)}_2\text{SO}_3 + \text{Ba(OH)}_2 \rightarrow \text{BaSO}_3 + 2 \text{H}_2\text{O} + \text{NCNH}_2.
\]

On heating the dioxide with dilute caustic soda thiosulphate is formed (on acidification separation of S and formation of SO₂) and a little sulphide (positive reaction on S²⁻).

If to a dilute solution of the dioxide is first added H₂O₂ and then barium hydroxide; two equivalents of this basis appear to be used; on
subsequent acidification and titration of the amount of $\text{H}_2\text{O}_2$ still present with KMnO$_4$, two molecules appear to be used.

Repetition of this reaction with the calculated amount of $\text{H}_2\text{O}_2$ and baryta, filtrating off the $\text{BaSO}_4$ and evaporation of the solution leaves the calculated amount of urea.

The decomposition of the dioxide consequently takes place as follows:

$$\text{C(}\text{NH}_2\text{)}_2\text{SO}_2 + 2 \text{H}_2\text{O}_2 + \text{Ba(OH)}_2 \rightarrow \text{BaSO}_4 + \text{C(}\text{NH}_2\text{)}_2\text{O} + 3 \text{H}_2\text{O}.$$  

This may be interpreted in this manner: In the same way as the tri-oxide with baryta is decomposed into sulphite and cyanamide, from the dioxide is formed the hypothetical barium sulphoxylate, $\text{BaSO}_2$, which is immediately oxidized by the $\text{H}_2\text{O}_2$ to $\text{BaSO}_4$. Instead of cyanamide here the hydrate, urea, is formed.

The formation of thiosulphate by warming with dilute caustic soda is in perfect agreement with this supposition, since the unstable sodium sulphoxylate will probably be converted as follows:

$$2 \text{Na}_2\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2 \text{NaOH}.$$  

The temporary formation of ammonium sulphoxylate explains the extremely powerful reducing properties of an ammoniacal solution, particularly with excess of the dioxide. In dilute solution and especially after some time no cadmium, for example, can be deposited as a metal, but only $\text{CdS}$ is obtained; the sulphoxylate has consequently changed into other substances lacking this capacity.

It is highly remarkable that recently $^1$) the diethyl ester of sulphoxylic acid has been prepared. By spontaneous oxidation to the air this is changed into diethyl sulphite; on saponification with dilute caustic soda it yields thiosulphate by the side of a little sulphide and sulphite. It is to be expected that this ester in the presence of alkali will have the same strongly reducing properties as formamidine-sulphinic acid.

In connection with these observations we studied the behaviour of thio-urea towards peracetic acid.

On addition of half a molecule of peracetic acid in acetic acid solution to thio-urea in the presence of sodium nitrate, the hardly soluble dithio-formamidine nitrate is practically quantitatively precipitated.

$$\text{CH}_3\text{COOH} + 2 \text{SC(}\text{NH}_2\text{)}_2 + \text{CH}_3\text{CO}_2\text{H} + 2 \text{NaNO}_3 \rightarrow [\text{HNCNH}_2\text{S}]_2[\text{HNO}_3]_2 + 2 \text{CH}_3\text{COONa} + \text{H}_2\text{O}.$$  

If to one mol. of thio-urea two mol. of peracetic acid are added in acetic acid solution and the solvent is quickly evaporated with an electric drier, the dioxide crystallizes, which by means of the nickel, chromic acid and cadmium reactions can be easily detected.

$^1$) A. MEUWSEN and H. GEBHARDT. Berichte 69, 937 (1936).
With three molecules of peracetic acid formamidine-sulphonic acid may be prepared directly from thio-urea.

Dithioformamidine sulphate is only very slowly attacked by peracetic acid. If first this oxidant is added and then the amount of baryta which is calculated for the $\text{SO}_4^2-$ present, the oxidation takes place very rapidly and, according to the amount of peracetic acid, either the dioxide or the trioxide is obtained.

Thus the behaviour of thio-urea towards oxidants is explained and also the most important properties of the oxidation products have been found.

On decomposition with caustic alkalies the dioxide probably yields the salts of sulphoxylic acid, the hydrate of the hypothetical $\text{sulphur monoxide}$. The experimental details of this investigation will be published elsewhere.

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**Psychology. — Physical Resemblance in connection with mental similarity. I. By E. D. Wiersma.**

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The connection between physical and mental functions has been frequently pointed out. In order to determine this connection more accurately I composed the somato-psychological inquiry, in which Dutch physicians were asked to give information concerning bodily build, physiological phenomena and psychological qualities of a large number of persons. This investigation has been elaborately discussed elsewhere. Moreover, I took the length and breadth measurements of numerous patients suffering from melancholia and dementia praecox, in order to ascertain which psychical qualities are mainly found in case of a large lateral growth and which with a greater length. The results of this investigation have been published in a monograph: Bodily Build, Physiological and Psychological Functions ¹).

The **thick-set or eurysomics**, who are characterized by a greater breadth with regard to the length of the body and all its parts, psychologically make a quiet, level-headed and thoughtful impression. They are more active, more strongly secondary and less emotional than the average. They show similarity to the phlegmatic type of temperament. Physiologically, with respect to the automatic movements, they have to be classified with the quick, quiet, sure tempo-type. The movements of the body, walking,