L.—*The Action of Water on Cupric Thiocyanate.*

By James Charles Philip and Arthur Bramley.

Some time ago (T., 1913, **103**, 795) the authors published the results of a research on the progressive change which solutions of ferric thiocyanate undergo. Even at the ordinary temperature and in an indifferent atmosphere, the ferric iron is reduced, whilst a corresponding oxidation of the thiocyanogen radicle takes place. The investigation of this reaction brought out the novel and interesting fact that the great bulk of the carbon which is thus oxidised is eliminated in the form of carbon dioxide.

It appeared probable that the change which cupric thiocyanate undergoes in contact with water might be of the same character, and that carbon dioxide might be produced in this case also. A simple experiment designed to test this point gave a positive result, and it was therefore decided to examine in some detail the action of water on cupric thiocyanate.

It has been long known that the black precipitate obtained on mixing solutions of cupric salts with alkali thiocyanates is slowly acted on by water, the copper being finally converted into cuprous thiocyanate. The reaction attracted the attention of several investigators about eighty years ago, and attempts were made to identify the products of change other than the cuprous salt. Claus (*J. pr. Chem.*, 1838, **15**, 401) and Meitzendorff particularly (*Ann. Phys. Chem.*, 1842, [ii], **56**, 88) showed that amongst these other products were thiocyanic, hydrocyanic, and sulphuric acids, but the efforts of the latter author to find a satisfactory quantitative basis for the reaction were unsuccessful. So far as can be discovered, there is no record in the literature of any investigation carrying the problem beyond the point at which it was left by Meitzendorff.

EXPERIMENTAL.

The vessel in which the reaction took place was a large bottle or round-bottomed flask, provided with a trebly-bored rubber stopper. Through two of the holes there passed glass tubes, one of which reached almost to the bottom of the vessel, and admitted a current of air or nitrogen, freed from carbon dioxide, the other providing for the passage of the escaping gases to the train of absorption flasks. The third hole carried the stem of a dropping funnel, from which a measured quantity of the cupric salt (chloride or acetate) could be delivered into the excess of alkali thiocyanate solution previously placed in the flask. The precipitate formed in the reaction vessel was kept in intimate contact with water by shaking the vessel until the completion of the change—a period of ten to twenty days, according to the conditions.

With the object of making a quantitative study of the reaction, and on the basis of the experience gained in the examination of ferric thiocyanate solutions, preparations were first made to estimate hydrogen cyanide, carbon dioxide, sulphuric acid, and ammonia. The first two of these substances were drawn out of the reaction mixture by means of an aspirator and absorbed in successive trains of flasks containing silver nitrate and baryta solutions respectively. The reaction vessel, containing the alkali thiocyanate solution, and the absorption flasks, containing the silver nitrate and the baryta, were filled from the beginning with air or nitrogen freed from carbon dioxide.

The preliminary experiments showed that it was desirable to have more than one flask containing silver nitrate solution, for, although the absorption of hydrogen cyanide was complete in the first flask, there was formed, even in a second flask, a very small quantity of a black precipitate, arising apparently from the hydrolysis of some compound by the silver nitrate. Experience showed that a train of four silver nitrate flasks was adequate, the formation of the black precipitate never being observed in any flask beyond the third. When too few silver nitrate flasks were employed, sulphide was found in the first succeeding flask containing baryta solution. It is suggested that the black precipitate is silver sulphide, arising from the hydrolysis of a trace of carbonyl sulphide produced in the reaction. The quantity of this black precipitate was extremely small and it was not estimated.

The carbon dioxide was estimated by absorption in a train of flasks charged with known quantities of standard baryta solution, the excess of baryta being found by subsequent titration with standard oxalic acid solution. A complication arose when the cupric salt employed for the production of the cupric thiocyanate was the acetate, for in this case cyanogen is formed and passes off through the silver nitrate solution into the baryta solution. Here it is hydrolysed, giving rise to cyanide, carbon dioxide, and ammonia, and its amount was ascertained by estimating the cyanide in the baryta flasks, subsequent to the titration with oxalic acid. The result obtained in this way was checked by a determination of the ammonia in the united contents of the baryta flasks. From the cyanide found, the quantity of carbon dioxide produced by the hydrolysis of the cyanogen was calculated, and deducted from the total quantity of carbon dioxide absorbed in the baryta.

The sulphuric acid and the ammonia arising from the action of water on cupric thiocyanate would naturally remain in the reaction mixture, which becomes increasingly acid as the change proceeds. In order, therefore, to estimate these two substances, aliquot portions of the filtrate from the cuprous thiocyanate finally obtained were employed. The estimation of the sulphuric acid presented no difficulty. One characteristic, however, of the ammonia determination, observed in the earlier experiments, indicated that, in addition to thiocyanic acid and ammonium salts, the reaction mixture contained some other nitrogenous compound, for the expulsion of the ammonia never came to a definite end, but continued for hours. There was evidently present some nitrogenous compound slowly hydrolysed by boiling alkali hydroxide, and carbamide was accordingly suspected. The presence of this compound was definitely established by the xanthhydrol test (Fosse, *Compt. rend.*, 1913, **157**, 948), and it was finally estimated by the soja-bean method, after the ammonia had been removed by treatment with alkali hydroxide at 40—50° and aspiration (compare Plimmer and Skelton, *Biochem. J.*, 1914, **8**, 70). The hydrobromite method of estimating the carbamide, after the removal of the ammonia, was also employed, but was not found so satisfactory.*

So far, then, as the merely qualitative side of the investigation is concerned, it is clear that the action of water on cupric thiocyanate, formed by mixing cupric chloride with excess of potassium thiocyanate, leads to the production of the following substances, in addition to cuprous thiocyanate: Carbon dioxide, hydrogen cyanide, ammonia, sulphuric acid, and carbamide. Further, as found by Meitzendorff, considerable quantities of thiocyanic acid are formed during the reaction. When, on the other hand, the cupric thiocyanate is obtained by mixing cupric acetate with excess

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* The presence of carbamide in ferric thiocyanate solutions which have been allowed to remain for some time was also proved with the aid of the soja-bean method. This observation probably accounts for the previously unexplained deficiency of nitrogen in the recognised products of the action of water on ferric thiocyanate (T., 1913, **103**, 796).

of potassium thiocyanate, the products of the action of water include cyanogen as well as the substances just specified.

That the foregoing list covers all the products of the action of water on cupric thiocyanate, with the possible exception of any, such as carbonyl sulphide, which occur in mere traces, appears certain from a consideration of the quantitative results of the investigation. It is clear that if no essential product has escaped detection, then, in any particular experiment, the total quantities of carbon, nitrogen, and sulphur found in one or other of the substances estimated should be in the atomic ratio 1 : 1 : 1, since they arise from the oxidation of the thiocyanogen radicle. It is further plain that, in applying this test, the quantities of cuprous thiocyanate and thiocyanic acid need not be considered, since these compounds contain the thiocyanogen radicle intact.

The data for the four final experiments only are recorded below, no account being taken of the many preliminary and incomplete trials which were made before carbamide was definitely detected and estimated in the reaction products.

EXPERIMENT I.

2000 *c.c. potassium thiocyanate solution containing* 100 *grams* KCNS.

250 *c.c. cupric chloride solution containing* 9·25 *grams* Cu.

	Found.	C.	N.	S.
CO_2	0·412	0·1124	—	—
NH_3	0·1376	—	0·1133	—
HCN..............	0·242	0·1076	0·1255	—
H_2SO_4	1·860	—	—	0·6073
$CO(NH_2)_2$	0·0795	0·0159	0·0371	—
		0·2359	0·2759	0·6073
Atomic ratio		1	1	0·96

EXPERIMENT II.

100 *c.c. potassium thiocyanate solution containing* 20 *grams* KCNS.

125 *c.c. cupric chloride solution containing* 4·12 *grams* Cu.

775 *c.c. water.*

	Found.	C.	N.	S.
CO_2	0·221	0·0603	—	—
NH_3	0·0680	—	0·0560	—
HCN	0·0798	0·0355	0·0414	—
H_2SO_4	0·900	—	—	0·294
$CO(NH_2)_2$	0·0619	0·0124	0·0289	—
		0·1082	0·1263	0 294
Atomic ratio		1	1	1·02

EXPERIMENT III.

1500 *c.c. potassium thiocyanate solution containing* 80 *grams* KCNS.

500 *c.c. cupric acetate solution containing* 10·2 *grams* Cu.

	Found.	C.	N.	S.
CO_2	0·646	0·1762	—	—
NH_3	0·239	—	0·1968	—
HCN	0·0498	0·0221	0·0258	—
H_2SO_4	2·228	—	—	0·7275
C_2N_2	0·1144	0·0528	0·0616	—
$CO(NH_2)_2$	0·0334	0·0067	0·0156	—
		0·2578	0·2998	0·7275
Atomic ratio		1	0·997	1·06

EXPERIMENT IV.

100 *c.c. potassium thiocyanate solution containing* 20 *grams* KCNS.

200 *c.c. cupric acetate solution containing* 4·08 *grams* Cu.

700 *c.c. water.*

	Found.	C.	N.	S.
CO_2	0·273	0·0745	—	—
NH_3	0·097	—	0·0800	—
HCN..............	0·0207	0·0092	0·0107	—
H_2SO_4	0·947	—	—	0·3092
C_2N_2	0·059	0·0272	0·0317	—
$CO(NH_2)_2$.........	0·0319	0·0064	0·0149	—
		0·1173	0·1373	0·3092
Atomic ratio		1	1·004	0·988

The figures recorded in the foregoing tables show that the action of water on cupric thiocyanate is restricted to the production of the substances specified, but, in order to account for the appearance even of those, it is necessary to assume the occurrence of fairly complicated reactions. Without attempting to indicate the mechanism of these reactions, one may suggest the following equations as representing the different ways in which water acts on cupric thiocyanate, equations based on the assumption that in each reaction the products account for an equal number of carbon, nitrogen, and sulphur atoms:

(*a*) $8Cu(CNS)_2 + 6H_2O = 8CuCNS + 7HCNS + CO_2 + \underbrace{NH_3 + H_2SO_4}$

(*b*) $6Cu(CNS)_2 + 4H_2O = 6CuCNS + 5HCNS + HCN + H_2SO_4$

(*c*) $14Cu(CNS)_2 + 8H_2O = 14CuCNS + 12HCNS + C_2N_2 + 2H_2SO_4$

(*d*) $16Cu(CNS)_2 + 11H_2O = 16CuCNS + 14HCNS + CO_2 + CO(NH_2)_2 + 2H_2SO_4$.

It is possible to test the appropriateness of these equations by comparing the final acidity of the reaction mixture, which was determined in each of the four experiments detailed above, with the acidity calculated on the basis of the equations. In experiment I, for example, the filtrate from the cuprous thiocyanate was made up to three litres, and the solution was then found to be 0·0508N in regard to acid. On the other hand, the number of equivalents of acid which should be formed according to equation (*a*), the calculation being based on the quantity of ammonia found, is $\frac{0{\cdot}1376\times 8}{17}=0{\cdot}0648$. Similarly, the number of equivalents of acid formed according to equation (*b*) and the amount of hydrogen cyanide found should be $\frac{0{\cdot}242\times 7}{27}=0{\cdot}0627$. Finally, the number of equivalents of acid formed according to equation (*d*) and the quantity of carbamide found should be $\frac{0{\cdot}0795\times 18}{60}=0{\cdot}0238$. In all, the number of equivalents of acid which, on the basis of the equations proposed, should be formed in experiment I, is 0·1513. If the solution containing this quantity of acid were made up to 3 litres, as was actually done, it would then be 0·0504N in regard to acid, a figure which agrees closely with the experimental value quoted above.

The extent of the agreement between the observed and calculated figures for the final acidity in the other experiments is seen from the following table:

	Acidity calculated.	Acidity found.
Experiment II.	0·0713N	0·0709N
,, III.	0·0855N	0·0895N
,, IV.	0·0789N	0·0790N

It thus appears that the equations proposed are in fact capable of representing satisfactorily the relation between the experimentally determined quantities of the various reaction products.

Summary.

(1) When cupric chloride solution is mixed with excess of potassium thiocyanate solution, the precipitated cupric thiocyanate is slowly acted on by the water present. Reduction to cuprous thiocyanate is ultimately complete, and the other products formed concurrently are carbon dioxide, ammonia, carbamide, hydrogen cyanide, thiocyanic and sulphuric acids.

(2) When the cupric thiocyanate is obtained by acting on cupric

acetate with excess of potassium thiocyanate, a further product of the reaction, in addition to those already specified, is cyanogen.

(3) A quantitative basis for the action of water on cupric thiocyanate is supplied by the equations proposed on page 601.

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