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Abstract

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ON THE FORMATION OF SULFANE-MONOSULFONIC ACIDS DURING THE DECOMPOSITION OF THIOSULFATE

The well-known decomposition of thiosulfates upon acidification, usually expressed by the simple equation

$$H_2S_2O_3 \rightarrow S + SO_2 + H_2O, \tag{1}$$

is undoubtedly a complex process, since the sulfur that separates consists mainly of S_8 molecules; moreover, this reaction is accompanied by the formation of polythionic acids and a small amount of hydrogen sulfide ([1,2]). A careful experimental study of the kinetics of thiosulfate decomposition in dilute solutions acidified with hydrochloric acid led La Mer et al. ([3]) to the following expressions for the rate of sulfur separation (V) and for the formation of SO_2 (V')

$$V = K\,[Na_2S_2O_3]^{3/2}\,[HCl]^{1/2}, \tag{2}$$

respectively

$$V' = K'\,[Na_2S_2O_3]^{2}\,[HCl]^{1}. \tag{3}$$

An explanation of these kinetic equations was recently achieved by Davis ([4]) on the basis of the reaction mechanism he proposed, which consists of the following series of consecutive reactions:

$$S_2O_3^{2-} + H^+ \rightleftarrows HS_2O_3^-, \tag{4}$$

$$HS_2O_3^- + S_2O_3^{2-} \rightarrow HS_3O_3^- + SO_3^{2-}, \tag{5}$$

$$HS_3O_3^- + S_2O_3^{2-} \rightarrow HS_4O_3^- + SO_3^{2-}, \tag{6}$$

$$HS_4O_3^- + S_2O_3^{2-} \rightarrow HS_5O_3^- + SO_3^{2-}, \tag{7}$$

$$HS_5O_3^- + S_2O_3^{2-} \rightarrow HS_6O_3^- + SO_3^{2-}, \tag{8}$$

$$HS_6O_3^- + S_2O_3^{2-} \rightarrow HS_7O_3^- + SO_3^{2-}, \tag{9}$$

$$HS_7O_3^- + S_2O_3^{2-} \rightarrow HS_8O_3^- + SO_3^{2-}, \tag{10}$$

$$HS_8O_3^- + S_2O_3^{2-} \rightarrow HS_9O_3^- + SO_3^{2-}, \tag{11}$$

$$HS_9O_3^- \rightarrow S_8 + HSO_3^-. \tag{12}$$

The intermediate compounds appearing here are ions of sulfane-monosulfonic acids $H_2S_{xO}3$, the initial member of whose series is thiosulfuric acid (5). Starting from the scheme given above, Davis derives the kinetic equations (2) and (3), obtained experimentally by La Mer. On the basis of the same scheme, the formation of polythionic acids during thiosulfate decomposition is also very simply explained (4), for example by condensation of sulfane-monosulfonic acids with elimination of hydrogen sulfide:

$$HO_3S \cdot S \cdot SH + HS \cdot S \cdot SO_3H \rightarrow HO_3S \cdot S \cdot S \cdot S \cdot SO_3H + H_2S. \tag{13}$$

The mechanism of decomposition of thiosulfuric acid proposed by Davis is thus very plausible, but for its firm substantiation it would be desirable to detect experimentally the intermediate compounds proposed here—sulfane-monosulfonic acids.

For this purpose we carried out the decomposition of thiosulfate in an acidic medium in the presence of nitron—a strong organic base giving large cations, which we had successfully used for the separation of higher polythionic acids (6). It turned out that, with careful introduction of thio-

sulfate in dilute hydrochloric acid containing a sufficient amount of nitron, sulfur is not liberated, but sulfurous acid is formed and a precipitate gradually separates, consisting of completely colorless, transparent needle-like crystals.

Table 1

	Found	Found	Found	Found	Found	Found	Found	Found	Calculated
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	
S, %	42.12	42.07	41.83	41.83	41.47	41.46	41.46	41.47	41.45
N, %	9.07	9.01	9.01	9.68	–	–	–	–	9.05
S : Nt	8.12 : 1	8.15 : 1	8.05 : 1	7.56 : 1	–	–	–	–	8.00 : 1
x^* by decomposition with ammonia	8.13	–	7.85	8.09	–	–	–	–	8.00
x by the sulfide method	7.96	8.12	7.99	7.94	7.88	–	–	–	8.00
x by the cyanide method	–	–	–	–	–	8.0	7.99	8.0	8.00

* x is the number of S atoms in the molecule.

Analysis of the precipitate for sulfur and nitrogen content (Table 1) showed a composition very close to that calculated from the formula $Nt \cdot H_2S_8O_3 = HS_7SO_3HNt^*$ for nitron heptasulfane-monosulfonate. Determination of the number of sulfur atoms in the molecule (x), carried out by three different methods (decomposition with ammonia, the sulfide method, and Kurtenacker’ s cyanide methods ([7],[5])), in all cases gave a value close to $x = 8$.

The compound obtained by us cannot be nitron polythionate $Nt_2H_2S_{16}O_6$, having the same sulfur and nitrogen content, since in the case of a polythionate the cyanide decomposition according to Kurtenacker should have given

Table 2

Stoichiometry of the formation of $Nt \cdot H_2S_8O_3$

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Taken, mmol:								
$Na_2S_2O_3$	28.6	71.6	76.4	76.4	38.2	34.6	42.7	42.7
$Nt = C_{20}H_{16}N_4$	17.6	17.6	12.8	12.2	8.0	15.0	8.7	8.8
HCl	115	345	575	575	460	275	330	330
Found:								
H_2SO_3, mmol. (c)	20.0	46.2	63.0	62.2	32.8	27.1	–	–
$S_2O_3^{2-}$, mmol.	3.7	3.6	2.4	1.6	1.6	2.2	–	–
$Nt \cdot H_2S_8O_3$, g	2.066	6.013	6.526	6.558	3.230	2.840	3.760	3.746
$Nt \cdot H_3S_8O_3$, mmol. (b)	3.34	9.72	10.55	10.60	5.22	4.59	6.08	6.06
Reacted $S_2O_3^{2-}$, mmol. (a)	24.9	68.0	74.0	74.8	36.6	32.4	–	–
$a : b : c$	7.46 : 1 : 6.0	7.00 : 1 : 4.8	7.01 : 1 : 5.97	7.06 : 1 : 5.87	7.02 : 1 : 6.28	7.06 : 1 : 5.91	–	–

one mole of thiosulfane per two moles of nitron. We, however, obtained in this way 1 mole of thiosulfate per 1 mole of nitron (acid equivalent), as should also be expected for salts of polysulfane-monosulfonic acids, which are monobasic acids (^{5}). In addition, ammoniacal decomposition in the case of a polythionate should have given considerably more than one mole of thiosulfate per acid equivalent (^{8}), whereas the amount of thiosulfate found by us here in all cases corresponded to the equation

$$H_2S_{xO}3 + OH^- \rightarrow S_2O_3^{2-} + (x-2)\,S + H^+ + H_2O. \tag{14}$$

Thus, the compound obtained by us should be regarded as nitron heptasulfane-monosulfonate, $HS_7 \cdot SO_3HNt$. Its formation proves to be direct confirmation of the mechanism, given above, of the acid decomposition of thiosulfate. The reason why we succeeded in capturing only one heptasulfane-monosulfonic acid probably lies

* Nt –nitron = $C_{20}H_{16}N_4$.

in that the latter apparently has, among the intermediate compounds of Davis' scheme, the greatest stability and the lowest solubility of the nitrone salt.

A check of the stoichiometry of formation of the above-described compound (Table 2) showed that the reaction proceeds according to the equation

$$7H_2S_2O_3 \rightarrow H_2S_8O_3 + 6H_2SO_3. \tag{15}$$

The amount of sulfurous acid found to be low in some cases is explained by the volatility of SO_2.

Experimental Part

To obtain nitrone heptasulfanemonosulfonate, a weighed portion of pure nitrone* (2.5–5.5 g) is dissolved in 5% acetic acid, and 100–200 ml of dilute HCl is added (see Table 2). Into the cooled solution ($t < 15^\circ$), from an immersed pipette, a solution of the calculated amount of $Na_2S_2O_3$ with a slight excess is carefully introduced. The reaction does not proceed rapidly: the product forms gradually, at first as a turbidity, from which a finely crystalline precipitate settles to the bottom of the vessel. The bulk of the precipitate forms at 16–18° over 1–2 h, but its separation is completed only after about 12 h, after which the solution becomes completely clear. The filtered precipitate is dried in a desiccator or in air at room temperature. Drying at elevated temperature (35–40°) leads to partial decomposition: the product becomes gray and no longer dissolves without residue in warmed alcohol. Pure preparations dissolve completely in alcohol, but recrystallization without a change in composition cannot be achieved, since the product decomposes with liberation of hydrogen sulfide and sulfur.

For the determination of sulfur, a weighed portion of the preparation is fused with a mixture of Na_2CO_3, K_2CO_3, and Na_2O_2 by the method of Ashboth (9). The cooled mass is dissolved in warm water, the solution is filtered and acidified with a solution of bromine in hydrochloric acid. After removal of the excess bromine by boiling, sulfur is precipitated as $BaSO_4$, which is weighed. The nitrogen content is determined by the known method of organic microanalysis.

The number of sulfur atoms in the molecule (x) is given by the ratio of the total sulfur content to the amount of thiosulfate formed as a result of decomposition of a separate weighed portion of the preparation by solutions of Na_2S, respectively KCN or NH_3. In all cases, 1 mole of sulfanemonosulfonate gives one mole of thiosulfate, which, after blocking of sulfite with formaldehyde and acidification, is titrated with iodine (5,7). To remove the nitrone or the products of its decomposition that have separated out, before acidification (also in the cases of cyanide or ammonia decomposition) a little zinc acetate is added; the precipitating zinc hydroxide carries down the separated organic precipitates and facilitates their removal by filtration, and also binds traces of hydrogen sulfide that may form. Decomposition by ammonia is accelerated by heating to 40°.

The sulfurous acid formed during synthesis of the product and the unreacted thiosulfate (when checking the stoichiometry of the reaction) are determined iodometrically (7).

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* We used nitrone from the firm "Merck."

Note: Figure translations are in progress. See original paper for figures.