

The Reaction Between Tetrathionate and Azide Ions

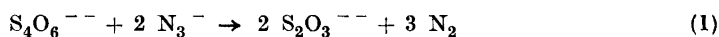
A Kinetic Investigation

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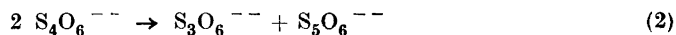
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Dodd and Griffith¹ and Hofman-Bang² have found that the rate determining reaction step of the iodine-azide reaction, catalyzed by tetrathionate ions, is a bimolecular reaction between azide ions and tetrathionate ions. Further it was found² that potassium tetrathionate and sodium azide in aqueous solution react with the evolution of free nitrogen. Keeping in mind that the carbon disulphide catalyzed iodine-azide reaction³ is closely related to the direct reaction between azide ions and carbon disulphide molecules⁴, it would seem natural that the tetrathionate catalyzed iodine-azide reaction was also in some way related to the reaction between tetrathionate and azide ions. This seems to be the case, and the relationship will be dealt with in a following publication.

Tetrathionate and azide ions interact according to the scheme:



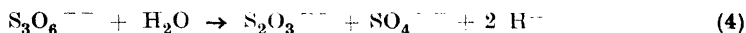
As will appear later, this reaction is not quantitative. Even when tetrathionate is allowed to react with a very large excess of sodium azide, a precipitate of sulphur is formed after some time. The explanation of this phenomenon is presumably as follows: As soon as thiosulphate ions are formed according to (1), they start to catalyze the conversion of tetrathionate ions into trithionate and pentathionate ions:



This conversion was studied by Kurtenacker *et al.*⁵ and recently by Goehring *et al.*⁶. Pentathionate ions decompose at a considerable rate:



and trithionate ions decompose slowly:



EXPERIMENTAL

The nitrogen evolution from a solution containing sodium azide and potassium tetrathionate was followed manometrically in the shaking apparatus used in the investigation ^{2,p.874} of the tetrathionate catalyzed iodine-azide reaction. The volume of the flask (including volume of the elastic connection to the manometer), in which the reaction took place, was determined in two different ways. Reaction between sodium bicarbonate, dried at 60° C, and 1 *M* hydrochloric acid gave the volume 227.9 ml. Reaction between sodium azide and an excess of 0.1 *M* ceric sulphate (1 *M* with respect to sulphuric acid) gave 228.7 ml.

Performance of an experiment: A known amount of sodium azide solution was pipetted with a Krogh syringe pipette into the reaction flask and also into the compensation flask. In the "vessel" was weighed 100 % pure potassium tetrathionate, $\text{K}_2\text{S}_4\text{O}_6$, usually 0.1000 g, which was dissolved in 2.000 ml water. The whole shaking apparatus was evacuated until the solutions began to bubble briskly, and was then allowed to stand for 30 minutes for the sake of complete temperature adjustment. The "vessel" with tetrathionate solution was caused to fall down into the azide solution by starting the shaking motor. In the following calculations the expansion of the reacting mixture from about 20° C to the experimental temperature was not compensated for. Neither was the alteration of volume due to the addition of potassium tetrathionate, nor to the mixing, taken into consideration. These corrections were of no importance compared with the experimental error.

In Table 1 are given the corresponding values of time of reaction, *t*, and pressure of nitrogen evolved, *p*, in three typical experiments. With the concentrations used (see Table), the azide ion concentration could be considered as constant during an experiment. From expt. no. 1, Table 1, is seen that the rate of reaction decreases much more than can be expected from the decrease in tetrathionate ion concentration. *E. g.* the increase in pressure is 0.29 cm Hg in the period 2–5 min., *i. e.* ca 0.1 cm Hg per min. In the period 20–30 min the increase in pressure is 0.33 cm Hg, *i. e.* ca 0.03 cm Hg per min. The last rate is ca. one third of the first, although decrease in tetrathionate concentration is only about 20 % (the concentration of azide ions is constant). It seems as though some sort of inhibitor were being produced. The immediate thought is that thiosulphate must be the inhibitor. In expt. no. 2, Table 1, 1.000 ml 0.1007 *M* sodium thiosulphate was added to the sodium azide solution in the reaction flask. The concentrations of potassium tetrathionate and

Table 1. Reaction between potassium tetrathionate and sodium azide at 25° C. In expt. no. 1 10.46 ml 4.00 M sodium azide were used in the reaction flask, and 0.1007 g potassium tetrathionate plus 2.000 ml water in the "vessel". In expt. no. 2 10.46 ml 4.00 M sodium azide and 1.000 ml 0.1007 M sodium thiosulphate were used in the reaction flask, and 0.1001 g potassium tetrathionate plus 1.000 ml water in the "vessel". In expt. no. 3 10.46 ml 4.00 M sodium azide, which at the same time was 0.0238 M with respect to potassium iodide, were used in the reaction flask, and 0.1000 g potassium tetrathionate plus 2.000 ml water in the "vessel".

Expt. 1		Expt. 2		Expt. 3	
<i>t</i> Time in min	<i>p</i> cm Hg	<i>t</i> Time in min	<i>p</i> cm Hg	<i>t</i> Time in min	<i>p</i> cm Hg
0	0	0	0	0	0
2	0.32	1	0.02	1	0.21
5	0.61	2	0.04	2	0.35
10	0.91	3	0.10	5	0.62
15	1.17	5	0.14	10	0.92
20	1.41	10	0.28	15	1.14
30	1.74	15	0.45	20	1.35
45	2.20	20	0.62	25	1.55
60	2.57	25	0.76	30	1.72
90	3.19	30	0.89	40	2.00
130	3.84	40	1.13	60	2.55
1140	6.74	50	1.40	90	3.18
1620	6.86	60	1.64	120	3.72
4030	7.00	90	2.28	150	4.11
5400	7.06	1125	6.42	180	4.47
6850	7.06	5400	6.81	435	5.99
		5820	6.82	1200	6.76
		7080	6.85		
		9840	6.86		
		14300	6.86		
82.8 % N ₂		80.9 % N ₂			

sodium azide were the same as in expt. no. 1. The results show, as was to be expected, that thiosulphate exercises a rather strong retarding effect on the rate of reaction.

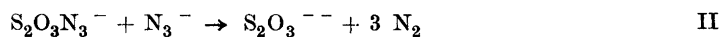
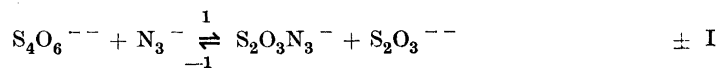
Expt. no. 3, Table 1, shows that the addition of potassium iodide (0.02 *M*) does not alter the rate of reaction. A similar experiment, which is not tabul-

ated, was carried out with the reacting mixture 0.2 *M* with respect to potassium iodide. Neither in this case was a specific effect of the iodide ion ascertained. These two experiments with addition of potassium iodide were carried out because variation of iodide ion concentration was shown^{1,2} to have a remarkable effect on the rate of the tetrathionate catalyzed iodine-azide reaction.

In Table 1 are given the final amounts of nitrogen evolved, calculated as percentages of the theoretical amounts according to (1). Quite a number of similar experiments have been carried out with variations in azide and tetrathionate concentrations. Variation of these concentrations did not effect the final amount of nitrogen evolved. All the results were between 82 and 83 %. One experiment carried out at 30° C instead of 25° C gave 83.4 %, so maybe an increase of temperature slightly increases the percentage of nitrogen. Addition of thiosulphate (see expt. no. 2, Table 1) seems to slightly decrease the total nitrogen evolution, which is not surprising, keeping in mind that thiosulphate ions catalyze degradation of polythionates.

A TENTATIVE MECHANISM OF REACTION

In the following considerations the thiosulphate catalyzed decomposition of tetrathionate will not be taken into consideration. As the over-all reaction takes place between one tetrathionate ion and two azide ions, it seems likely that the sequence of reactions consists of two bimolecular reaction steps. The striking decrease of the rate of reaction caused by thiosulphate ions can be accounted for by assuming one of the reaction steps to be reversible. The formation of free nitrogen can not be reversible, so only one possibility remains:



According to Christiansen⁷ the reciprocal velocity is:

$$\frac{1}{s_+} = \frac{1}{a_1} \left(\frac{1}{w_1} + \frac{w_{-1}}{w_1} \cdot \frac{1}{w_2} \right) \quad (5)$$

or

$$\frac{dt}{dx} = \frac{1}{[\text{S}_4\text{O}_6^{--}]} \left(\frac{1}{k_1[\text{N}_3^-]} + \frac{k_{-1}[\text{S}_2\text{O}_3^{--}]}{k_1[\text{N}_3^-]} \cdot \frac{1}{k_2[\text{N}_3^-]} \right) \quad (6)$$

When we consider an experiment with no pre-addition of thiosulphate, and only consider very small degrees of reaction, the thiosulphate ion concentration is the only concentration that is not constant, and we have:

$$\frac{1}{k_1[\text{S}_4\text{O}_6^{2-}][\text{N}_3^-]} = A = \text{const. and } \frac{1}{k_1[\text{S}_4\text{O}_6^{2-}][\text{N}_3^-]} \cdot \frac{k_{-1}}{k_2[\text{N}_3^-]} = B = \text{const.}$$

which give:
$$\frac{dt}{dx} = A + B(2x) \quad (7)$$

where x is the decrease in tetrathionate concentration.

By integration of (7) we get:

$$t = Ax + Bx^2 \quad (8)$$

Let us now consider an experiment with sodium thiosulphate added in advance, but with the same initial concentrations of azide and tetrathionate ions. As before, only small degrees of reaction are considered, so that azide, tetrathionate and also thiosulphate ion concentrations are nearly constant. In this case we have:

$$\frac{dt}{dx} = A + B \cdot y \quad (9)$$

where y is the constant concentration of thiosulphate. By integration of (9) we get:

$$t = Ax + Bxy \quad (10)$$

Equation (9) was checked by carrying out a series of kinetic experiments with different concentrations of thiosulphate. In each experiment 10.46 ml 4.00 *M* sodium azide and 1.000 ml sodium thiosulphate (of known concentration) were used in the reaction flask, and 0.1000 \pm 0.0002 g potassium tetrathionate plus 1.000 ml water in the "vessel". At first a few experiments, in which the tetrathionate, water and thiosulphate were introduced into the "vessel", were carried out. But this procedure did not give correct results, because, during the 30 minutes temperature adjustment, the thiosulphate caused some decomposition of the tetrathionate.

The experiments showed that the rate of reaction was constant as long as the degree of reaction was so small that the concentrations of tetrathionate and thiosulphate could be considered constant. The initial reciprocal rates of reaction were determined graphically. They are — together with the molar concentrations of thiosulphate — given in Table 2. The reciprocal rates,

Table 2. Reaction between potassium tetrathionate and sodium azide with simultaneous presence of sodium thiosulphate at 25° C. In each experiment 10.46 ml 4.00 M sodium azide and 1.000 ml sodium thiosulphate were used in the reaction flask, and 0.1000 ± 0.0002 g potassium tetrathionate plus 1.000 ml water in the "vessel". $\frac{dt}{dx}$ min/cm Hg is the initial reciprocal rate of reaction, and y is the corresponding initial concentration of thiosulphate ions.

Expt. no.	1	2	3	4	5	6	7	8	9	10
$\frac{dt}{dx}$ min/cm Hg	ca. 4	28.7	33.9	52.1	79.2	81.0	107.9	122.0	147.5	153.8
y Initial concentration of thio-sulphate	0	0.00647	0.00809	0.01617	0.03234	0.03234	0.04851	0.0647	0.0809	0.0970
$\alpha = \frac{\left(\frac{dt}{dx}\right)_n - \left(\frac{dt}{dx}\right)_1}{y_n}$		3820	3700	2980	2330	2380	2140	1820	1770	1540

expressed in minutes per cm Hg nitrogen pressure, were plotted against the thiosulphate concentration (abscissa). This plot did not give a straight line in accordance with equation (9), but a curve which was downwards convex, as shown by the α -values, which are the slopes calculated from the $\frac{dt}{dx}$ and y values in expt. no. 1 and n . In other words, with increasing thiosulphate concentration the rate of reaction did not decrease quite as much as was to be expected. Nevertheless it seems likely that the sequence \pm I and II represent the essentials of the mechanism. As already mentioned thiosulphate catalyzes the conversion of tetrathionate into trithionate and pentathionate. Pentathionate ions also react with azide ions to give free nitrogen — and at a considerably larger rate than do tetrathionate ions^{8,p.460}. This observation explains qualitatively why the rate of nitrogen evolution, from a solution containing tetrathionate, azide and thiosulphate was higher than expected according to \pm I and II.

It may be mentioned that when two experiments from Table 2 were used for the calculation of the coefficients A and B in (9), then the numerical values obtained agreed better and better with (8), the smaller the concentrations of thiosulphate were in the two first-mentioned experiments.

Table 3. Energy of activation of the reaction between tetrathionate and azide ions. In each experiment 10.46 ml 4.00 M sodium azide were used in the reaction flask, and 0.1000 ± 0.0002 g potassium tetrathionate plus 2.000 ml water in the "vessel". The read nitrogen pressures were all corrected to 25° C. From the time of reaction-nitrogen pressure curves were found the times of reaction, t' and t'' , corresponding to 1 and 2 cm Hg nitrogen pressure respectively. The reciprocal values of t' and t'' were used as relative rate constants. $t'_{calc.}$ and $t''_{calc.}$ were calculated by inserting the experimental temperatures in the found Arrhenius equation.

Expt. no.	Temp. °C	t' min	$t'_{calc.}$ min	t'' min	$t''_{calc.}$ min
1	20°	21.5	21.8	73.8	73.8
2	25°	11.3	11.1	38.1	37.2
3	30°	5.75	5.73	18.6	19.1
4	33°	3.85	3.90	13.3	13.0
Energy of activation cal/mole		23590		23790	

ENERGY OF ACTIVATION

The energy of activation of the nitrogen formation was measured by running, at different temperatures, experiments with identical concentrations (the same as those used in expt. no. 1, Table 1). From the time — nitrogen pressure curves were read the times of reaction, t' and t'' in Table 3, at 1 and 2 cm Hg nitrogen pressure respectively. The reciprocal values of t' and t'' were used as relative rate constants, k . Using the method of least squares, the numerical values of H and A were calculated according to the Arrhenius equation:

$$\log k = H - \frac{A}{T}$$

where T is the absolute temperature. From this equation values of reaction times ($t_{calc.} = \frac{1}{k}$) were calculated by substituting T with the experimental temperatures. These values, $t'_{calc.}$ and $t''_{calc.}$, are, together with the experimental ones, recorded in Table 3. At the nitrogen pressure 1 cm Hg was found the energy of activation:

$$A \times 4.571 = 5161 \times 4.571 = 23590 \text{ cal/mole}$$

At the nitrogen pressure 2 cm Hg was found:

$$A \times 4.571 = 5204 \times 4.571 = 23790 \text{ cal/mole}$$

The difference between the two energies of activation is not larger than can be accounted for by the experimental error. Consequently it seems that the energy of activation does not alter through an experiment.

SUMMARY

Tetrathionate ions and azide ions react to give thiosulphate ions and free nitrogen (1). Kinetic investigations on this reaction have been carried out. The most noticeable feature is, that the rate of reaction decreases rather much with increasing concentration of thiosulphate ions. The over-all rate seems to agree qualitatively with the mechanism \pm I and II. That the accordance is only qualitative can be explained by the disproportioning of tetrathionate into tri- and pentathionate (2). The energy of activation was found to be 23700 cal/mole.

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