The Iodine-azide Reaction

I. The Catalytic Effect of the Tetrathionate Ion

NIELS HOFMAN-BANG

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

No reaction will take place in a solution containing triiodide and azide ions without the presence of a catalyst. Raschig[1], who was the first to describe this phenomenon, was of the opinion that the iodine-azide reaction was a typical catalytic reaction. Raschig ascertained that sodium thiosulphate and sodium sulphide act as catalysts.
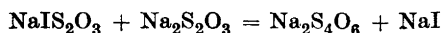
The overall equation of the iodine-azide reaction is:

$$2 \ N_3^- + I_2 = 3 \ N_2 + 2 \ I^-$$
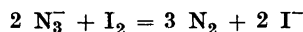
Raschig[2] has proposed the following reaction mechanism for the iodine-azide reaction catalyzed by thiosulphate:

$$Na_2S_2O_3 + I_2 = NaIS_2O_3 + NaI$$
$$NaIS_2O_3 + 2 \ NaN_3 = NaI + Na_2S_2O_3 + 3 \ N_2$$
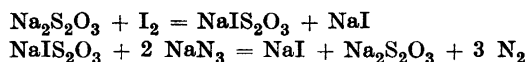
while tetrathionate is formed at the same time according to the equation:

$$NaIS_2O_3 + Na_2S_2O_3 = Na_2S_4O_6 + NaI$$

In his proposal, Raschig assumes that the tetrathionate does not catalyze the iodine-azide reaction. This has now been proved incorrect, and for this reason alone his mechanism of reaction must be held as rather unlikely.

Feigl[3] and others have shown that many compounds, which contain sulphide sulphur, catalyze the iodine-azide reaction. Examples are all inorganic sulphides[3], thiocyanates[3], carbon disulphide[4], tri-, tetra- and penta-thionate[5] and many organic sulphur compounds[6] containing sulphidic sulphur.

Neither the authors mentioned above, nor the rather many others who have made use of the iodine-azide reaction, have tried to elucidate the reaction mechanism by kinetic measurements. Alkali metal salts of tetrathionic acid should be suitable for that purpose, since according to the literature, tetrathionate ions do not react with iodine or azide ions. According to Kurtenacker et al. [7], tetrathionate decomposes in aqueous solution to tri- and pentathionate. The rate of decomposition is fairly small at 25° C and is, within a pH-range of 9—5, independent of the pH.

REAGENTS

Sodium azide. Sodium azide, *p. a.* — after drying — was analyzed by oxidizing hydrazoic acid to free nitrogen by means of ceric salt [8] in excess.

NaN$_3$ (65.02)   Calc. N 64.63   Found N 64.64, 64.59

Potassium tetrathionate: This salt is prepared according to the method of Raschig [9] which, in principle, consists of oxidation of thiosulphate by means of cupric ions:

$$3 \text{ K}_2\text{S}_2\text{O}_3 + 2 \text{ CuSO}_4 = \text{Cu}_2\text{S}_2\text{O}_3 + 2 \text{ K}_2\text{SO}_4 + \text{K}_2\text{S}_4\text{O}_6$$

The raw product of potassium tetrathionate was recrystallized four times from water. A polythionate analysis, as outlined by Kurtenacker [10] was carried out. The improved method of Foss [11] was used for analysis of the reaction between tetrathionate and potassium cyanide:

$$\text{S}_4\text{O}_6^{--} + 3 \text{ CN}^- + \text{H}_2\text{O} = \text{S}_2\text{O}_3^{--} + \text{SO}_4^{--} + \text{SCN}^- + 2 \text{ HCN}$$
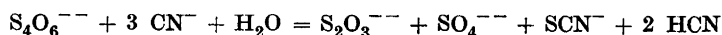
This consists in principle of the titration of the thiosulphate formed with iodine in a solution acidified with acetic acid instead of sulphuric acid.

The potassium tetrathionate prepared was found to be 99.6 % pure and to contain no sulphate or potassium pentathionate. Furthermore, it was ascertained that the use of further recrystallized sodium azide and potassium tetrathionate did not alter the experimental results.

The other reagents used were all of analytical grade.

FIRST EXPERIMENTAL METHOD

According to Raschig [1, 2], the iodine-azide reaction takes place without interfering side reactions, and the amount of nitrogen evolved is proportional to the amounts of iodine and azide consumed. This result has been confirmed by Sommer and Pincas [12] and by Browne [13]. The present author has analyzed the gas evolved using tetrathionate as the catalyst and found that it consists only of nitrogen.

The original experiments were carried out by measuring the pressure, at constant volume, of the nitrogen evolved in a shaking apparatus rather similar to that described in detail by Brønsted[14] in 'Nitramidkatalytische Studien. II'. The volume of the flask, in which the reaction takes place, was about 200 ml. The flask — through an elastic glass spiral — was connected to a manometer, which was filled with mercury. The other side of the manometer was connected, also through an elastic glass spiral, to a compensation flask matching the reaction flask. During an experiment, the compensation flask contained sodium azide and iodine solution of the same concentration as in the reaction flask. Thus it was possible to compensate for vapour pressure. The necks of the two flasks were provided with a ground male connection and could be closed with a cap with a corresponding female connection. At the bottom of the cap a glass rod was fastened, the lower end of which was hook shaped. On this hook a small glass container — a 'vessel' could be placed. The catalyst solution was placed in this 'vessel'. By shaking, the 'vessel' can be made to fall into the solution of sodium azide and iodine in potassium iodide. The entire shaking apparatus, including the manometer, was, during an experiment, lowered into a water thermostat, which was kept at $25.00° \pm 0.02°$ C. Stopcocks and ground joints were greased with a wax-containing stopcock grease which was not attacked by water at 25° C.

Performance of an experiment: A known amount of sodium azide solution and iodine, in potassium iodide solution, was pipetted with a Krogh syringe pipette into the reaction flask as well as into the compensation flask. Into the 'vessel', which was placed on the hook in the reaction flask, a known amount of potassium tetrathionate solution was introduced. When all the joints had been greased and connected, the entire shaking apparatus was lowered into the thermostat and the system evacuated until the solutions of azide and iodined bubble briskly. At this time the apparatus was allowed to stand for 30 minutes for the sake of complete temperature adjustment. The experiment was started by switching on the motor which works the shaking mechanism. The 'vessel' containing the tetrathionate thereby fell into the azide-iodine solution, and the evolution of nitrogen began. The nitrogen pressure, which is directly proportional to the amounts of iodine and azide consumed, was read at definite intervals. The shaking is sufficient when a still more rapid shaking does not alter the pressure-time curve.

Solutions used in the experiments: The concentrations of the solutions used were adjusted so that the ionic strength in the reaction mixture was as close to 0.37 as possible. The sodium azide solutions were made by weighing dried sodium azide and dissolving in water in a volumetric flask. For each experiment, 11.344 ml sodium azide solution was pipetted off. The iodine, in potassium iodide solution, was made by weighing out dried potassium iodide, p. a., and resublimated iodine, and dissolving in water in a volumetric flask. Furthermore, the iodine concentration was determined by titration with standard sodium thiosulphate. 11.344 ml of the iodine in potassium iodide solution was used in each experiment. Potassium tetrathionate was weighed off in the 'vessel', after which 1.038 ml of water was added. The volumes mentioned above are the volumes of the syringe-pipettes measured at 20° C. In the following calculations the expansion of the reacting mixture from 20 to 25° C is not compensated for. This correction is, for pure water, about 0.12 %. Neither, is the alteration of volume due to the addition of potassium tetrathionate nor to the mixing taken into consideration. Since the largest amount of tetrathionate added is 20 mg, this correction is also without importance.

EXPERIMENTAL RESULTS

From the experimental results it is evident that the rate of reaction is proportional to the concentration of potassium tetrathionate and approximately proportional to the concentration of sodium azide. Consequently we have:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = k \cdot a \cdot c$$

where c is the concentration of potassium tetrathionate, and a is the concentration of sodium azide. The integrated form of this rate equation is:

$$k = \frac{2.303}{c \cdot t} \log \frac{a}{a-x} \tag{1}$$

where t is the time of reaction, a is the initial concentration of sodium azide, and $a-x$ is the concentration of sodium azide at the time t.

To illustrate the treatment of the experimental results, an experiment (expt. no. 1) with the appurtenant calculations (Table 1) is shown; for each reading of the nitrogen pressure p (mm Hg) at the time t, the rate constant k according to (1) is calculated.

The rate constants of two other experiments, calculated in an analogous manner, are given in Table 2.

Many other experiments have been carried out, but as it turned out to be possible to use a much simpler method, the results of these experiments are not tabled. All the experiments carried out with a shaking apparatus show that the rate of reaction is: 1) directly proportional to the concentration of the catalyst, 2) approximately proportional to the concentration of sodium azide, and 3) independent of the concentration of iodine. Furthermore, the experiments seem to indicate that the iodide ions have a specific effect on the absolute rate of reaction; but there does not seem to be a simple dependence between rate constant and iodide ion concentration. The large rate constant in expt. no. 3 is partly due to the large concentration of iodide ions and partly to the very small concentration of sodium azide. A small concentration of azide ions seems to give a higher rate constant than a large concentration does (see later).

As the rate of reaction is independent of the concentration of iodine, it should be possible to carry out the rate experiments in such a manner that a relatively small amount of iodine solution is added to a solution which contains potassium tetrathionate, a relatively large amount of sodium azide, and

*Table 1. Reaction between sodium azide and iodine at 25° C. Catalyst: Potassium tetra -
thionate. The initial concentrations were: a = 0.2719 M; c = 0.00279 M; c_{I-} = 0.0957 M ;
c_{I_2} = 0.0476 N. x, which is the amount of azide consumed, is calculated from the equation :*

$$x = \frac{p}{13.41} \cdot 0.0476. \text{ The ionic strength was 0.376}$$

Experiment 1

p mm Hg	t Time in min	x	$a-x$	$\log \frac{a}{a-x}$	$k = \frac{2.303}{c \cdot t} \cdot \log \frac{a}{a-x}$
0	0	0	0.2719		
0.71	1	0.0025	0.2694	0.0040	3.30
1.52	2	0.0054	0.2665	0.0087	3.59
2.21	3	0.0079	0.2640	0.0128	3.52
2.99	4	0.0106	0.2613	0.0173	3.57
3.78	5	0.0134	0.2585	0.0219	3.62
4.47	6	0.0159	0.2560	0.0262	3.60
5.14	7	0.0182	0.2537	0.0301	3.55
5.80	8	0.0206	0.2513	0.0342	3.53
6.47	9	0.0230	0.2489	0.0384	3.52
7.16	10	0.0254	0.2465	0.0426	3.52
7.76	11	0.0276	0.2443	0.0465	3.49
8.32	12	0.0295	0.2424	0.0499	3.43
8.92	13	0.0317	0.2402	0.0538	3.42
9.50	14	0.0337	0.2382	0.0575	3.39
9.96	15	0.0354	0.2365	0.0605	3.33
10.53	16	0.0374	0.2345	0.0642	3.31
11.10	17	0.0394	0.2325	0.0679	3.30
11.61	18	0.0412	0.2307	0.0714	3.27
12.13	19	0.0431	0.2288	0.0749	3.26
12.64	20	0.0449	0.2270	0.0784	3.24
13.17	21	0.0467	0.2252	0.0819	3.22
13.41	22	0.0476			
13.41	23	0.0476			

some starch solution. When all iodine is used up, the blue colour of the solu-
tion should disappear, and the time of reaction should be inversely proportional
to the rate of reaction. This assumption has proved to be correct.

NEW EXPERIMENTAL METHOD

Into a 300 ml Erlenmeyer flask was pipetted 30 ml of a solution, which was 4.013 M
with respect to sodium nitrate and 0.1 M to potassium iodide, 10 ml potassium tetra-
thionate solution, 0.2 ml 0.5 % starch solution, and 10 ml of a solution, which was 0.01 N

Table 2. Reaction between sodium azide and iodine at 25° C. Catalyst: Potassium tetrathionate. The initial concentrations in experiment No. 2 were: $a = 0.1767\,M$; $c = 0.00279$ M; $c_{I^-} = 0.1903\,M$; $c_{I_2} = 0.0473\,N$; and the ionic strength was 0.375. The initial concentrations in experiment No. 3 were: $a = 0.02389\,M$; $c = 0.00279\,M$; $c_{I^-} = 0.2721\,M$; $c_{I_2} = 0.0480\,N$; and the ionic strength was 0.304.

Experiment 2			Experiment 3		
p mm Hg	t Time in min	$k = \dfrac{2.303}{c \cdot t} \log \dfrac{a}{a-x}$	p mm Hg	t Time in min	$k = \dfrac{2.303}{c \cdot t} \log \dfrac{a}{a-x}$
0.55	1	3.96	0.33	1	17.4
1.20	2	4.33	0.62	2	16.6
1.83	3	4.43	0.90	3	16.4
2.43	4	4.44	1.16	4	16.3
3.04	5	4.46	1.42	5	16.3
3.62	6	4.43	1.68	6	16.4
4.20	7	4.42	1.91	7	16.3
4.75	8	4.40	2.12	8	16.2
5.30	9	4.38	2.36	9	16.4
5.81	10	4.36	2.60	10	16.7
6.83	12	4.33	3.00	12	16.7
7.81	14	4.29	3.39	14	17.0
8.82	16	4.28	3.78	16	17.4
9.78	18	4.26	4.11	18	17.6
10.70	20	4.24	4.42	20	17.9
11.58	22	4.22	4.99	24	18.6
12.41	24	4.19	5.43	28	19.1
13.22	26	4.16	5.80	32	19.7
13.61	28		6.10	36	20.4
13.61	30		6.29	40	20.5
			6.42	44	20.3
			6.53	50	19.3
			6.64	60	17.6
			6.70	70	16.1
			6.78	90	
			6.83	110	
			7.00	310	
			7.00	390	

with respect to iodine and 0.02 M to potassium iodide. The flask was placed in a water thermostat, so that only the neck was above the water. Behind the flask a plate of white glass was inserted, and in front of the thermostat, the front of which was clear glass, an electric bulb was mounted and screened so that a ray of light was directed through the Erlenmeyer flask against the white glass plate. It was now very easy to see any colour change. Before continuing the experiment the Erlenmeyer flask was allowed to stand in

Table 3. Reaction between sodium azide and iodine at 25° C. Catalyst: Potassium tetra-thionate. In all four experiments — besides the solutions mentioned in the table — were added 0.2 ml starch solution and 39 ml solution, which was 4.013 M with respect to sodium nitrate and 0.1 M to potassium iodide. In experiments 2 and 4 (in which 5 ml 0.5 M sodium azide is added instead of 10 ml) for the sake of constant ionic strength, 5 ml 0.5 M sodium nitrate was added. The concentrations of the stock solutions used were: Potassium tetrathionate: 0.01 M; iodine: 0.00982 N with respect to iodine and 0.02 M to potassium iodide; and sodium azide: 0.5 M.

Expt. no.		c	a	x	t Time in min	$k = \dfrac{2.303}{c \cdot t} \log \dfrac{a}{a-x}$
1	5 ml tetrathionate 5 ml water 10 ml iodine 10 ml sodium azide	0.000831	0.0831	0.001631	5.70	4.13
2	5 ml tetrathionate 5 ml water 5 ml iodine 5 ml water 5 ml sodium azide 5 ml sodium nitrate	0.000831	0.04153	0.000816	5.57	4.31
3	5 ml tetrathionate 5 ml water 5 ml iodine 5 ml water 10 ml sodium azide	0.000831	0.0831	0.000816	2.78	4.19
4	10 ml tetrathionate 10 ml iodine 5 ml sodium azide 5 ml sodium nitrate	0.001661	0.04153	0.001631	5.42	4.45

the thermostat for 15 minutes (this has proved to be sufficient for temperature adjustment). In addition a bottle containing 0.5 *M* sodium azide solution was placed in the thermostat. After the elapse of 15 minutes, 10 ml 0.5 *M* sodium azide was sucked into a pipette. This was immediately allowed to run down into the Erlenmeyer flask, which

Table 4. Effect of addition of various salts on the rate of reaction of the tetrathionate-catalyzed iodine-azide reaction. In each experiment 10 ml 0.00982 N iodine in 0.02 M potassium iodide, 10 ml 0.01 M potassium tetrathionate, 0.2 ml starch solution, and 5 ml 0.5 M sodium azide were used. Furthermore, the various solutions mentioned in the table were added. The concentrations in the reacting solutions were: c = 0.003105; a = 0.07762 and x = 0.00305.

Expt. no.		t Time in min	$k = \dfrac{2.303}{c \cdot t} \log \dfrac{a}{a-x}$
1	5 ml water	10.13	1.28
2	5 ml 0.5 M sodium chloride	9.17	1.42
3	5 ml 0.5 M potassium iodide	5.57	2.33
4	5 ml 0.5 M sodium nitrate	9.37	1.39
5	5 ml 0.5 M sodium acetate	9.32	1.39
6	5 ml 6 M sodium nitrate	5.57	2.33
1 a	5 ml water	10.15	1.28

at the same time — partly immersed in the thermostat water — was kept in a rotary motion with the left hand. When half the sodium azide had run out of the pipette, a stopwatch was started. The last drop in the pipette was blown out, and the flask was kept rotating for an additional 10 sec. The instant the colour in the experimental solution disappeared, the watch was stopped.

The volume in each experiment was 60.2 ml. The reason the solution was made approx. 0.05 M with respect to potassium iodide, is that the reduction of iodine to iodide ions would otherwise cause a considerable increase in the concentration of iodide ions. All the pipettes used were controlled by weighing out with water.

The results (see Table 3) of this experimental method are quite in accordance with those previously obtained, since the rate of reaction is found to be independent of the concentration of iodine, proportional to the concentration of the catalyst, and approximately proportional to the azide ion concentration, although decreasing azide ion concentration seems to give a slightly too large rate of reaction.

Table 4 represents an investigation of the effect of addition of various salts. It will be noticed that increasing concentration of a salt causes an increase in the rate of reaction. This is to be expected since the rate determining reaction step is a reaction between an azide ion and a tetrathionate ion (see later),

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which are both negatively charged. Of course, the ionic strength of the solutions in question is too large to allow for quantitative considerations. From the results it is seen that sodium chloride, sodium nitrate and sodium acetate have practically the same effect. Potassium iodide, however, has a specific rate increasing effect, which is in accordance with what the original measurements seemed to indicate. This effect cannot be explained by a shift in the equilibrium $I_2 + I^- \rightleftharpoons I_3^-$. There does not seem to be a simple dependency between iodide ion concentration and rate of reaction.

THE EFFECT OF pH ON THE RATE OF REACTION

Hydrazoic acid is approximately of the same strength as acetic acid. According to Hughes [15] the ionization constant of hydrazoic acid is about 2×10^{-5} at 25° C, *i. e.* the pH of a 0.1 M sodium azide solution is roughly 9, and very close to 100 % of the sodium azide dissolved will be on hand as free azide ions.

Two experiments with tetrathionate as the catalyst were carried out in boric acid — borate buffered solutions with identical concentrations of sodium nitrate, sodium azide, potassium tetrathionate, and starch. As usual the time of decoloration of identical amounts of iodine were measured at 25° C. In two solutions of pH 9.19 and 8.69 respectively, the times of decoloration were the same within 1 %. From this fact it follows that it is the azide ions which take part in the reaction, because the concentration of free azide ions is practically constant, whereas the concentration of undissociated hydrazoic acid varies considerably in the two experiments.

A series of experiments was carried out (without addition of sodium nitrate), in such a way that the concentrations of sodium azide, potassium tetrathionate and iodine were the same in all experiments. In addition, varying amounts of hydriodic acid were added, so that the azide ions were partly converted into un-ionized hydrazoic acid. Accordingly varying amounts of potassium iodide were added, so that the total concentration of iodide ions was the same in all experiments. The solution of hydriodic acid was made from iodine and water by reduction with hydrogen sulphide. The excess of hydrogen sulphide was removed by boiling out in a current of carbon dioxide. The concentration of hydriodic acid was determined by titration with standard sodium hydroxide. The result showed an approx.- but not exact-proportionality between the rate of reaction and the concentration of free azide ions. When an excess of hydriodic acid was added, so that all azide ions were converted into hydrazoic acid, the rate of reaction was extremely small. Consequently we have good reason to assume that only free azide ions — and not hydrazoic acid — take part in the iodine-azide reaction.

EXPERIMENTS WHICH SHOW THAT TETRATHIONATE IONS DO NOT DECOMPOSE WHEN CATALYZING THE IODINE-AZIDE REACTION

A few experiments were carried out as follows: A small amount of tetrathionate solution and some starch were added to a solution with a large concentration of sodium azide and small concentration of iodine. The time of decoloration was determined. At the instant the colour changed from light blue to colourless, a small amount of additional iodine solution was added, and the time of decoloration determined. From these two reaction times two rate constants can be calculated according to equation (1). The two constants were the same within the range of experimental error.

In this connection it is worth mentioning that a water solution of potassium tetrathionate shows an increased activity after standing some days, and the older the solution becomes the more the activity increases. This phenomenon is undoubtedly due to the fact that tetrathionate gradually decomposes to tri- and pentathionate [7].

Although tetrathionate does not seem to decompose essentially when acting as catalyst, it has been nevertheless ascertained that when rather concentrated solutions of sodium azide and potassium tetrathionate are mixed, a visible reaction takes place evolving a gas. An experiment was carried out by dissolving 1 g potassium tetrathionate in 10 ml 0.5 M sodium azide. After two hours approx. 10 ml of a gas had been evolved. The gas was analyzed * according to Christiansen and Wulff [16]. The result was 98.9 % nitrogen and 1.2 % oxygen. This small percentage of oxygen was probably due to contamination by atmospheric air. Consequently, it is believed that tetrathionate ions oxidize azide ions essentially to free nitrogen.

ENERGY OF ACTIVATION

The energy of activation of the tetrathionate catalyzed iodine-azide reaction was determined by experiments analogous to those previously described. The rate of reaction was determined in the temperature range 20° to 40° C. The experiments were carried out partly without addition of sodium nitrate and partly in a solution, which was 1 M with respect to sodium nitrate. In each experiment of the first series 10 ml 0.0200 N iodine in 0.500 M potassium iodide, 1 ml 0.05 M potassium tetrathionate, 9 ml water, 20 ml water, 0.2 ml starch solution and 10 ml 0.1 M sodium azide were used. In the second series the 20 ml water was substituted by 20 ml 2.5 M sodium nitrate solution.

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* I am greatly indebted to Miss I. Wulff, who carried out the analysis.

Table 5. Energy of activation of the tetrathionate catalyzed iodine-azide reaction. Concentrations in all experiments: c = 0.000996 M; a = 0.01992 M; x = 0.00398. $k_{exp.}$ is the rate constant calculated in each case from equation (1). $k_{calc.}$ is calculated from the equation $\log k = H - \dfrac{A}{T}$, which is a straight line fitted to the experimental k and T values.

| Temp. °C | No sodium nitrate added | | | The solution is 1 M as to sodium nitrate | | |
	Time in min	$k_{exp.}$	$k_{calc.}$	Time in min	$k_{exp.}$	$k_{calc.}$
20°	102.03	2.194	2.168	48.57	4.608	4.603
	103.25	2.168		48.33	4.631	
25°	70.40	3.179	3.126	33.18	6.745	6.730
	70.42	3.179		33.38	6.708	
30°	50.67	4.418	4.467	23.60	9.484	9.728
	50.55	4.428		23.58	9.493	
35°	36.72	6.095	6.295	16.55	13.52	13.86
	36.80	6.083		16.52	13.55	
40°	24.63	9.089	8.790	11.32	19.77	19.54
	24.82	9.018		11.33	19.75	

Using the method of least squares, the numerical values of H and A were calculated according to the equation

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

In the first series of experiments, in which no sodium nitrate was added, the result is

$$\log k = 9.842 - \frac{2786}{T}$$

Values of k calculated from this equation are, together with the experimental values, shown in Table 5. The energy of activation was:

$$A \times 4.571 = 2786 \times 4.571 = 12740 \text{ kcal/mole}$$

From the second series of experiments, in which the solution was 1 M with respect to sodium nitrate, was analogously calculated

$$\log\ k = 10.47 - \frac{2874}{T}$$

The experimental as well as the calculated values of k are shown in Table 5. The energy of activation was calculated to be 13140 kcal/mole. The frequency exponents H, which had values of 9.842 and 10.47, were — with 1 sec. as unit — respectively 9.84 — log 60 = 8.06 and 10.47 — log 60 = 8.69. These values agree well with those to be expected, when an ion of two negative charges (the tetrathionate ion) reacts with an ion of one negative charge (the azide ion) (*cf.* Moelwyn-Hughes: *Kinetics of reactions in solution* [17]). As was expected the addition of a neutral salt increased the rate of reaction.

DISCUSSION

It has been shown that the rate of the tetrathionate catalyzed iodine-azide reaction is proportional to both the concentration of potassium tetrathionate, and to the concentration of sodium azide, but is independent of the concentration of iodine. From the investigations of the effect of pH on the rate of reaction it is evident that only azide ions participate in the process. The integrated rate equation is consequently:

$$k = \frac{2.303}{c \cdot t}\ \log\ \frac{a}{a-x} \tag{1}$$

where k is the rate constant, c is the concentration of potassium tetrathionate, t is the time, a is the initial concentration of azide ions, and $a—x$ is the concentration of azide ions at the time t.
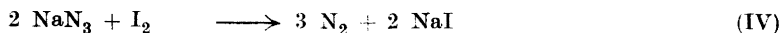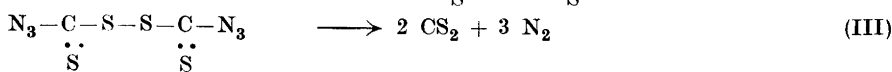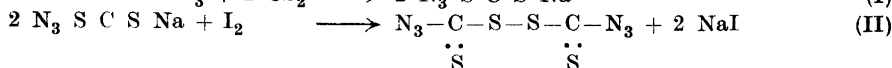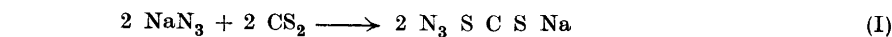
Tetrathionic acid is a rather strong acid and therefore potassium tetrathionate, in a slightly basic solution as is the case in a sodium azide solution, will be on hand as potassium ions and tetrathionate ions. The rate determining reaction step must therefore be:

$$N_3^- + S_4O_6^{--} \rightarrow N_3S_4O_6^{---} \tag{2}$$
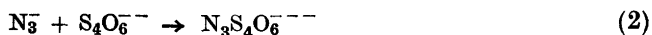
The reversal of reaction (2) must be without importance in this case. This reaction (2) can be shown to take place (*cf.* a following publication) even if iodine is not present. Therefore it is reasonable to assume that it is also the
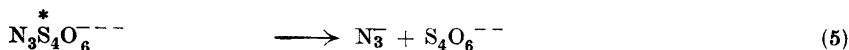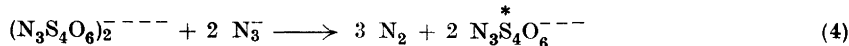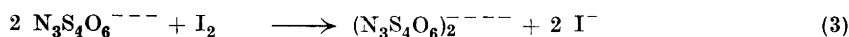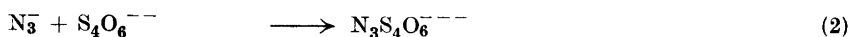
first step in a sequence of reactions. As the reaction between the complex and the iodine is instantaneous, it is impossible by kinetic investigations to elucidate the mechanism of this reaction.

Feigl[4] assumes, on the basis of diverse qualitative experiments and the fact that carbon disulphide and azide ions in water solution react with the formation of azido-dithiocarbonate ions, that the mechanism of the carbon disulphide catalyzed iodine-azide reaction is as follows:

$$2 \text{ NaN}_3 + 2 \text{ CS}_2 \longrightarrow 2 \text{ N}_3 \text{ S C S Na} \qquad \text{(I)}$$

$$2 \text{ N}_3 \text{ S C S Na} + \text{I}_2 \longrightarrow \underset{\overset{|}{\text{S}}}{\text{N}_3 - \text{C}} - \text{S} - \text{S} - \underset{\overset{|}{\text{S}}}{\text{C}} - \text{N}_3 + 2 \text{ NaI} \qquad \text{(II)}$$

$$\underset{\overset{|}{\text{S}}}{\text{N}_3 - \text{C}} - \text{S} - \text{S} - \underset{\overset{|}{\text{S}}}{\text{C}} - \text{N}_3 \longrightarrow 2 \text{ CS}_2 + 3 \text{ N}_2 \qquad \text{(III)}$$

$$2 \text{ NaN}_3 + \text{I}_2 \longrightarrow 3 \text{ N}_2 + 2 \text{ NaI} \qquad \text{(IV)}$$

Browne[13] has also investigated the iodine-azide reaction with carbon disulphide as the catalyst — although without carrying out kinetic measurements. Browne has shown the existence of the azido-carbondisulphide, which Feigl had postulated, and shown that it reacts very rapidly with sodium azide solution with the liberation of nitrogen. Browne proposes a reaction mechanism rather similar to that of Feigl, but with the difference that the azido-dithiocarbonate ion is assumed to be the actual catalyst.

As long as no other mechanism is proved, it is natural to formulate the mechanism of the tetrathionate catalyzed iodine-azide reaction analogous with the mechanism of the carbon disulphide catalyzed reaction:

$$\text{N}_3^- + \text{S}_4\text{O}_6^{--} \longrightarrow \text{N}_3\text{S}_4\text{O}_6^{---} \qquad \text{(2)}$$

$$2 \text{ N}_3\text{S}_4\text{O}_6^{---} + \text{I}_2 \longrightarrow (\text{N}_3\text{S}_4\text{O}_6)_2^{-----} + 2 \text{ I}^- \qquad \text{(3)}$$

$$(\text{N}_3\text{S}_4\text{O}_6)_2^{-----} + 2 \text{ N}_3^- \longrightarrow 3 \text{ N}_2 + 2 \overset{*}{\text{N}_3}\text{S}_4\text{O}_6^{---} \qquad \text{(4)}$$

$$\overset{*}{\text{N}_3}\text{S}_4\text{O}_6^{---} \longrightarrow \text{N}_3^- + \text{S}_4\text{O}_6^{--} \qquad \text{(5)}$$

where (2) is the rate determining reaction step, and (3), (4) and (5) are instantaneous. $\overset{*}{\text{N}_3}\text{S}_4\text{O}_6^{---}$ is assumed to be an activated ion which decomposes readily. As the reaction step, in which iodine participates, is instantaneous, it is impossible to decide whether it is triiodide ions or iodine molecules — or both — which react. It is worth mentioning that a solution of iodine in alcohol reacts in the same way as a solution of iodine in potassium iodide.

SUMMARY

Kinetic investigations were carried out on the iodine-azide reaction catalyzed by potassium tetrathionate. The reaction was a second order reaction with respect to azide ions and tetrathionate ions. The rate of reaction was found to be independent of the concentration of iodine. The rate determining reaction step was a reaction between azide ions and tetrathionate ions. The old theory of Raschig [2] and Feigl [3], assuming formation of complex compounds between iodine and sulphur compounds, must be abandoned, and in its place a reaction mechanism is proposed, which shows a considerable analogy with that proposed by Feigl [4] and Browne [13] for the carbon disulphide catalyzed iodine-azide reaction. The energy of activation of the tetrathionate catalyzed iodine-azide reaction was determined.

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