

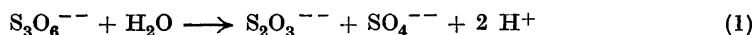
The Iodine-Azide Reaction

V. The Catalytic Effect of Trithionate Ions, and Their Decomposition in Aqueous Solution

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Kinetic investigations of the iodine-azide reaction catalyzed by tetrathionate ions^{1, 2}, pentathionate ions³, and carbon disulphide⁴ have shown that the rate of reaction is proportional to the concentrations of catalyst and of azide ions, but independent of the concentration of iodine. Therefore, it would have seemed natural if the trithionate catalyzed iodine-azide reaction had shown a similar kinetic picture, but this is not the case. According to Kurtenacker *et al.*⁵ trithionate decomposes in aqueous solution to thiosulphate and sulphate:



The rate of reaction is, within a pH-range of 9—5, independent of the pH. The thiosulphate ions formed according to (1) seem to be responsible for the iodine-azide reaction of trithionate.

EXPERIMENTAL

Potassium trithionate, $\text{K}_2\text{S}_3\text{O}_6$, was prepared according to the method of Kurtenacker and Matejka⁶. A polythionate analysis, as outlined by Kurtenacker⁷, was carried out. A double analysis gave the results: 99.8 and 100.0 % potassium trithionate, and no detectable impurities.

In case of the tetra²- and pentathionate³ catalyzed iodine-azide reaction, kinetic experiments could be carried out in a very simple way by determining the time of consumption of a definite amount of iodine with starch as the indicator, because the rate of reaction was independent of the concentration of iodine. The same method was used for trithionate, and although the rate of

reaction was proportional to the iodine concentration to a varying power of α , where $0 < \alpha < 1$, there was a clear and abrupt colour change when all the iodine was consumed. In other words, the rate of reaction did not become very small when the iodine concentration was very small.

Into a 300 ml Erlenmeyer flask were 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 freshly prepared 0.05 *M* potassium trithionate solution, and 0.2 ml 0.5 % starch solution. For the sake of temperature adjustment the flask was left in the thermostat water for 15 min. 0.00982 *N* iodine solution was now added dropwise until a faint blue colour was visible (1 or 2 drops were enough). The purpose of this addition of iodine was to convert the thiosulphate formed during the temperature adjustment, to tetrathionate. Thereafter 10 ml 0.00982

Table 1. Reaction between sodium azide and iodine at 25° C, catalyzed by potassium trithionate.

In all four experiments — besides the solutions mentioned in the table — were added 0.2 ml starch solution, and 30 ml solution which was 4.013 *M* with respect to sodium nitrate and 0.1 *M* to potassium iodide. The concentrations of the stock solutions used were: Potassium trithionate: 0.05 *M*; sodium azide: 0.5 *M*; iodine: 0.00982 *N* with respect to iodine and 0.02 *M* to potassium iodide; sodium acetate: 0.5 *M*.

Expt. no.		<i>t</i> Time of reaction in min
1	10 ml trithionate 10 ml iodine 10 ml sodium azide	8.65
2	10 ml trithionate 5 ml iodine 5 ml water 10 ml sodium azide	5.67
3	5 ml trithionate 5 ml iodine 10 ml water 10 ml sodium azide	12.28
4	10 ml trithionate 5 ml iodine 5 ml water 5 ml sodium acetate 5 ml sodium azide	6.95

N iodine, and after an additional 1 min. 10 ml 0.5 *M* sodium azide solution were added and the time of reaction determined. Carried out in this way the experiments were reproducible.

Expt. nos. 2 and 3 in Table 1 show that the time of reaction (*t*) was approx. inversely proportional to the concentration of trithionate, *i. e.* that the rate of reaction was directly proportional to the concentration of the catalyst. Expt. nos. 2 and 4 show that when the sodium azide concentration was halved, the time of reaction increased only by about 20 %.

When similar experiments were carried out in such a way that iodine solution was added *after* sodium azide solution, it was unmistakable that a considerable part of the iodine was consumed immediately with a brisk evolution of nitrogen. The only reasonable explanation is that the very small amounts of thiosulphate formed when the solution of trithionate, neutral salt, and starch was left for temperature adjustment, caused an instantaneous thio-sulphate catalyzed iodine-azide reaction. As the presence of sodium azide during the temperature adjustment did not alter the amount of thiosulphate formed, it seems evident that the trithionate catalyzed iodine-azide reaction actually is a thiosulphate catalyzed iodine-azide reaction, and that the thio-sulphate is formed by spontaneous decay of trithionate ions.

ENERGY OF ACTIVATION OF THE TRITHIONATE CATALYZED IODINE-AZIDE REACTION

The energy of activation was determined by experiments analogous to those previously described. In each experiment were used: 30 ml of a solution which was 4.013 *M* with respect to sodium nitrate and 0.1 *M* to potassium iodide, 10 ml 0.05 *M* potassium trithionate, 0.2 ml starch indicator, 10 ml 0.00982 *N* iodine which was 0.02 *M* with respect to potassium iodide, and 10 ml 0.5 *M* sodium azide. The reacting solution was 2 *M* with respect to sodium nitrate.

The reciprocal of the time of reaction (*t*) was used as a relative rate constant ($k_{\text{exp.}}$). Using the method of least squares, the numerical values of *H* and *A* were calculated according to the equation:

$$\log k_{\text{exp.}} = H - \frac{A}{T}$$

where *T* is the absolute temperature. The result is

$$\log k = 13.060 - \frac{4173}{T}$$

From this equation values of k were calculated by substituting T with the experimental temperatures. These values ($k_{\text{calc.}}$) are, together with the experimental ones, recorded in Table 2. The energy of activation is:

$$A \times 4.571 = 4173 \times 4.571 = 19\,070 \text{ cal/mole}$$

The frequency exponent H , of course, is not a true one, because the rate constants are only relative.

Table 2. Energy of activation of the trithionate catalyzed iodine-azide reaction.

In all the experiments were used: 30 ml of a solution which was 4.013 M with respect to sodium nitrate and 0.1 M to potassium iodide, 10 ml 0.05 M potassium trithionate, 0.2 ml starch indicator, 10 ml 0.00982 N iodine which was 0.02 M with respect to potassium iodide, and 10 ml 0.5 M sodium azide. The reacting solution was 2 M with respect to sodium nitrate. $k_{\text{exp.}}$ is the reciprocal of the time of reaction (t). $k_{\text{calc.}}$ was calculated from the equation $\log k = H - \frac{A}{T}$, which is a straight line fitted to the experimental k and T values.

Expt. no.	Temp. °C	t Time of reaction min	$k_{\text{exp.}}$	$k_{\text{calc.}}$
1	25	8.65	0.1156	0.1152
2	25	8.58	0.1165	
3	30	5.15	0.1942	0.1961
4	30	5.08	0.1969	
5	35	3.13	0.3195	0.3278
6	35	3.12	0.3205	
7	40	1.83	0.5464	0.5394
8	40	1.82	0.5494	

DECOMPOSITION OF TRITHIONATE IN AQUEOUS SOLUTION

According to Kurtenacker *et al.*⁵, trithionate — as already mentioned — decomposes in aqueous solution to thiosulphate and sulphate (eq. (1)). Within a pH-range of 9—5 no side reactions take place, and the rate of reaction is independent of the pH. Kurtenacker writes that the reaction probably is unimolecular when autocatalytic phenomena can be excluded. As thiosulphate ions usually catalyze decomposition of polythionates, it is to be expected that the rate of (1) will be proportional to the concentration of trithionate ions only when the degree of decomposition is small. Concerning the iodine-azide reaction, formation of only a small amount of thiosulphate is of interest, because just after formation the thiosulphate ions react rapidly with azide ions and iodine.

It was chosen to measure the rate of decomposition of trithionate ions in sodium acetate solutions because they yield a pH nearly the same as that of sodium azide solutions. According to Hughes⁸ the ionization constant of hydrazoic acid is about 2×10^{-5} at 25° C. Of course, sodium acetate solutions are not buffer solutions, and when the decomposition of trithionate ions takes place, the pH will be slightly altered due to the formation of hydrogen ions according to (1). But as the same would be the case in sodium azide solutions, and as experiments showed that the pH in the range 9—5 was of no influence, it was not necessary to use buffered solutions.

EXPERIMENTAL

100 ml aqueous solution, which was 0.1 *M* with respect to potassium trithionate and 0.5 *M* to sodium acetate, was placed in a water thermostat. Every 15 minutes 10.00 ml solution was taken out, and the thiosulphate formed was titrated with *y* ml 0.00978 *N* iodine solution. The degree of decomposition of trithionate was in none of the experiments larger than 1 per cent, so the concentration of trithionate ions could be considered constant.

From Table 3 it can be seen that the number of ml of 0.00978 *N* iodine used in the titration is directly proportional to the time of reaction (*t*). Using the method of least squares, the number of ml iodine solution per one minute time of reaction, were calculated. In Expt. no. 1 the concentration of trithionate was 0.2 *M*, while in no. 2 it was 0.1 *M*. The relation between ml iodine per minute time of reaction is seen to be as 2 to 1. Using the method of least squares, the relation between *y* and *t* in Expt. no. 1 was found to be: $y = 0.104 + 0.00888 \times t$. From this equation values of *y* were calculated by substituting *t* with the experimental times of reaction. These values ($y_{\text{calc.}}$) are, together with the

experimental ones, recorded in Table 3. The concentrations in Expt. no. 3 were the same as those in no. 2, except that acetic acid was added, so that pH was 5.1. This is about the pH at which reaction (1) no longer is the only one taking place. As was to be expected, the number of ml iodine per minute time of reaction was somewhat different from that in Expt. no. 2.

Table 3. Decomposition of potassium trithionate in aqueous solution at 25° C.

Concentrations in the experiments: Potassium trithionate: 0.2 *M* in no. 1, and 0.1 *M* in nos. 2 and 3. Sodium acetate: 0.5 *M* in all 3 experiments. In Expt. no. 3 was added acetic acid, so that the pH was 5.1. *y* is the number of ml 0.00978 *N* iodine used for titration of the thiosulphate formed in 10 ml of the reacting solution. *y*_{calc.} (Expt. no. 1) was calculated from the equation: $y = 0.104 + 0.00888 \times t$, which is a straight line fitted to the experimental *y* and *t* values.

<i>t</i> Time of reaction min	Expt. no. 1		Expt. no. 2	Expt. no. 3
	<i>y</i>	<i>y</i> _{calc.}	<i>y</i>	<i>y</i>
15	0.21	0.24	0.14	0.12
30	0.40	0.37	0.19	0.18
45	0.51	0.50	0.26	0.22
60	0.64	0.64	0.34	0.28
75	0.76	0.77	0.41	0.32
90	0.90	0.90	0.47	0.37
105			0.53	0.44
Ml iodine per minute time of reaction	0.00888		0.00448	0.00343
pH	~ 9		~ 9	5.1

ENERGY OF ACTIVATION OF THE DECOMPOSITION OF TRITHIONATE IONS

The rate of decomposition of trithionate ions in aqueous sodium acetate solution was determined at different temperatures by experiments analogous to those described above. The concentrations used were the same as in Expt. no. 2, Table 3.

Table 4. Energy of activation of the decomposition of trithionate ions into sulphate and thiosulphate ions.

Concentrations in the experiments: Potassium trithionate: 0.1 *M*; sodium acetate: 0.5 *M*. *y* is the number of ml 0.00978 *N* iodine used for titration of the thiosulphate formed in 10 ml of the reacting solution. $k_{\text{exp.}}$ is the rate constant calculated when assuming that the decomposition is a bimolecular reaction between trithionate ions and water molecules.

<i>t</i> Time of reaction min	Expt. 1. 25° C	Expt. 2. 30° C	Expt. 3. 35° C	Expt. 4. 40° C
	<i>y</i>	<i>y</i>	<i>y</i>	<i>y</i>
15	0.14	0.21	0.50	0.12
30	0.19	0.33	0.71	0.47
45	0.26	0.47	0.90	0.85
60	0.34	0.61	1.08	1.22
75	0.41	0.70	1.28	1.61
90	0.47	0.85	1.48	
105	0.53	0.97	1.66	
120		1.08		
Ml iodine per minute time of reaction	0.00448	0.00835	0.01286	0.02487
$k_{\text{exp.}} \times 10^7$	8.27	15.41	23.73	45.89
$k_{\text{calc.}} \times 10^7$	8.28	14.73	25.70	44.06

In Table 4 are given the number of ml 0.00978 *N* iodine (*y*) used for the titration of 10 ml of the reacting solution at different times of reaction. Using the method of least squares, the number of ml iodine solution per one minute time of reaction, were calculated for all 4 experiments. From these values the rate constants ($k_{\text{exp.}}$) were derived by assuming that the stoichiometric scheme (1) was also the kinetic equation of the reaction, so that:

$$\frac{da}{dt} = k_{\text{exp.}} \cdot a \cdot b$$

where *a* is the concentration of trithionate, *b* is the concentration of water, and $\frac{da}{dt}$ is the change in trithionate concentration per minute. For *b* was inserted the value 53, which is about the molar concentration of water in an

aqueous solution, which is 0.1 *M* with respect to potassium trithionate and 0.5 *M* to sodium acetate. Of course, it is most likely that the activity coefficient of water has not the value 1, but it is difficult to tell what the exact value is.

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

$$\log k_{\text{exp}} = H - \frac{A}{T}$$

where *T* is the absolute temperature. The result was:

$$\log k = 9.074 - \frac{4518}{T}$$

From this equation values of *k* were calculated by substituting *T* with the experimental temperatures. These values (*k*_{calc.}) are, together with the experimental ones, recorded in Table 4. The energy of activation is:

$$A \times 4.571 = 4518 \times 4.571 = 20650 \text{ cal/mole.}$$

DISCUSSION

The experimental evidence for thiosulphate ions (formed according to (1)) being responsible for the trithionate iodine-azide reaction is as follows. When sodium azide was added to an aqueous solution of potassium trithionate, which had been kept for *x* minutes in a thermostat, titration with iodine could be carried out with starch as the indicator. The consumed amount of iodine was of the same order of magnitude as the amount that was consumed when a comparable solution of trithionate, azide and iodine was allowed to react for *x* minutes.

The rate of reaction of the trithionate catalyzed iodine-azide reaction was not proportional to the azide ion concentration, as was the case with carbon disulphide⁴, tetrathionate^{1, 2}, and pentathionate³ ions. The energy of activation was found to be 19 070 cal. This value was surprisingly high keeping in mind that the energies of activation of the penta³⁻ and tetrathionate² catalyzed iodine-azide reactions were found to be respectively about 11 000 and 13 000 cal. When two kinetic experiments were carried out respectively with trithionate and tetrathionate as the catalysts, so that all concentrations were identical, the two rates of consumption of iodine were of the same order of

magnitude irrespective of the actual concentrations. This fact, together with the large difference in energies of activation, also indicated a different reaction mechanism.

The energy of activation of the decomposition of trithionate ions to thiosulphate and sulphate ions was found to be 20 650 cal. This value is 1580 cal. larger than that of the iodine-azide reaction (19 070 cal.). Assuming that the thiosulphate formed by the decomposition of trithionate was responsible for the iodine-azide reaction, this difference could be accounted for by an observation of Dodd and Griffith¹, p. 548. If thiosulphate acts as catalyst on the iodine-azide reaction, a considerable number of iodine molecules will be consumed per molecule thiosulphate consumed. The thiosulphate will be converted partly to tetrathionate and partly to sulphate. The ratio R (moles I_2 consumed/moles $Na_2S_2O_3$ consumed) is somewhat dependent on temperature. A decrease of temperature from 18° to 1° C increases R by about 20 %. This temperature dependency, found by Dodd and Griffith, could be calculated to correspond to an apparent, negative energy of activation of 1700 cal., which agrees very well with the found difference of 1580 cal.

SUMMARY

Kinetic investigations have been carried out on the iodine-azide reaction catalyzed by trithionate ions. The energy of activation was determined to be 19 070 cal/mole. The mechanism of reaction was definitely different from that of the tetra²- and pentathionate³ catalyzed. Determination of the energy of activation of the spontaneous decomposition of trithionate ions to sulphate and thiosulphate ions, seemed to show that the thiosulphate ions formed by this decomposition were responsible for the trithionate catalyzed iodine-azide reaction.

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