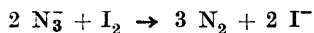# The Iodine-Azide Reaction

III. The Catalytic Effect of the Pentathionate Ion

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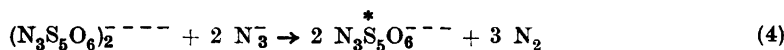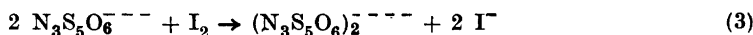
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The iodine-azide reaction was discovered by Raschig [1], who found that sodium thiosulphate and sulphide act as catalysts. The overall equation of the reaction is:

$$2 \text{ N}_3^- + \text{I}_2 \rightarrow 3 \text{ N}_2 + 2 \text{ I}^-$$

It is believed that only compounds which contain sulphide sulphur catalyze the reaction. Metz [2] has shown that tri-, tetra-, and pentathionate act as catalysts. The tetrathionate catalyzed reaction was investigated kinetically by Dodd and Griffith [3] and Hofman-Bang [4]. The rate of reaction was found to be directly proportional to the concentrations of tetrathionate and of azide ions, and independent of the concentration of iodine. It was shown [4] that 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. A few introductory experiments with potassium pentathionate as the catalyst, showed that the rate of reaction, also in this case, was independent of the concentration of iodine, so that the same simple method could be used.

A reaction mechanism similar to that of the tetrathionate catalyzed iodine-azide reaction is proposed in analogy with that of the carbon disulphide catalyzed iodine-azide reaction [5,6]:

$$\text{N}_3^- + \text{S}_5\text{O}_6^{--} \rightarrow \text{N}_3\text{S}_5\text{O}_6^{---} \tag{2}$$

$$2 \text{ N}_3\text{S}_5\text{O}_6^{---} + \text{I}_2 \rightarrow (\text{N}_3\text{S}_5\text{O}_6)_2^{----} + 2 \text{ I}^- \tag{3}$$

$$(\text{N}_3\text{S}_5\text{O}_6)_2^{----} + 2 \text{ N}_3^- \rightarrow 2 \overset{*}{\text{N}}_3\text{S}_5\text{O}_6^{---} + 3 \text{ N}_2 \tag{4}$$

$$\overset{*}{\text{N}}_3\text{S}_5\text{O}_6^{---} \rightarrow \text{N}_3^- + \text{S}_5\text{O}_6^{--} \tag{5}$$

where (2) is the rate determining reaction step, and (3), (4), and (5) are instantaneous. $N_3\overset{*}{S}_5O_6^{---}$ is assumed to be an activated ion which decomposes readily.

REAGENTS

Sodium azide: Sodium azide as previously described [4], was used. Potassium pentathionate, $K_2S_5O_6$, $1\frac{1}{2}$ H_2O: This salt was prepared according to Stamm, Seipold, and Goehring [7], and analyzed according to Kurtenacker [8] and Foss [9]. The prepared salt was found to be 98.2 % pure, and dissolved in water without any sulphur being seen. An impurity of approx. 2 % tetrathionate was in this case of no importance, because pentathionate turned out to be a much more powerful catalyst than tetrathionate.

The other reagents used were all of analytical grade.

EXPERIMENTAL PROCEDURE

(For further details see ref. 4.) 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, 0.2 ml 0.5 % starch solution, 10 ml 0.00978 N iodine in potassium iodide, and 10 ml 0.5 M sodium azide. The flask was placed in a water thermostat, and after the elapse of 15 minutes (for sake of temperature adjustment), 10 ml approx. 0.0002 M potassium pentathionate solution was added. The instant all the iodine present had been consumed, the blue colour of the experimental solution disappeared. When less than 10 ml iodine solution was used, water was added, so that the volume of the reacting solution was the same. Also for potassium pentathionate solution, water was used as substitute, whereas the substitute for sodium azide solution was 0.5 M sodium nitrate, so that the ionic strength did not change. The reacting solution was 2 M with respect to sodium nitrate. The purpose of the addition of potassium iodide is partly to prevent a considerable percentile change of the iodide ion concentration during the reaction, and partly to produce a sharp colour change.

EXPERIMENTAL RESULTS

The concentrations in the kinetic experiments were chosen so that the time of reaction would be only a few minutes. According to Kurtenacker et al. [10] pentathionate decomposes in aqueous solution to predominantly sulphur and tetrathionate. The rate of decomposition is fairly large at 25° C and is, within a pH-range of 9—5, independent of pH. In each experiment a fresh solution of potassium pentathionate was prepared by dissolving the salt

Table 1. Reaction between sodium azide and iodine at 25° C. Catalyst: Potassium penta-
thionate. In all 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: 0.000193
M potassium pentathionate; 0.5 M sodium azide; 0.00978 N iodine, which was 0.02 M with
respect to potassium iodide. The rate constants, k, were calculated according to equation (1).

Expt. no.		c	a	x	t Time in min	k
1	10 ml pentathionate 10 ml iodine 10 ml sodium azide	0.0000321	0.0831	0.00163	3.18	194
2	5 ml pentathionate 5 ml water 10 ml iodine 10 ml sodium azide	0.0000160	0.0831	0.00163	7.07	175
3	5 ml pentathionate 5 ml iodine 10 ml water 10 ml sodium azide	0.0000160	0.0831	0.00081	3.27	187
4	10 ml pentathionate 5 ml iodine 5 ml water 5 ml 0.5 M sodium nitrate 5 ml sodium azide	0.0000321	0.0415	0.00081	2.85	215
5	10 ml pentathionate 10 ml iodine 10 ml sodium azide	0.0000321	0.0831	0.00163	3.22	192

in water preheated to the experimental temperature, so that an experiment
could be started about one minute later. In none of the experiments was any
sulphur seen immediately after the iodine-starch colour had disappeared, but
when the solution was allowed to stand for an additional 30 minutes, a slight
opalescence was noticeable.

From the experimental results (see Table 1) it is seen that the rate of reac-
tion is approx. proportional to the concentrations of potassium pentathionate
and sodium azide, and independent of the concentration of iodine. The results
are not really fine, but the reason is probably that pentathionate so easily

decomposes to tetrathionate and sulphur; it is, in this connection, worth noticing that the rate constant seems to increase with decreasing time of reaction. The rate constants, k, in Table 1, are calculated from the integrated rate expression:

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

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

ENERGY OF ACTIVATION

The energy of activation of the pentathionate catalyzed iodine-azide reaction was determined by experiments analogous to those described above. The rate of reaction was determined at 20°, 25°, and 30° C. 30 ml solution, which was 4.013 M with respect to sodium nitrate and 0.1 M to potassium iodide, 10 ml 0.00978 N iodine, 10 ml 0.5 M sodium azide, 0.2 ml starch indicator, and 10 ml 0.000193 M potassium pentathionate were used in each experiment. In Table 2 are given the rate constants ($k_{exp.}$) calculated according to

Table 2. Energy of activation of the pentathionate catalyzed iodine-azide reaction. Concentrations in all experiments: $a = 0.0831$ M; $c = 0.0000321$ M; $x = 0.00163$ M. $k_{exp.}$ is the rate constant in each case calculated 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. The reacting solution was 2 M with respect to sodium nitrate.

Expt. no.	Temp. °C	t Time in min	$k_{exp.}$	$k_{calc.}$
1	20°	4.40	140	140
2	20°	4.45	139	140
3	25°	3.22	192	192
4	25°	3.25	190	192
5	30°	2.37	260	260
6	30°	2.37	260	260

equation (1). 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 resulting expression is:

$$\log\ k = 10.337 - \frac{2401}{T}$$

By substituting the experimental temperature for T, is calculated $k_{\text{calc.}}$,
which also is given in Table 2. The energy of activation was found to be:

$$A \times 4.571 = 2401 \times 4.571 = 10970 \text{ kcal/mole}$$

The energy of activation of the tetrathionate catalyzed iodine-azide reaction [4]
is approx. 2000 kcal larger, which is also to be expected, as the tetrathionate
reaction is ca. 30 times slower than the pentathionate reaction. The frequency
exponents are nearly identical, resp. 10.34 and 10.47 with minutes as unit.

Although pentathionate does not seem to decompose much in the experi-
ments carried out, it was nevertheless ascertained that a visible evolving of
a gas took place, when rather concentrated solutions of sodium azide and
potassium pentathionate were mixed. This reaction was definitely more rapid
than the corresponding tetrathionate-azide reaction [4]. The gas was analyzed *
according to Christiansen and Wulff [11]; the result was 98.4 % nitrogen, 0.7 %
oxygen, and perhaps a trace of hydrogen. A buffered solution with pH approx.
5, and a solution of sodium azide and potassium pentathionate only, gave
practically the same results. The small percentage of oxygen was probably due
to contamination by atmospheric air. Consequently it is believed that penta-
thionate ions oxidize azide ions essentially to free nitrogen.

EXPERIMENTS WITH POTASSIUM HEXATHIONATE

Potassium hexathionate was prepared according to Weitz and Achterberg [12]
and Stamm, Seipold and Goehring [7]. A few experiments with hexathionate
as the catalyst were carried out in the same way as with pentathionate. The
results were the same as those with pentathionate, and even the rate constant

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

was the same within a few percent. The reason presumably is that hexathionate decomposes almost instantaneously to pentathionate and sulphur in a slightly basic solution.

SUMMARY.

Kinetic investigations were carried out on the iodine-azide reaction catalyzed by potassium pentathionate. It was a second order reaction with respect to azide and pentathionate ions. The rate of reaction was found to be independent of the concentration of iodine. This kinetic behaviour is analogous to that of the tetrathionate catalyzed iodine-azide reaction [3,4]. The energy of activation was determined to be 10970 kcal/mole in 2 M sodium nitrate solution.

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