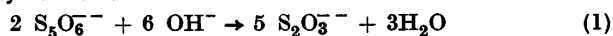# The Kinetics of Decomposition of Potassium Pentathionate in Alkaline Solution

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The velocity of the reaction

$$2 \ S_5O_6^{--} + 6 \ OH^- \rightarrow 5 \ S_2O_3^{--} + 3H_2O \qquad (1)$$

has been found to be proportional to the concentrations of pentathionate and hydroxyl ions to the first power and to show a positive salt effect as to be expected from a rate-determining step involving two ions with one and two charges of the same sign, respectively.

The velocity is — *ceteris paribus* — independent of the presence of $S_2O_3^{--}$, $S_4O_6^{--}$, NH_3 or CH_3COO^-.

A discussion of these results shows that the first and rate-determining step in the sequence of reactions resulting in (1) is

$$S_5O_6^{--} + HO^- \rightarrow S_2O_3^{--} + HOSS_2O_3^-$$
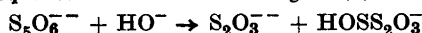
An automatic device called a potentiostat is described.

Previous investigations (for references see Foss [1] and Goehring [2]) have shown that pentathionate ions in aqueous alkaline solution are decomposed into thiosulphate ions, free sulphur and tetrathionate ions.

At the beginning of the reaction the only changes which are observed are the disappearance of pentathionate and hydroxyl ions and the formation of thiosulphate. Then, very sudden liberation of free sulphur occurs which makes the solution opaque and, at the same time, an equivalent amount of tetrathionate is formed [2,4]. This reaction is catalysed by sulphur [4] and thiosulphate [4] *i.e.* it is autocatalytic. Analysing the reaction mixture before the occurrence of free sulphur Kurtenacker [4] showed that the initial reaction stoichiometrically agrees with

$$2 \ S_5O_6^{--} + 6 \ OH^- \rightarrow 5 \ S_2O_3^{--} + 3 \ H_2O \qquad (1)$$
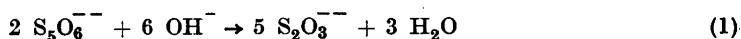
We have been able to show that, within 0.5 per cent, this is also the case when the reaction is performed under the experimental conditions used by us, which

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allow us to measure the amount of base consumed and, by titration with iodine, of the thiosulphate formed. Also the consumption of pentathionate was found to agree stoichiometrically with the consumption of base within a few per cent.

Kurtenacker [4] concluded, from experiments by Foerster [5] and his own results, that reaction (1) proceeds through the following steps:

$$S_5O_6^{--} + 2\ OH^- \rightarrow S(OH)_2 + 2\ S_2O_3^{--} \tag{2}$$

$$2\ S(OH)_2 + 2\ OH^- \rightarrow S_2O_3^{--} + 3\ H_2O \tag{3}$$
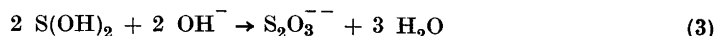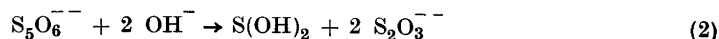
The assumption of sulphoxylic acid $S(OH)_2$ as an intermediate and of its conversion into thiosulphate is strongly supported by the experiments of Goehring [2], by the reaction between pentathionate and piperidine to yield sulphur dipiperidide described by Foss [1] and, finally, by the experiments of Meuwsen and Gebhardt [6] on the reaction between sulphur diethoxide and base to form thiosulphate, alcohol and alcoholate. As precise kinetic measurements on reaction (1) have not been published we decided to undertake such measurements, in an attempt to elucidate its mechanism. In consequence of the side reaction producing sulphur and tetrathionate, reaction (1) could be followed only until about 20 per cent of the pentathionate was converted. For this reason the technique chosen consisted in making a number of experiments with different initial concentrations, continuing each experiment only long enough to determine the initial velocity with the necessary accuracy.

EXPERIMENTAL

Potassium pentathionate was prepared according to Goehring [3] and recrystallized four times. The product formed a clear solution with water and analysis by the method of Foss [1] gave 98.2 per cent assay. No traces of sulphate, sulphite, thiosulphate, trithionate, chloride or free sulphur were found. The remainder was tetrathionate. The reactions were performed in a thin-walled glass cylinder 4 cm high, 15 ml capacity, which was fitted with a stirrer of glass, glass electrode, calomel electrode, inlet capillary for the addition of the base and inlet and outlet tubes for passing nitrogen freed from carbon dioxide over the solution. This reaction vessel was immersed in a water thermostat, operating at $20.00° \pm 0.05°$ C. By means of the E.M.F. between the electrodes in the reaction mixture, an automatic device described below maintained the OH^- activity at a constant value by adding the required amounts of N or $0.1\ N$ potassium hydroxide to the mixture.

The electrodes were connected to a pH-meter (valve potentiometer) with constant zero point reading and constant amplification factor (Radiometer's A.C. fed "PHM 22"), which instrument furnishes a current varying linearly with pH. Across a rheostat the current produces a voltage which is nearly compensated. The "unbalance" is sent

through a mirror galvanometer. When the pH reaches a certain value, the mirror galvano-meter permits a light beam to act upon a photocell which in turn controls a pulse genera-tor. The electrical pulses drive a relay which acts upon a micrometer screw through a saw-toothed gear to push in the glass piston in a hypodermic syringe, thus delivering the reagent to the reaction mixture. This addition of base changes the pH and causes the galvanometer mirror to turn the light beam away from the photocell. The pulses then cease until the pH value desired is again passed by the consumption of hydroxyl ions in the reaction with pentathionate ions. After calibration of the micrometer screw and syringe this device, called a pH-stat or potentio-stat, permits the measurement of the amount of base consumed which is a measure of the degree of conversion. The apparatus works satisfactorily only when care is taken to keep the glass electrode sufficiently con-stant from the very beginning of the experiment. For this reason the glass electrode was placed for some hours before each run in a dilute buffer solution with the required pH. Then it was wiped off with a piece of filtering paper (but not rinsed) before it was immer-sed in the reaction mixture, the pH of which had been previously adjusted by means of an empirically determined amount of base. The pH-meter readings were standardized at closely spaced values over the whole pH range investigated, by means of standard buffer solutions. The constancy of the pH during each run was $\pm$ 0.01 to $\pm$ 0.02 pH units. The reaction mixture was composed of measured volumes of freshly prepared potassium pentathionate, hydroxide and chloride solutions. In order to follow the reac-tion during the first few seconds it was necessary in case of the fastest reactions that the apparatus was in operation before the addition of pentathionate. The results for a typical experiment are given below.

Table 1.

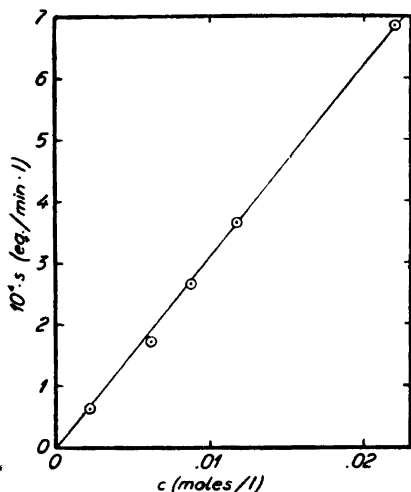| Time minutes	Micrometer screw readings cm	
	exp.	calc.
0.00	(3.739) *	(3.739)
0.65	3.753	3.753
1.00	60	60
1.25	64	65
1.50	69	70
1.75	75	76
2.00	81	81
2.25	86	86
2.50	91	92
3.00	3.800	3.802
3.50	09	12
4.00	17	23
4.50	26	34
5.00	35	44

* extrapolated

Fig. 1. The initial velocity s *measured in equivalents of potassium pentathionate per minute per litre reaction mixture versus the pentathionate concentration* c *in moles per litre.*

pH = 9.81; μ = 1.50; temperature 20.0° C; base: 0.100 N Potassium hydroxide; total volume 10.0 ml.

In the reaction vessel: 12 ml solution with $c_{S_5O_6}^{--}$ = 0.00897, μ = 0.83 (by means of KCl), pH = 10.50. Calibration of syringe: 1 cm = 0.418 ml. Titrator: 1.00 N KOH.

From a plot of micrometer screw readings *versus* time the initial velocity is found as the slope of a straight line fitting with the first 8 points. Slope = 0.0210 cm/min. = $8.78 \cdot 10^{-6}$ eq./min.

$s = 8.78 \cdot 10^{-6}/0.012 = 7.32 \cdot 10^{-4}$ eq./min. l; $k = s/3c_{S_5O_6}^{--} = 2.72 \cdot 10^{-2}$ min^{-1}.

RESULTS

1. From Fig. 1 it is seen that at constant pH and ionic strength the initial base consumption velocity *s* measured in equivalents of potassium hydroxide per minute per liter reaction mixture is proportional to the pentathionate concentration. So we may write

$$s = k_1 \cdot c_{S_5O_6}^{--}$$

From (1) we derive, at constant c_{OH}^{-}

$$-\frac{dc_{S_5O_6}^{--}}{dt} = \frac{1}{3} s$$

or

$$-\frac{dc_{S_5O_6}^{--}}{dt} = k \cdot c_{S_5O_6}^{--}$$

where

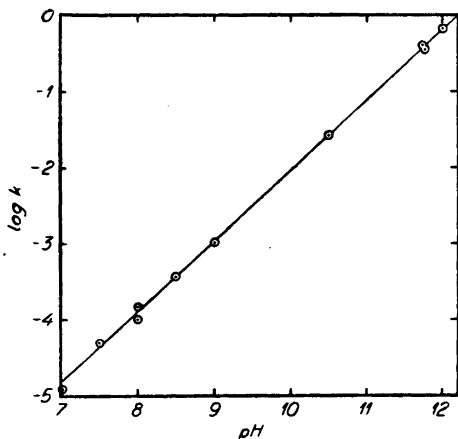$$k = \frac{1}{3} k_1 = \frac{s}{3 \, c_{S_5O_6}^{--}} = \text{a constant}$$

Fig. 2. The logarithm of the velocity constant $k = d \ln c/dt$ (min^{-1}) versus pH. $\mu = 0.83$; temperature 20.0° C.
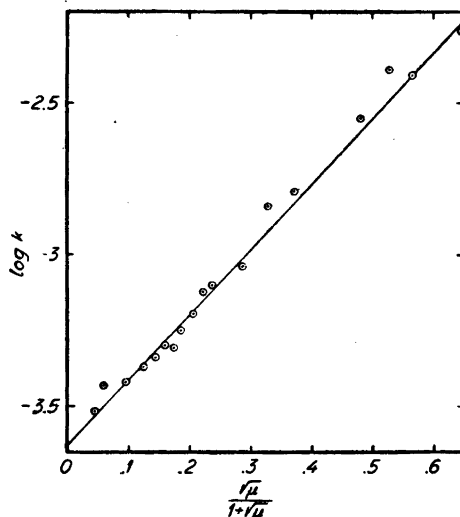
Fig. 3. log k versus $V\mu/(1 + V\mu)$. pH = 10.50. Temperature 20.0° C. Except at the lowest ionic strengths the concentration of pentathionate was 0.00673 M.

This shows that the reaction is of the first order with regard to pentathionate and the last equation allows us to calculate the rate constant from the experimental results.

  2. From Fig. 2 we find

$$\log k = 0.96 \text{ pH} + \text{a constant} \quad (7 \leq \text{pH} \leq 12)$$

so the reaction is almost first-order with regard to the hydroxyl ion concentration. The deviation from first order is only four per cent, which corresponds to the factor $10^{0.2} = 1.6$ over the interval investigated. This deviation is most probably due to systematic errors although we have not been able to trace their origin. In the following discussion we shall consider the reaction to be first order with respect to hydroxyl ion as well as to pentathionate ion.

  Therefore the rate-determining step is a reaction between a pentathionate ion and a hydroxyl ion. As these two ions have the same sign, the rate must show a positive salt effect.

  3. Fig. 3 provides a qualitative proof of this. To test it quantitatively we calculate the influence of changing the ionic strength at constant hydroxyl ion activity (activity because a potentiometric method was used).

Assuming, according to Brønsted [7] that a pentathionate ion A and a hydroxyl ion B form a complex M

$$A + B \rightleftharpoons M \rightarrow \ldots$$
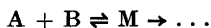
and the velocity is proportional to the concentration of this complex, we have

$$-\frac{dc_A}{dt} = k' \, c_M$$

Using the thermodynamic equilibrium constant

$$K = \frac{a_M}{a_A \, a_B}$$

and the relation between activity, activity coefficient and concentration

$$a = f \, c$$

we derive

$$-\frac{dc_A}{dt} = k' \, K \, c_A \, a_B \frac{f_A}{f_M} = k'' \, c_A \frac{f_A}{f_M}$$

or

$$\log k = \log\left(-\frac{d \ln c_A}{dt}\right) = \log f_A - \log f_M + \text{a constant}$$

Introducing the Debye-Hückel equation as modified by Güntelberg [8]

$$\log f_z = -0.50 \, z^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}}$$

which gives a good approximation up to $\mu = 0.1$ we arrive at

$$\log k = 0.50 \, (z^2_M - z^2_A) \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + \text{a constant.}$$

With $z_A = -2$, $z_B = -1$, $z_M = z_A + z_B = -3$, this salt effect equation becomes

$$\log k = 2.5 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + \text{a constant}$$

whilst with $z_A = z_B = -1$, $z_M = -2$ it becomes

$$\log k = 1.5 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + \text{a constant.}$$

The experimental value 2.2 obtained from the slope of the line in Fig. 3 is close to 2.5 and seems therefore to decide for the first choice.

4. Investigation has shown that the velocity is not influenced by the presence of thiosulphate, trithionate or tetrathionate ions, except for their contribution to the ionic strength. This enables us to exclude certain mechanisms otherwise possible.

5. Finally we have examined whether the reaction is generally base-catalysed. At pH 10.50 and $\mu = 0.83$ a part of the potassium chloride was substituted by ammonium chloride to such an extent that the concentration of free ammonia was 0.067 M (calculated) and in other experiments by potassium acetate to give an acetate ion concentration of 0.083 M (calculated). In both instances we found within 10 per cent the same velocity as usually at this pH and ionic strength. This agrees with results obtained by Foss [1, p. 113] concerning the influence of acetate ions.

Therefore we conclude that the reaction is a reaction with the hydroxyl ion.
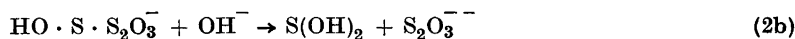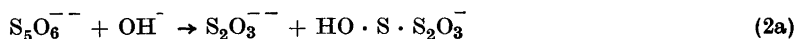
6. The numerical results of the present investigation can be expressed in the following empirical equation

$$\log k = -12.7 + 0.96 \text{ pH} + 2.2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \pm 0.1 \text{ at } 20.0° \text{ C}$$

where $k = \dfrac{\mathrm{d}\ln c_{S_5O_6}{}^{--}}{\mathrm{d}t} \text{min}^{-1}$, $7 \leq \text{pH} \leq 12$, $0 < \mu \leq 3.3$.

CONCLUSION

All our results agree with the equations (2) and (3), when (2) is split up in (2a) and (2b)

$$S_5O_6{}^{--} + OH^- \rightarrow S_2O_3{}^{--} + HO \cdot S \cdot S_2O_3^- \tag{2a}$$

$$HO \cdot S \cdot S_2O_3^- + OH^- \rightarrow S(OH)_2 + S_2O_3{}^{--} \tag{2b}$$

(2a) is rate determining and (2b) is not.

This is seen as follows: If (2b) were rate determining (2a) must be reversible. But in that case the overall velocity would be proportional to the square of the hydroxyl ion concentration and the reaction would be inhibited by thiosulphate ions, both of which results disagree with the experiments.

According to Foss [1] (2a) is also the first step in the reaction yielding sulphur + tetrathionate (l.c.p.113) the next step being

$$HO \cdot S \cdot S_2O_3^- + S_2O_3{}^{--} \rightarrow S_4O_6{}^{--} + S + OH^-$$
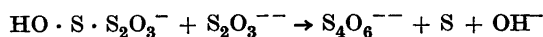
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