Kinetics of the Oxydation of Red Phosphorus by Potassium Bromate

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(Received September 20, 1955)

Potassium bromate is a powerful oxidising agent in acid solution. Reducing agents convert it smoothly into the bromide:

$$BrO_3^- + 6H^+ + 6\epsilon = Br^- + 3H_2O.$$

At the end of the reaction free bromine appears:

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O.$$

Numerous quantitative oxidation processes involving the use of potassium bromate show that its oxidising property is almost equivalent to that of potassium iodate[1-5].

Many quantitative oxidation reactions with potassium bromate[6], iodate[7], periodate[8], ceric sulphate[9], and iodine[10] as powerful oxidising agents for the oxidation of red phosphorus have been studied by earlier workers.

The use of potassium bromate in the volumetric determination of elementary red phosphorus has been investigated by Deshmukh and Sant[6]. They have observed that the addition of acidified potassium bromate solution to phosphorus leads to its gradual disappearance accompanied with a rapid evolution of bromine. The method is based on the oxidation and subsequent conversion of phosphorus into phosphoric acid. Bromine liberated during the process or the unreacted bromate after the completion of the reaction is estimated iodometrically and the amount of phosphorus is calculated from the following reaction mechanism:

$$2P + 2KBrO_3 + H_2SO_4 + 2H_2O \longrightarrow 2H_3PO_4 + Br_2 + K_2SO_4.$$

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[1] S. Győry, *Z. anal. Chem.*, **32**, 415 (1893).

[2] A. Kurtenacker and J. Wagner, *Z. anorg. allgem. Chem.*, **120**, 261 (1922).

[3] R. Lang, *Z. anal. Chem.*, **106**, 12 (1935).

[4] R. Lang, *Z. anorg. allgem. Chem.*, **142**, 229 (1925).

[5] E. Rimini, *Gazz. chim. ital.*, **29**, 265 (1899).

[6] G.S. Deshmukh and B.R. Sant, *Anal. chem.*, **24**, 901 (1952).

[7] T.F. Büehrer and O.E. Schupp, *J. Am. Chem. Soc.*, **49**, 9-15 (1927).

[8] G.S. Deshmukh and M. Venugopalan, *J. Ind. Chem. Soc.*, **32**, 309-312, (1955).

[9] G.S. Deshmukh, *Analyst*, **76**, 604, (1951).

[10] G.S. Deshmukh and M. Venugopalan, *J. Ind. Chem. Soc.*, **30**, 747-750 (1953); **32**, 305-308 (1955).

Experience, however, has shown that the rate of the above oxidation process is measurably slow at ordinary temperatures. Hence, it was of interest to study the kinetics of this oxidation process in some detail.

Experimental

Red phosphorus of British Drug House laboratory reagent grade quality was purified by Buehrer and Schupp's method[7] and subsequently by the copper phosphide process[3]. Its purity was checked by the magnesium pyrophosphate and bromate procedures.

An accurately weighed quantity of the sample was introduced in a ground-glass stoppered Erlenmeyer flask to which a known excess of standard potassium bromate solution was added, followed by 5 to 10 ml. of carbontetrachloride. Acidified with about 5 to 10 ml. of 4N sulphuric acid so that the overall acidity of the system was maintained at or about 0.5N sulphuric acid. The flask was maintained at a desired constant temperature for thirty minutes prior to the addition of potassium bromate and also during the course of subsequent observations in an electrically heated thermostat fitted with an accurately calibrated automatic thermoregulator. The contents of the flask were swirled from time to time and an aliquot portion (5 ml.) of the clear supernatent aqueous layer was pipetted out carefully at different time intervals and titrated iodometrically by standard thiosulphate[11]. Series of experiments were carried out at different temperatures, viz., 30°, 35°, 40°, 45°, 50° atd 55°C using the same conditions for concentrations and also by varying the concentrations of potassium bromate and the weight of red phosphorus over a fairly wide range.

Results and Discussion

From the initial titre value of bromate and that obtained at various time intervals during the course of the oxidation, the order of the reaction was calculated by the integration method. Under the given operative conditions the value of K was found to be constant and within limits of experimental error according to the following equation:

$$K=\frac{2.303}{tC_\infty}\log_{10}\frac{C_t(C_0-C_\infty)}{C_0(C_t-C_\infty)}$$

where C_0—initial concentration of potassium bromate;

C_t—concentration of potassium bromate at time t;

C_∞—concentration of potassium bromate at time ∞;

and t—time in minutes.

A representive group of results is shown in Table I.

TABLE I

Temperature: 45°C Weight of phosphorus: 0.02 g.
Reaction mixture: 5 ml. Concentration of $KBrO_3$: 40 ml. N/5 solution.

Time	N/10 Thiosulphate	$\log_{10}\frac{C_t(C_0-C_\infty)}{C_0(C_t-C_\infty)}$	$K\times10^{-3}$
0 min.	8.5 ml.	—	—
5	8.2	0.0174	1.8
15	7.85	0.0405	1.4
30	7.3	0.0774	1.4
50	6.7	0.1438	1.5
85	6.05	0.2477	1.5
∞	4.4	—	—

Mean $K=1.5\times10^{-3}$

The results in Table I therefore show that the oxidation of red phosphorus by potassium bromate is an overall second order reaction.

A reaction of the second order depends principally on the initial concentration of the reactants, the half value period and the temperature at which the reaction is carried out. The variation of the velocity constant K with temperature for the same initial concentrations of the reactants is represented in Table II.

TABLE II

Weight of Phosphorus taken: 0.02 g.
Concentration of bromate: 40 ml. N/5 solution.
Normality of thiosulphate: 0.1 N.

Temperature (t)	Mean $K\times10^{-3}$
30°C	0.35
35	1.00
40	1.40
45	1.50
50	1.90
55	4.85

From the results, it can be inferred that the velocity constant K increases as the temperature increases; the values of $\log_{10}\frac{C_t(C_0-C_\infty)}{C_0(C_t-C_\infty)}$ plotted against time t for different temperatures, at which the reaction has been studied, are represented graphically in Fig. 1.

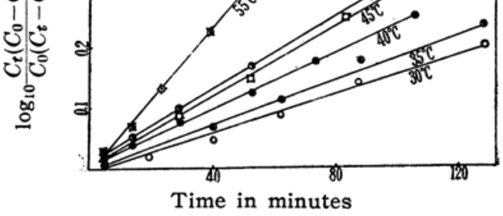

Fig. 1. Variation of $\log_{10}\frac{C_t(C_0-C_\infty)}{C_0(C_t-C_\infty)}$ with temperaure.
Wt. of P=0.02 g.
Conc. of $KBrO_3$=40 cc. N/5 soln.

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[11] A. I. Vogel, "Text Book of Quantitative Inorganic Analysis," London, Longmans, Green and Co., 1945, p. 451.

The variation of the velocity constant K for different initial concentrations of the reactants has been studied by varying the concentration of bromate solution and keeping the weight of phosphorus constant in all the experiments. A typical set of results is returned in Table III.

TABLE III

Temperature: 30°C.
Weight of phosphorus taken: 0.02 g.
Normality of thiosulphate: 0.1 N.

Expt. No.	Concentration of $KBrO_3$ added	Mean $K\times10^{-3}$
1.	40 ml. N/5 solution	0.35
2.	〃 N/6 〃	0.52
3.	〃 N/9 〃	0.94

TABLE IV

Temp. absolute T_1-T_2	$K_1\times10^{-3}$	$K_2\times10^{-3}$	Temp. coeff. K_2/K_1	Energy of activation $E=\frac{2.303\log_{10}K_2/K_1\times R\times T_1\times T_2}{T_2-T_1}$
303–313°	0.35	1.40	4.00	26290 g. cals.
308–318	1.00	1.50	1.50	7942
313–323	1.40	1.90	1.36	6215
318–328	1.50	4.85	3.23	24450

Fig. 2 represents graphically the variation of $\log_{10}\frac{C_t(C_0-C_\infty)}{C_0(C_t-C_\infty)}$ with time for different initial concentrations of bromate at the same temperature.

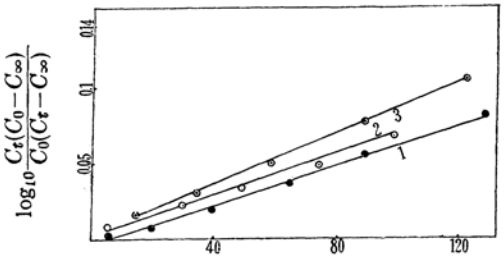

Fig. 2. Variation of $\log_{10}\frac{C_t(C_0-C_\infty)}{C_0(C_t-C_\infty)}$ with time for different concentration of potassium bromate.

Wt. of P=0.02 g. Conc. of $KBrO_3$
1. 40 ml. N/5 soln.
2. 〃 N/6 〃
3. 〃 N/9 〃

The energy of activation and the temperature coefficient were calculated from the values obtained for K at different temperatures T_1 and T_2 as indicated in Table IV.

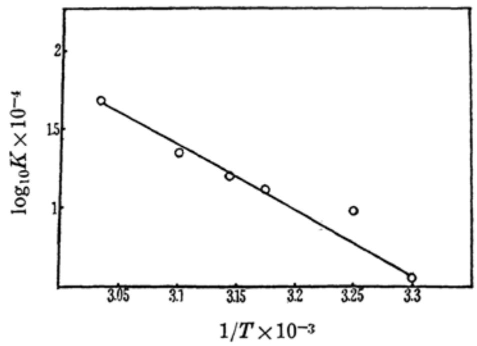

Fig. 3. Variation of $\log_{10}K$ with $1/T$.

The variation of log K with $1/T$ is shown in Table V; the results are plotted in Fig. 3. The linear relationship between log K and $1/T$ (Fig. 3) is in accord with the Arrhenius equation[12] which expresses the influence of temperature on reaction velocity.

TABLE V

Temp. absolute	$1/T\times10^{-3}$	$K\times10^{-4}$	$\log_{10}K\times10^{-4}$
303	3.30	3.5	0.5441
308	3.25	10.0	1.0000
313	3.17	14.0	1.1461
318	3.14	15.0	1.1761
323	3.10	19.0	1.2788
328	3.05	48.5	1.6857

The essential bimolecularity of the overall oxidation process shows that the molecular ratio of P to $KBrO_3$ is 1:1 which is in agreement with the earlier observation of Deshmukh and Sant[6].

Nature of the Reactions involved

The reactions involved in the oxidation of phosphorus by $KBrO_3$ have been found to take place as follows:

$$5P+3BrO_3^-+3H^++6H_2O=3/2Br_2+5H_3PO_3 \qquad (i)$$

This reaction is slow and goes partially to phosphoric acid.

$$2P+3Br_2+6H_2O=6H^++6Br^-+2H_3PO_3 \qquad (ii)$$

This reaction is quite rapid.

$$5H_3PO_3+2BrO_3=Br_2+3H^++5H_2PO_4^-+H_2O \qquad (iii)$$

This reaction is very slow as is strikingly shown by adding $KBrO_3$ to a phosphorus

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[12] Arrhenius, *Z. phys. Chem.*, 4, 226 (1889); *Trans. Farad. Soc.*, 33, 72 (1937).

acid solution. Very little bromine is liberated even on refluxing the solution for some time.

$$H_3PO_3+Br_2+H_2O=3H^++2Br^-+H_2PO_4^- \quad (iv)$$

This reaction has been shown by a number of authors to be slow, and to depend in large measure upon the acid concentration. It appears that the oxidation of phosphorus acid by bromine determines the rate of reaction as a whole.

$$5Br^-+BrO_3^-+6H^+=3Br_2+3H_2O \quad (v)$$

This latter reaction is instantaneous and complete. The possibility of adopting this reaction for a quantitative oxidation of red phosphorus to phosphoric acid bromometrically is being investigated.

Summary

Kinetics of the oxidation of Red Phosphorus by Potassium Bromate in acid solution has been studied. Using varying concentrations of potassium bromate and the quantity of red phosphorus between 0.01 g. and 0.02 g., the reaction has been found to be bimolecular with respect to potassium bromate over a temperature range of 30–55°C. The energy of activation and temperature coefficient of the reaction have been calculated. Further work on the oxidation of red phosphorus by bromide-bromate mixture in acid solution is suggested.

Grateful thanks of the authors are due to Professor S. S. Joshi for facilities and kind interest in the work.

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