Bromometric Oxidation of Red Phosphorus by Bromide Bromate Mixtures

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In a previous communication, Venugopalan and George[1] suggested the utility of the instantaneous and complete reaction

$$5Br^- + BrO_3^- + 6H^+ = 3Br_2 + 3H_2O \qquad \text{(i)}$$

for a quantitative oxidation of red phosphorus to phosphoric acid bromometrically. Various substances react quantitatively with an excess of bromine, and acid solutions of bromine of exactly known concentration can readily be obtained from a standard potassium bromate solution by adding acid and an excess of bromide. In this reaction one mole of bromate yields six atoms of bromine and hence the equivalent weight is identical with that of potassium bromate alone. Bromine is very volatile and hence the experiments are carried out at as low a temperature as possible and in Erlenmeyer flasks provided with ground glass stoppers. The excess of bromine is determined iodometrically and from the reacted bromine the amount of phosphorus can be calculated.

Earlier workers[2] have shown that bromine reacts with red phosphorus at a very rapid rate at the ordinary temperature; but the reaction could proceed with a measurable speed at low temperatures and hence, it was of interest to undertake a kinetic study of the oxidation process.

Experimental

Solutions of bromide and bromate were prepared in the proportions given in equation (i) so that when mixed together in presence of an acid (H_2SO_4) both bromide and bromate react together instantaneously and completely to give a known amount of bromine.

Pure dry red phosphorus was weighed into a ground-glss stoppered Erlenmeyer flask. Equal volumes (40 cc.) of bromide and bromate solutions were added, followed by 20 ml. of 1 N sulphuric acid so that the overall normality of the system was maintained at or about 0.2 N H_2SO_4. The phosphorus dissolved in the evolved bromine in solution, thereby indicating that the initial reaction is very rapid and almost instantaneous. The system was maintained at a desired constant temperature for a few minutes prior to the addition of the oxidant and also during the course of subsequent observations in an ice-cooled water bath provided with an accurate thermometer. The contents of the flask were swirled from time to time and an aliquot portion (5 ml.) of the clear solution was pippetted out carefully at different time intervals and titrated iodometrically with standard thiosulphate[3]. Experiments were carried out at different temperatures, viz., 5, 10, 15, 20°C using the same concentration and by varying the concentration of the oxidant.

Results and Discussion

The order of the reaction was calculated by the integration method from the initial titre value of bromide bromide-bromate mixture and that obtained at various time intervals during the course of the oxidation, applying the equation

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

where C_o—initial concentration of bromide-bromate mixture
C_t—concentration at time t
C_∞—concentration at time ∞
and t—time in minutes

A representative group of results is shown in Table I. These results therefore show

TABLE I

Temperature: 20°C
Reaction Mixture: 5 ml.
Weight of P: 0.02 g.
Strength of KBr—$KBrO_3$ Mixture: N/35 solution

Time in Minutes	N/40 Thio ml.	$\frac{C_t(C_o-C_\infty)}{C_o(C_t-C_\infty)}$	$K\times10^3$
0	3.40	—	—
15	3.05	0.0363	3.98
30	2.80	0.0706	3.87
45	2.60	0.1053	3.85
60	2.45	0.1375	3.86
90	2.20	0.2088	3.82
∞	1.40	—	—

Mean $K=3.87\times10_3$

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[1] M. Venugopalan and K. J. George, *Bull. Chem. Soc. Japan*, **29** (3), 350-353, (1956).

[2] J. W. Mellor, "A comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. VIII, Longmans Green & Co. (1928). p. 785.

[3] A. I. Vogel, "Text Book of Quantitative Inorganic Analysis", Longmans Green & Co., London (1953). p. 369.

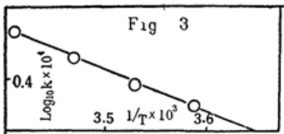
that the oxidation of red phosphorus by bromide-bromate mixture is an overall bimolecular reaction.

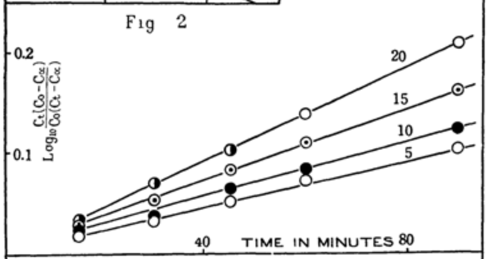
The influence of temperature on the velocity constant K, when the concentrations of the reactant are kept constant are given in Table II. The above results show that the velocity constant K increases with a rise in temperature; the values of $\log_{10}\frac{C_t(C_o-C_\infty)}{C_o(C_t-C_\infty)}$ plotted against time t for different temperatures, at which the reaction has been studied are represented graphically in Fig. 2.

TABLE II

Weight of P Taken: 0.02 g.
Strength of Bromide-bromate Mixture: N/35
Normality of Thiosulphate: N/40

Temperature (t) °C	Mean $K\times10^3$
5	2.0
10	2.4
15	3.1
20	3.87





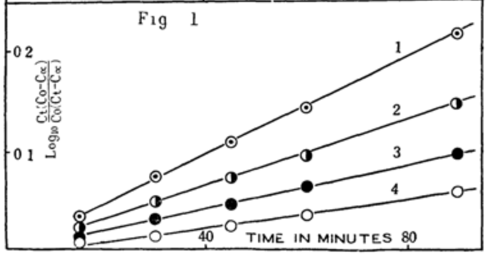


Fig. 1. Variation of $\log_{10}\frac{C_t(C_o-C_\infty)}{C_o(C_t-C_\infty)}$ with time t for different initial concentrations of bromide-bromate mixture at the same temperature.

Fig. 2. Variation of $\log_{10}\frac{C_t(C_o-C_\infty)}{C_o(C_t-C_\infty)}$ with time t for different temperatures.

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

Variation of the velocity constant K for different initial concentrations of the reactants has been studied by varying the concentration of bromide-bromate mixture and keeping the weight of phosphorus constant in all the experiments.

TABLE III

Temperature: 5°C
Weight of Phosphorus Taken: 0.02 g.
Normality of Thiosulphate: N/30

Expt. No.	Concentration of $KBr-KBrO_3$Mixture	Mean $K\times10^3$
1	N/35	4.0
2	N/40	2.9
3	N/45	2.1
4	N/50	1.2

Fig. 1 represents graphically the variation of $\log_{10}\frac{C_t(C_o-C_\infty)}{C_o(C_t-C_\infty)}$ with time for different concentrations of the oxidant (bromide-bromate mixture) at the same temperature.

The temperature coefficient and energy of activation were calculated from the values obtained for K at different temperatures T_1 and T_2 and are given below:

TABLE IV

Temp. T_1-T_2	K_1	K_2	Temp. Coeff. K_2/K_1	Energy of Activation/g. kcal.
278-288	2.0	3.1	1.56	7.00
283-293	2.4	3.87	1.60	7.78

The variation of $\log_{10}K$ with $1/T$ is shown in Table V; the results are plotted in Fig. 3.

TABLE V

Temperature Absolute T°	$1/T\times10^3$	$K\times10^3$	$\log_{10}K\times10^3$
278	3.59	2.0	0.3010
283	3.53	2.4	0.3802
288	3.47	3.1	0.4914
293	3.41	3.87	0.5877

The linear relationship between $\log_{10}K$ and $1/T$ (Fig. 3) is in accord with the Arrhenius equation[4] which expresses the influence of temperature on reaction velocity.

Bromometric Determination of Red Phosphorus

A series of experiments was carried out in which the difference in the quantity of bromide-bromate mixture added initially

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

to a given weight of phosphorus and that left over after its complete disappearance i. e. the titre value at infinite time served as a measure of the quantity of bromide-bromate mixture required for the oxidation reaction. Hence a knowledge of the quantity of bromide-bromate mixture utilized in the reaction is useful for the direct determination of red phosphorus bromometrically. A typical set of results of such determinations are given in Table VI.

TABLE VI

Wt. of P Taken g.	Wt. of P Calculated* g.	Difference in g.
0.018	0.01788	−0.00012
0.015	0.01488	−0.00012
0.028	0.02772	−0.00028
0.017	0.01693	−0.00003
0.029	0.02909	+0.00009
0.018	0.01788	−0.00012
0.032	0.03208	+0.00008
0.023	0.02272	−0.00028
0.020	0.01983	−0.00013

* Weight of P calculated from reacted bromine according to the equations:

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

and $$2P + 5Br_2 + 8H_2O = 12H^+ + 10Br^- + 2H_2PO_4^-$$

Mechanism of the Reaction

Since the interaction of bromide-bromate mixture is instantaneous and complete

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

bromine is quantitatively liberated. This bromine oxidizes phosphorus to phosphoric acid according as

$$2P + 3Br_2 + 6H_2O = 6H^+ + 6Br^- + 2H_3PO_3$$

$$H_3PO_3 + Br_2 + H_2O = 3H^+ + 2Br^- + H_2PO_4^-$$

The former reaction is quite rapid, whereas the tatter one is slow and depends on the H^+ ion concentration. It appears that the oxidation of phosphorus acid by bromine (obtained from acid bromide-bromate mixture) determines the rate of reaction as a whole.

Summary

Bromometric oxidation of red phosphorus using an acid solution of bromide-bromate mixture has been studied and applied in the volumetric determination of red phosphorus. The kinetics of the oxidation process show that the reaction is of the second order. The influence of temperature and concentration of the reactants, have been investigated and the energy of activation calculated. Further the applicability of this procedure for a bromometric determination of red phosphorus is emphasized and such determinations can be carried out over a period of three to four hours.

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