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Studies on the Oxidation of Red Phosphorus by Potassium Permanganate in an Acid Medium

By

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With 3 figures in the text

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Potassium permanganate is a powerful oxidising agent, whose reduction in an acid solution proceeds as:

$$MnO_4 - + 8H^+ + 5 e \rightleftharpoons Mn^{++} + 4H_2O_2$$

Sulphuric acid is the most suitable acid, as it has no action upon permanganate in dilute solution; with hydrochloric acid there is the likelihood of the reaction⁹

 $2 \text{KMnO}_4 + 16 \text{HCl} = 2 \text{KCl} + 2 \text{MnCl}_2 + 5 \text{Cl}_2 + 8 \text{H}_2 \text{O}$

taking place and some permanganate may be consumed in the formation of chlorine, which is a powerful oxidising agent capable of oxidising red phosphorus drastically, especially when suspended in solution⁶, and hence an hydrochloric acid medium can normally interfere with the P-KMnO₄ reaction.

Numerous oxidation studies with potassium permanganate led the above authors to investigate the possibility of using it for the oxidation of red phosphorus to phosphoric acid. Even though SLATER⁷ suggested the use of yellow phosphorus as a reductant in the reduction of permanganate to manganese dioxide and ROSENSTEIN⁵ observed that solutions of permanganates are reduced to manganous salts by a few minutes boiling with red phosphorus, the available information in the literature about the quantitative oxidation of red phosphorus by permanganate is meagre. The addition of acidified potassium permanganate solution to red phosphorus leads to its gradual disappearance accompanied with a simultaneous fading of the pink colour of the permanganate. The rate of the above change is measurably slow at ordinary temperatures and with excess of permanganate, complete oxidation of red phosphorus could be effected.

The present work was therefore undertaken to study the factors affecting this reaction and to determine its applicability to the determination of elementary phosphorus.

Experimental

Red phosphorus of B.D.H. laboratory reagent grade quality was purified by BUEHRER and SCHUPPS method³ and subsequently by the copper phosphide process⁴. Its purity was checked by the bromate procedure^{4.8}.

An accurately weighed quantity (0.02-0.03 gm.) of the sample of red P was introduced in a ground glass stoppered Erlenmeyer flask to which a known excess of standard potassium permanganate solution (75 ml. N/6) was added, followed by the required quantity of dilute sulphuric acid (25 ml. 4N), so as to maintain the overall acidity of the system at or about 1N sulphuric acid. The flask containing the red P and permanganate and sulphuric acid solutions was maintained at a desired constant temperature for nearly 30 minutes before commencing the reaction, as also during the course of subsequent observations in an electrically heated thermostat fitted with an accurately calibrated automatic thermoregulator or in an ice-cooled bath, for low temperatures. The contents of the flask were swirled from time to time and an aliquot portion (2 ml.) of the clear supernatent solution was pipetted out carefully at different time intervals into known excess of ferrous ammonium sulphate solution (10 ml. 0.05 N) to arrest the reaction and the ferrous ammonium sulphate left over was titrated against standard potassium permanganate¹⁰. Series of experiments were carried out at different temperatures, viz., 0, 10, 20, 30 and 40° C using the same concentrations and also by varying the concentrations of potassium permanganate and red P over a fairly wide range.

Results and Discussion

The concentrations of potassium permanganate as determined and represented in terms of number of ml. of ferrous ammonium sulphate solution in the experimental results, have been made use of, in calculating the order of the reaction by the integration method from the initial titre value of permanganate and that obtained at various time intervals during the course of the oxidation. 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:

$$K = \frac{2.303}{t T \alpha} \log_{10} \frac{T_t (T_o - T \alpha)}{T_o (T_t - T \alpha)}$$

where T_o initial concentration of permanganate, T_t concentration of permanganate at time t, $T\alpha$ concentration of permanganate at time α , and t time in minutes.

A representative group of results is shown in Table 1.

1 able 1.
Temperature: 10° C. Weight of phosphorus = 0.03 gm.
Reaction mixture: 2 ml. Concentration of $KMnO_4 = 75$ ml.
N/6 soln.

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Time min.	0.05 N ferrous amm. sulphate solution ml.	$\log_{10} \frac{T_t (T_0 - T\alpha)}{T_0 (T_t - T\alpha)}$	$K imes 10^{+3}$
0	8.3		
10	7.9	0.0346	1.60
30	7.3	0.1010	1.55
50	6.85	0.1679	1.55
70	6.50	0.2362	1.55
90	6.25	0.2984	1.50
110	6.0	0.3600	1.50
	5.0	· ·	_

The results in Table 1, therefore show that the oxidation of red phosphorus by permanganate is an overall bimolecular reaction.

The variation of the velocity constant (K) with temperature for the same initial concentrations of the reactants is given in Table 2.

Table 2. Weight of phosphorus:

0.03 gm. Concentration of

 $KMnO_4$: 75 ml. N/6 soln.

Normality of ferrous amm.

Table 3.

Temperature 25° C. Weight of phosphorus: 0.027 gm. Normality of ferrous amm. sulphate: 0.05 N.

sulphate: 0,05 N		of ferrous amin. surpliate: 0.05 N.			
Temperature °C Mean $K \times 10^{+3}$		Expt. No.	Conc. of KMnO ₄ ml. soln.	$rac{ ext{Mean}}{K imes 10^{+8}}$	
0	1.00	I	75 N/5	4.3	
10	1.54	2	100 N/6	4.0	
20	2.50	3	125 N/9	3.7	
30	4.80	4	150 N/10	3.2	
40	7.50	5	150 N/12	2.6	

The results (Table 2) show that the velocity coefficient (K) increases as the temperature increases; the values of $\log_{10} \frac{T_t (T_0 - T\alpha)}{T_0 (T_t - T\alpha)}$ plotted against time t for different temperatures at which the reaction has been studied, are represented graphically in Fig. 1.

The variation of the velocity coefficient (K) for different initial concentrations of the reactants has been studied by varying the concentration of permanganate solution and keeping the weight of P constant in all the experiments. A typical set of results are given in Table 3.

Fig. 2 represents graphically the variation of $\log_{10} \frac{T_t(T_o - T\alpha)}{T_o(T - T\alpha)}$ with time for different initial concentrations of permanganate at the same temperature.



Fig. 1. Variation of $\log_{10} \frac{T_t (T_0 - T\alpha)}{T_0 (T_t - T\alpha)}$ with temperature. Wt. of P = 0.03 gm. conc. of pot.



Fig. 2. Variation of $\log_{10} \frac{T_t(T_0 - T\alpha)}{T_0(T_t - T\alpha)}$ with time for different conc. of pot. permanganate. Temp. 25° C. Wt. of P = 0.027 gm.

No.	1	2	3	4	5
Cone of norman ganate	N	N	N	N	N
cone, of permanganate	5	6	9	10	12

The energy of activation and temperature coefficient were calculated from the values obtained for K at different temperatures T_1 and T_2 as indicated in Table 4.

Temp. absolute $T_1 \underset{\circ_C}{\sim} T_2$	$K_1 \times 10^{+3}$	$K_2 imes 10^{+3}$	Temp. coeff. K_2/K_1	$E = \frac{\frac{\text{Energy of activation}}{2.303 \log_{10} K_3/K_1 \times R \times T_1 \times T_2}}{\frac{T_2 - T_1}{g. \text{ cals.}}}$
273 - 283	1.00	1.54	1.54	6773
283 - 293	1.54	2.50	1.62	8020
293-303	2.50	4.80	1.92	11520
303 - 313	4.80	7.50	1.56	8433

Table 4

The variation of $\log_{10} K$ with 1/T is shown in Table 5, the results are plotted in Fig. 3.



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

T	ab	le	5
_			•

Temp. absolute °C	$1/T imes 10^{+3}$	$K imes 10^{+8}$	$\log_{10}{(K imes 10^{+3})}$
273	3.66	1.00	0.00
283	3.55	1.54	0.1875
293	3.41	2.50	0.3979
303	3.30	4.80	0.6812
313	3.20	7.50	0.8751

The linear relationship between $\log_{10} K$ and 1/T (Fig. 3) is in accord with the ARRHENIUS equation¹ which expresses the influence of temperature on reaction velocity.

Permanganate Method for the Determination of Red Phosphorus

A series of experiments were carried out in which the difference in the quantity of permanganate added initially 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 permanganate required for the oxidation reaction.

These results show that for a complete oxidation under the above experimental conditions, the mol. ratio of P to $KMnO_4$ is 1:1, which is in agreement with the essential bimolecularity of the overall oxidation process. Hence, a knowledge of the quantity of permanganate utilised in the reaction is useful for the direct determination of phosphorus. A typical set of results for the estimation of red phosphorus by permanganate method is given in Table 6.

Expt.	Weight of P taken	Weight of P calculated*	Difference
	gm.	gm.	gm
1	0.0138	0.0132	0.0006
2	0.0143	0.0151	+0.0008
3	0.0190	0.0205	+0.0015
4	0.0216	0.0202	-0.0014
5	0.0227	0.0223	-0.0004
6	0.0243	0.0252	+0.0009
7	0.0256	0.0262	+0.0006
8	0.0429	0.0424	-0.0005

 $Table \ 6$

* Weight of P calculated from reacted KMnO_4 according to the equation 2 P + 2 KMnO_4 + 3 H_2SO_4 = K_2SO_4 + 2 MnSO_4 + 2 H_3PO_4 .

The agreement between the calculated and weighed quantities of P proves the stoichiometry of the reaction and its utilisability in the determination of red phosphorus.

Mechanism of the Reaction

ROSENSTEIN⁵ suggested that in the reduction of permanganate solutions by red phosphorus in acid solutions manganous salts are formed as the end products. The reaction may be represented as:

$$P + MnO_4^- = Mn^{2+} + PO_4^{3-}$$
.

In complete agreement with the above suggestion, the oxidation of red P with $KMnO_4$ may be represented according to the equations:

$$MnO_4^- + 8 H^+ + 5 e = Mn^{2+} + 4 H_2O$$
 (i)

$$P + 4 H_2 O = PO_4^{3-} + 8 H^+ + 5 e.$$
 (ii)

On combining the above equations, we get,

$$P + MnO_4^{-} = Mn^{2+} + PO_4^{3-}.$$
 (iii)

From equation (iii) it is evident that one mol of P requires one mol of KMnO_4 for complete oxidation of P to phosphoric acid (H_3PO_4).

SLATER's⁷ observation that permanganate is reduced to manganese dioxide by yellow phosphorus may be explained as due to the reduction of permanganate according as:

$$\mathrm{MnO_4^{-+}e} = \mathrm{MnO_4^{--}} \ \mathrm{MnO_4^{--}} + 2 \mathrm{\,H_2O} + 2 \mathrm{\,e} = \mathrm{MnO_2} + 4 \mathrm{\,OH^{--}}$$

and

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both of which can proceed only in a strongly alkaline medium². However, the reaction:

 $2 \text{ MnO}_4^- + 3 \text{ Mn}^{2+} + 2 \text{ H}_2\text{O} = 5 \text{ MnO}_2^- + 4 \text{ H}^+$

is quite likely to take place, but it is observed that this reaction is very slow in cold acid solution and hence cannot play a major part in the oxidation-reduction process.

The nature of the P-KMnO₄ oxidation-reduction in an alkaline medium is being investigated.

Summary

Oxidation of red phosphorus by an acid solution of potassium permanganate has been studied and applied in the volumetric determination of red phosphorus. The kinetics of the oxidation-reduction process show that the reaction is of the bimolecular order. Influence of temperature on the velocity coefficient (K) as also the variation of (K) for different concentrations of the oxidant, observed, have been made use of in evaluating the activation energy of the reaction. Further the utilisability of this simple procedure for the volumetric determination of red phosphorus is emphasized.

The nature of the above oxidation reaction in an alkaline medium is being investigated.

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