

# OXIDATION POTENTIAL OF PEROXO-MONOPHOSPHORIC ACID

By

J. SCHNEIDER

Institute of Inorganic and Analytical Chemistry, Attila József University,  
Szeged\*

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The oxidation potential of peroxo-monophosphoric acid was determined as a function of the peroxo acid, hydrogen peroxide and phosphate ion concentrations and the pH. In the absence of hydrogen peroxide the potential can be described by the formula:

$$E = E^0 + \frac{RT}{F} \ln [\text{H}_3\text{PO}_5]^{10.95} [\text{H}^+]^{1.05}. \quad E^0 = 1.19 \pm 0.01 \text{ V.}$$

In the presence of hydrogen peroxide the empirical formula

$$E = E^0 + \frac{RT}{F} \ln \frac{[\text{H}_3\text{PO}_5]^{1.73} [\text{H}^+]^{0.96}}{[\text{H}_2\text{O}_2]^{1.73}}$$

is valid, with a value of  $E^0 = 0.88 \pm 0.01 \text{ V}$ . The oxidation potential is regarded as a mixed potential brought about by a local cell mechanism at the surface of the Pt electrode.

Peroxo-monophosphoric acid (in the following HOOA) is frequently used as a reagent of high oxidizing power and at the same time of high reactivity. However, reference can not be found in the literature with regard to the oxidation potential of HOOA. In the present paper we report the results of experiments made to determine the oxidation potential, and these are compared with earlier findings relating to peroxo-monosulphuric acid [1] and peroxo-acetic acid [2].

## Experimental

**Materials:** The chemicals used were Merck and Reanal products of p.a. purity. With the exceptions of sodium hydroxide and sodium perchlorate, from solutions of which heavy metal ion trace impurities were removed by the method of D'ANS and MATTNER [3], these chemicals were used without further purification.

A phosphate-free HOOA solution was prepared by perchloric acid hydrolysis of sodium peroxo-diphosphate (1,0 M perchloric acid, 298 K, ca. 4 hr). After neutralization with sodium hydrogen carbonate, barium perchlorate was used to precipitate the phosphate ions from the resulting solution. For the more complete removal of

\* Present address: VITUKI, 1095 Budapest IX., Kvassai u. 1.

barium phosphate, barium carbonate too was added to the solution, which was filtered after a standing period of 30 min. If the presence of phosphate ions was not disturbing, the hydrolysis was performed with 2 M phosphoric acid. During 90 min at 333 K the hydrolysis is quantitative; under these conditions there is practically no formation of hydrogen peroxide. Peroxo-diphosphate ( $K_4P_2O_8$ ) was prepared as described by FICHTER and GUTZWILLER [4], and was converted according to INDELLI and BONORA [5] to  $Na_4P_2O_8$ , which is more easily purifiable by recrystallization.

*Analysis:* After attainment of the equilibrium potential, the HOOA and possible hydrogen peroxide contents of the solutions were determined as described earlier [6], with the modification that the sulphuric acid concentration of the solution was raised to 1 M in order to avoid precipitation of cerium(IV) phosphate during the cerimetric titration in the case of higher phosphate ion contents. After flushing-out of the dissolved oxygen with  $CO_2$ , the total oxidizing capacity of the solutions was determined iodometrically, as described by CHULSKY [7].

*Potential measurement:* The pH of the HOOA solutions was adjusted with acetate and phosphate buffer, and by the addition of perchloric acid or sodium hydroxide, while the ionic strength was adjusted by the addition of sodium perchlorate. The potential was determined as described previously [2]. Prior to the measurements, the electrodes (in the present case 1.0 · 0.6 cm Pt sheets 0.15 mm thick) were left to stand for about 30 min in chromic acid cleaning mixture. They were then washed, immersed for 10 min in 3% hydrogen peroxide solution acidified nitric acid, re-washed, and left to stand for several hours in distilled water short-circuited to one another. By this means it was generally possible to achieve equalization of the initially different potentials of the individual electrodes. The potential data given in the Figures and Tables are the means of the potentials of three Pt electrodes immersed in a given solution in each case.

## Results

### a) Oxidation potential in the absence of hydrogen peroxide

In  $H_2O_2$ -free solution ( $[H_2O_2] < 10^{-6}$  M) in the range  $pH_3PO_5 = 2.0-5.0$ , the  $E$  vs.  $pH_3PO_5$  data determine a straight line, the slope of which (established by the GAUSS least squares method) is

$$\Delta E / \Delta pH_3PO_5 = -56 \text{ mV.}$$

The potential is independent of the phosphate ion concentration, and is not affected by changes in the ionic strength either. It is further independent of the quantity of dissolved  $O_2$  in the solution.

The potential of the HOOA depends on the pH of the solution. In the interval  $pH = 2.0-6.2$ , the  $E$  vs. pH data determine a straight line, the slope of which is

$$\Delta E / \Delta pH = -62 \text{ mV.}$$

The rest potential and the potential measured in the intensively-stirred solution virtually do not differ from each other.

On the above basis, in the absence of hydrogen peroxide the potential of HOOA can be described by the empirical formula

$$E = E^0 + \frac{RT}{F} \ln \{ [H_3PO_5]^{0.95} [H^+]^{1.05} \}. \quad (1)$$

The apparent oxidation normal potential calculated via formula (1) (see Table 1) is  $E^0 = 1.19 \pm 0.01$  V (referred to a hydrogen electrode).

Table 1

*Oxidation potential of peroxo-monophosphoric acid in the absence of hydrogen peroxide*

$H_3PO_5$ $M \cdot 10^4$	pH	$E_{obs.}$ (V) vs. SCE	$E^0$ (V)
53.5	3.50	0.564	1.148
43.4	4.09	0.560	1.186
30.3	3.55	0.570	1.171
27.3	2.55	0.640	1.182
26.0	3.91	0.584	1.211
24.8	3.90	0.566	1.194
18.5	2.55	0.629	1.180
17.4	3.86	0.573	1.206
14.4	2.45	0.636	1.187
12.5	2.60	0.635	1.199
11.7	2.40	0.642	1.195
11.5	3.00	0.603	1.194
9.6	2.70	0.616	1.192
8.6	2.40	0.636	1.196
6.5	4.50	0.506	1.203
6.0	3.40	0.576	1.207
5.5	4.50	0.490	1.192
3.8	2.90	0.572	1.183
3.5	2.45	0.614	1.199
2.5	2.80	0.580	1.195
2.4	2.71	0.586	1.197
2.1	4.50	0.480	1.205
1.8	2.60	0.574	1.185

*b) Oxidation potential in the presence of hydrogen peroxide*

If hydrogen peroxide is added to an HOOA solution, the peroxo acid and the hydrogen ion concentrations being maintained constant ( $pH_3PO_5 = 2.9$ ;  $pH = 3.9$ ), up to a hydrogen peroxide concentration of about  $2.5 \cdot 10^{-5}$  M the potential exhibits no, or scarcely any change. On further increase of the hydrogen peroxide concentration, the potential begins to fall significantly, (Fig. 1) the rate of the linear decrease being

$$\Delta E / \Delta (pH_2O_2)_{pH_3PO_5 = \text{const.}} = -97 \text{ mV.}$$

If the concentration ratio  $[H_3PO_5]/[H_2O_2]$  falls below 0.25, a stage is again observed in which the potential changes only slightly on further increase of the hydrogen peroxide concentration (Fig. 1). The slope of this stage is

$$\Delta E / \Delta pH_2O_2 = -10 \text{ mV.}$$

A similar result is found if the HOOA concentration of the solution is varied while the hydrogen peroxide concentration and the pH are maintained constant. The slope of the steeper section of the curve is

$$\Delta E / \Delta(p\text{H}_3\text{PO}_5)_{p\text{H}_2\text{O}_2 = \text{const.}} = -101 \text{ mV.}$$

On the above basis, the potential varies according to the function

$$E = f\{\log ([\text{H}_3\text{PO}_5]^x / [\text{H}_2\text{O}_2]^y)\}.$$

For a further checking of the exponents  $x$  and  $y$ , the potentials were measured in solutions with constant pH, but different concentration ratios  $[\text{H}_3\text{PO}_5]/[\text{H}_2\text{O}_2]$ . The resulting  $E$  vs.  $p$  ( $[\text{H}_3\text{PO}_5]/[\text{H}_2\text{O}_2]$ ) data determined a straight line (Fig. 2) which is possible only if  $x=y$ . The slope of the steep stage is  $\Delta E / \Delta p([\text{H}_3\text{PO}_5]/[\text{H}_2\text{O}_2]) = -102 \text{ mV}$ , while that of the less steep stage is  $-8 \text{ mV}$ .

The potential of HOOA does not depend on the phosphate ion concentration in the presence of hydrogen peroxide either, nor on the ionic strength of the solution. The potential again depends on the pH of the solution

$$\Delta E / \Delta \text{pH} = -57 \text{ mV.}$$

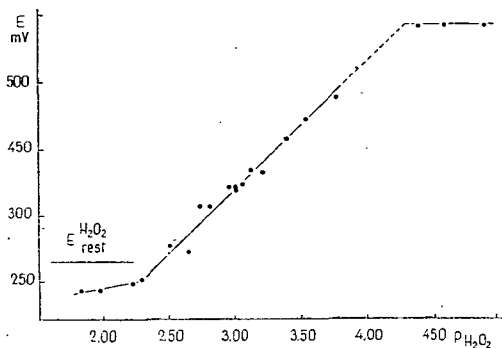


Fig. 1. Dependence of oxidation potential of  $\text{H}_3\text{PO}_5$  on hydrogen peroxide concentration.

$$p\text{H}_3\text{PO}_5 = 2.9, \quad \text{pH} = 3.9$$

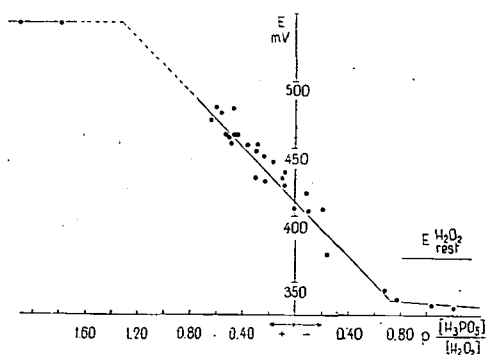


Fig. 2. Oxidation potential of peroxo-monophosphoric acid as a function of  $p([\text{H}_3\text{PO}_5]/[\text{H}_2\text{O}_2])$ .  $\text{pH} = 3.9$

It is noteworthy that in the presence of hydrogen peroxide, and predominantly in the range  $p([\text{H}_3\text{PO}_5]/[\text{H}_2\text{O}_2]) = -0.8 - +1.2$ , the potential depends strongly on the state of motion of the solution. The rest potential is about 80–100 mV more positive than the potential measured in the vigorously-stirred solution.

In the presence of hydrogen peroxide, therefore, the oxidation potential of peroxo-monophosphoric acid can be described by the empirical formula

$$E = E^0 + \frac{RT}{F} \ln \frac{[\text{H}_3\text{PO}_5]^{1.73} [\text{H}^+]^{0.96}}{[\text{H}_2\text{O}_2]^{1.73}} \quad (2)$$

The apparent standard oxidation potential, calculated on the basis of formula (2) is  $E^0 = 0.88 \pm 0.01 \text{ V}$  (Table 2).

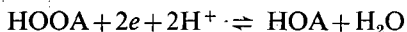
Table II

Dependence of the oxidation potential on the  $H_3PO_5/H_2O_2$  concentration ratio and pH

$H_3PO_5$ $M \cdot 10^3$	$H_2O_2$ $M \cdot 10^3$	pH	$p \frac{[H_3PO_5]}{[H_2O_2]}$	$E_{obs.} (V)$ vs. SCE	$E^0 (V)$
4.72	0.98	2.84	-0.683	0.562	0.894
1.25	0.28	3.20	-0.650	0.515	0.871
3.99	0.98	3.03	-0.609	0.536	0.865
3.92	1.06	3.19	-0.568	0.522	0.886
3.20	0.94	5.10	-0.532	0.386	0.862
3.07	0.95	3.90	-0.509	0.458	0.868
1.19	0.39	3.06	-0.484	0.507	0.872
3.04	0.98	2.77	-0.492	0.551	0.899
3.07	1.06	3.87	-0.462	0.462	0.875
3.08	1.07	3.87	-0.459	0.462	0.876
2.46	1.06	3.90	-0.366	0.458	0.883
1.98	0.98	2.77	-0.305	0.518	0.884
1.19	0.59	3.00	-0.305	0.485	0.865
2.08	1.06	3.96	-0.293	0.450	0.886
3.00	1.75	5.10	-0.234	0.369	0.876
1.24	0.73	3.33	-0.229	0.461	0.867
1.58	1.06	4.05	-0.173	0.431	0.884
1.35	1.06	2.98	-0.105	0.487	0.884
3.57	2.97	3.90	-0.080	0.422	0.876
1.29	1.06	4.03	-0.085	0.424	0.885
0.84	0.84	3.00	+0.000	0.462	0.873
0.87	1.06	3.90	0.086	0.416	0.887
1.19	1.55	3.00	0.104	0.460	0.881
0.64	1.06	3.08	0.219	0.456	0.894
1.22	2.16	2.45	0.248	0.462	0.867
1.06	5.00	2.25	0.676	0.447	0.884
0.96	5.78	2.25	0.779	0.440	0.888
0.93	10.25	2.25	1.042	0.434	0.909
0.89	14.57	2.25	1.214	0.432	0.924

## Discussion

For a qualitative explanation of the oxidation potential measured in HOOA solutions, we may set out from the finding that the potential in either the absence or the presence of hydrogen peroxide is not so „stable“ and well-reproducible as the potential to be measured in the solution of a well-poised redox system (e.g. iron(II)/iron(III)). Even after a waiting period of 20–60 min, the potentials measured at the individual electrodes exhibit differences of *ca.*  $\pm 10$  mV. From this behaviour it is concluded that in the absence of hydrogen peroxide the potential is not determined by the process



for then the potential would be „more stable“ (better poised), and should also depend on the concentration of phosphate ions, which was not supported by the measurements. It is probable, therefore, that the potential observed is a mixed potential, brought about by a local cell mechanism. The HOOA is reduced on the cathodic sites of the electrode, and oxidized on the anodic sites, and the potential is determined

by the  $i_c = i_a$  state. As regards the cathode reaction, we may consider the voltammetric findings of SECCO and VENTURINI [8], who suggested that, on the 1-electron reduction of HOOA on a platinized Pt electrode:



a phosphate species corresponding to the pH of the medium is formed, and an OH radical is transferred to the Pt electrode. The above authors state that the more acidic the leaving group, the easier it is for the reduction to occur. The OH radical next participates in a further electrode reaction, or is stabilized by disproportionation. Only assumptions are possible with regard to the anode reaction. It may be assumed that the HOOA is oxidized to a peroxo-phosphate radical:

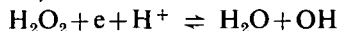


which is either oxidized to oxygen and phosphate ions, or undergoes dismutation to oxygen and HOOA.

In the presence of hydrogen peroxide, the potential-dependence changes. While the concentration ratio  $[\text{HOOA}]/[\text{H}_2\text{O}_2]$  is larger than 20, the potential decreases only slightly on the addition of hydrogen peroxide, but even this decrease disappears after a short waiting period, the potential being restored to the original value. The high potential gradient observed in the presence of somewhat more hydrogen peroxide is in all probability connected with the fact that the hydrogen peroxide interacts with the products of electrode reactions (3) and (4) on the surface of the electrode, and these Pt-surface reactions alter the concentration ratio  $[\text{HOOA}]/[\text{H}_2\text{O}_2]$  on the surface of the electrode. We consider it probable that the dependence of the potential on the state of motion of the solution can also be attributed to this. If the increase in the flux of reacting substances on the surface is enhanced not only by diffusion, but also by convection, the potential will become more negative. Under the conditions of potential measurement the ratio solution volume:surface is generally high, and therefore a change in the composition of the solution as a consequence of the surface reactions can not be observed, even after a longer time. However, if the ratio solution volume:surface is strongly decreased (*e.g.* to a value of about 1), by the use of a special vessel, a well-measurable concentration change can be observed even in a short time. The very slow reaction  $\text{HOOA} + \text{H}_2\text{O}_2$  with a stoichiometry of 1:1 under the homogeneous conditions is accelerated 20–25-fold on the effect of surface catalysis, but in addition the ratio  $[\text{HOOA}]/[\text{H}_2\text{O}_2]$  is increased because of the faster decomposition of the hydrogen peroxide. This is why we state that the concentration ratio  $[\text{HOOA}]/[\text{H}_2\text{O}_2]$  is larger on the surface of the electrode than in the bulk of the solution. The potential-dependence (eqn. (2)) observed in the presence of hydrogen peroxide does not only originate from the shift in the concentration ratio; a mixed potential arising as a result of several simultaneous electrode reactions (a multicouple system) is also involved. In other words, the hydrogen peroxide too participates in the local cell mechanism.

In the event of a larger excess of hydrogen peroxide, the role of the peroxomonophosphoric acid is forced into the background, and the potential gradient is then only 8–10 mV. This is probably related with the fact that primarily the

hydrogen peroxide predominantly occupying the active sites takes part in the local cell mechanism:



The effect of the HOOA can be observed even then, however, for the potential is more negative than the rest  $\text{H}_2\text{O}_2$  potential measured under similar conditions in the absence of HOOA ( $E_{\text{rest}}^{\text{H}_2\text{O}_2}$  is indicated on the left-hand side of Fig. 2).

We have already pointed out that oxidation potential of peroxo-monophosphoric acid is analogous with the potentials determined in the cases of peroxo-monosulphuric acid [1] and peroxo-acetic acid [2]. In all probability, the cause of this is that the peroxo acids give rise to analogous electrochemical and chemical reactions. Our findings show that the powers of the peroxo acid and the hydrogen peroxide in the potential dependence observed in the presence of hydrogen peroxide are functions of the rate of the reaction  $\text{HOOA} + \text{H}_2\text{O}_2$  on the Pt surface. The rate of this surface reaction is the highest for Caro's acid (power: 2.25), lower for peroxo-phosphoric acid, and the lowest for peroxo-acetic acid (power: 1.66). On the basis of these observations, we are of the opinion that, besides detailed electrode-kinetic investigations, a study of the Pt-catalyzed  $\text{HOOA} + \text{H}_2\text{O}_2$  reactions is necessary for a quantitative clarification of the oxidation potentials measured in solutions of the peroxo acids. Such measurements are now in progress.

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#### ОКИСЛИТЕЛЬНЫЙ ПОТЕНЦИАЛ ПЕРОКСО-МОНОФОСФОРНОЙ КИСЛОТЫ

Й. Шнейдер

Окислительный потенциал пероксо-монофосфорной кислоты определен как функция концентрации пероксо-кислоты, перекиси водорода, ионов фосфата и pH. В отсутствие перекиси водорода потенциал может быть выражен формулой:

$$E = E^0 + \frac{RT}{F} \ln [\text{H}_3\text{PO}_5]^{0.95} [\text{H}^+]^{1.05}. \quad E^0 = 1.19 \pm 0.01 \text{ V.}$$

В присутствии перекиси водорода эмпирическая формула

$$E = E^0 + \frac{RT}{F} \ln \frac{[\text{H}_3\text{PO}_5]^{1.78} [\text{H}^+]^{0.96}}{[\text{H}_2\text{O}_2]^{1.78}}$$

действительна при значении  $E^0 = 0.88 \pm 0.01$ . Окислительный потенциал рассматривается как смешанный потенциал, возникающий по клеточному механизму на поверхности платинового электрода.