347. *Complexes of Tartaric Acid with Peroxytungstate Ions.*

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Tartaric acid forms 1 : 1 complexes with both the tetraperoxyditungstate and the tetraperoxytungstate ions over a limited range of pH. The complex anions formed have been investigated by polarimetric, potentiometric, and spectrometric methods.

Addition of hydrogen peroxide to a solution of sodium tungstate results in the formation of peroxytungstate ions. These are unstable in the solid state although Pechard [1] isolated the compound H_2WO_8. In solution, however, they are stable for several hours. Jahr [2] showed the existence in solution of the tetraperoxytungstate ion WO_8^{2-} and indicated the conditions for its formation. The pH of solutions containing two moles of hydrogen peroxide per one mole of sodium tungstate is maximum immediately after preparation. With increasing hydrogen peroxide content the colourless solutions became yellow. The reactions involved are:

$$WO_4^{2-} + 2H_2O_2 \rightleftharpoons [HWO_6]^- + OH^- + H_2O$$

$$WO_4^{2-} + 4H_2O_2 \rightleftharpoons WO_8^{2-} + 4H_2O$$

Souchay,[3] whose work was confirmed by Jahr and Blanke [4] and by Tridot,[5] showed the presence of a condensed ion resulting from the dehydration of $[HWO_6]^-$:

$$2[HWO_6]^- \longrightarrow W_2O_{11}^{2-} + H_2O$$

Further proof for the existence of the ions $W_2O_{11}^{2-}$ and WO_8^{2-} was obtained by potentiometric methods.[6] The tetraperoxytungstate ion is converted into the tetraperoxyditungstate ion by acid:

$$W_2O_{11}^{2-} + 4H_2O_2 \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} 2WO_8^{2-} + 2H^+ + 3H_2O$$

In weak acid solution, where the hexatungstate ion $[HW_6O_{21}]^{5-}$ exists,[7] an excess of hydrogen peroxide appears to cause the reaction:

$$[H_6WO_{21}]^{5-} + 12H_2O_2 \rightleftharpoons 3[W_2O_{11}]^{2-} + H^+ + 12H_2O$$

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[1] Pechard, *Ann. Chim. Phys.*, 1893, **28**, 537.
[2] Jahr, *Z. angew. Chem.*, 1941, **55**, 94.
[3] Souchay, *Bull. Soc. chim. France*, 1949, 122.
[4] Jahr and Blanke, *Z. anorg. Chem.*, 1953, **272**, 45.
[5] Tridot, *Ann. Chim. (France)*, 1955, **10**, 255.
[6] Biehler, *Ann. Chim. (France)*, 1947, **2**, 489.
[7] Jander, *Z. anorg. Chem.*, 1930, **187**, 60.

The suggested structures [2] for these complex ions involve O_2^{2-} ions. The structure of a similar type of peroxide, the perchromic ion, has been worked out.[8] Here O_2^{2-} ions replace O^{2-} ions in such a way that the oxygen atoms are equidistant from the chromium ion, giving eight co-ordination. Thus in peroxytungstate, O_2^{2-} ions probably replace the O^{2-} ions of the normal tungstate and ditungstate ions. No complexes of these peroxytungstate ions with organic ligands have previously been described. D-Tartaric acid has now been investigated as a possible ligand because it forms stable complexes with normal tungstate ions and is stable in hydrogen peroxide solutions and also because the change in optical rotation enables complex-formation to be measured conveniently.

EXPERIMENTAL AND RESULTS

Adding an aqueous solution of sodium tetraperoxytungstate to one of D-tartaric acid increases the optical rotation but the yellow colour of the tetraperoxytungstate solution remains.

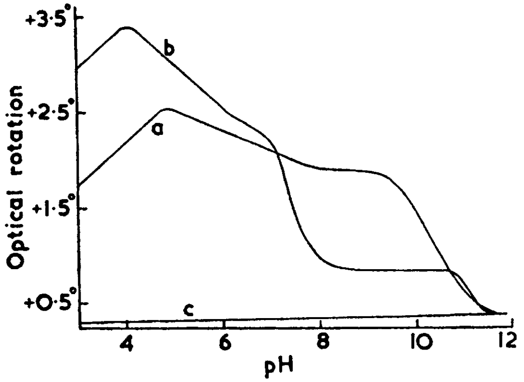

FIG. 1. Plots of optical rotation against pH for (a) 0·04M-(+)-tartratoperoxytungstate, (b) 0·04M-(+)-tartratotungstate, and (c) 0·04M-(+)-tartaric acid.

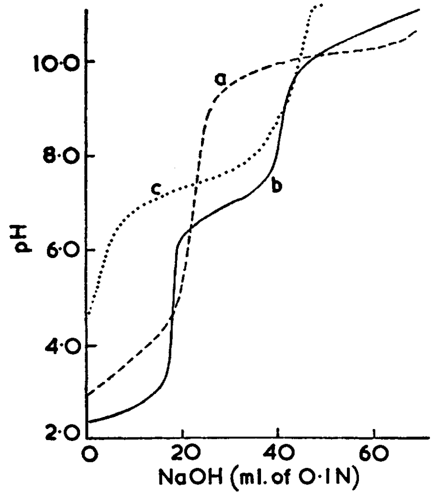

FIG. 2. Potentiometric titrations of (a) 0·04M - tartratoperoxytungstate, (b) 0·04M-peroxytungstate, and (c) 0·04M-tartratotungstate (each 50 ml.) with 0·1N-sodium hydroxide.

Using solutions 0·064M in D-tartaric acid, 0·04M in sodium tungstate, and 0·5M in hydrogen peroxide, we have measured the variation in optical rotation (20 cm. tube; sodium D light) with pH. Each solution was left for 1 hr. to reach equilibrium. Fig. 1 shows the results and corresponding optical rotations of D-tartratotungstate and D-tartaric acid. Curve (a) for tartratoperoxytungstate shows four turning points, at pH 4·8, 7·8, 9·1, and 11·2. Comparison with curve (b) suggests that, at least above pH 7·5, there is complex-formation between D-tartaric acid and peroxytungstate ions. At pH $>11·5$, the optical rotation falls to that of sodium D-tartrate solution, indicating breakdown of the complex.

Fig. 2 shows the potentiometric titration (a) of 50 ml. of a solution, 0·04M in sodium tungstate and tartaric acid and 0·5M in hydrogen peroxide, with 0·1M-sodium hydroxide. Comparable titrations of sodium tetraperoxyditungstate solutions are also shown. Curve (b), for peroxytungstate, is similar to that obtained by Biehler,[6] corresponding to the formation of the $W_2O_{11}^{2-}$ and WO_8^{2-} ions as the pH rises. Curve (c), for tartratotungstate, is similar to that obtained by Baillie and Brown.[9] Curve (a), which cannot be produced by a combination of (b) and (c), indicates, along with the polarimetric evidence, that there is some complex formation and that either the tartratoperoxytungstate ion titrates as a weak acid or a change in the nature of the complex takes place at higher pH's.

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[8] Stromberg and Brosset, *Acta Chem. Scand.*, 1960, **14**, 441.

[9] Baillie and Brown, *J.*, 1961, 3691.

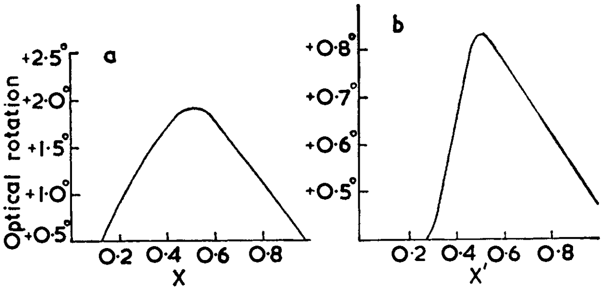

FIG. 3. Job's plot for 0·04M-tartaric acid and (a) 0·04M-tetraperoxyditungstate, or (b) 0·04M-tetraperoxytungstate.
For (a), $X = [W_2O_{11}^{2-}]/([W_2O_{11}^{2-}] + [C_4H_6O_6])$.
For (b), $X' = [WO_8^{2-}]/([WO_8^{2-}] + [C_4H_6O_6])$.

Ultraviolet spectra of solutions (10^{-2}M) of peroxytungstates and tartratoperoxytungstates were taken at different pH's for the region above 250 mμ (below 250 mμ sodium tungstate, hydrogen peroxide, and tartaric acid all absorb strongly). The results are tabulated. The stoicheiometry of the complexes was found by plotting optical rotation against molar fraction of D-tartaric acid. Curve (a) of Fig. 3 represents the values obtained at pH 5 where the ion $W_2O_{11}^{2-}$ is the dominant tungstate species, and curve (b) the results at pH 9 where WO_8^{2-} is the dominant species. In both cases a 1 : 1 complex was indicated.

	Peroxytungstate		Tartratoperoxy-tungstate			Peroxytungstate		Tartratoperoxy-tungstate	
pH	$\lambda_{\text{max.}}$ (mμ)	*D*	$\lambda_{\text{max.}}$ (mμ)	*D*	pH	$\lambda_{\text{max.}}$ (mμ)	*D*	$\lambda_{\text{max.}}$ (mμ)	*D*
4	287	0·96	287	1·14	8	330	1·08	330	0·76
5	287	0·96	287	1·18	9	330	1·08	330	0·80
6	287	0·78	287	1·14	10	287	0·90	330	0·68
7	330	1·08	287	1·10	11·5	287	0·36	330	0·30

DISCUSSION

Comparisons of the curves in Fig. 1 suggest that complex formation could occur between the tetraperoxytungstate ion and tartaric acid, at least above pH 7·5, and that a stable species is formed between pH 7·8 and pH 9·1. The enhanced optical rotation could be due to a greater electron shift away from the asymmetric carbon atoms in the tartratotetraperoxytungstate complex than in the tartratotungstate ion.[10] Below pH 7, the change in optical rotation shown in Fig. 1 is inconclusive, although the D-tartaric acid must be to some extent engaged as a complex. The optical densities tabulated indicate that the dominant species in the peroxytungstate solution below pH 6 is present in the tartratoperoxytungstate solution up to pH 7. This ion, as mentioned above,[3-5] is probably $W_2O_{11}^{2-}$. The slightly increased optical density, along with the wider pH range of stability, suggests that the $W_2O_{11}^{2-}$ ion is also united as complex to the tartaric acid. Thus the decreased optical rotation shown in Fig. 1(a) below pH 7 is due to complex formation and not to a decrease in the concentration of the tartratotungstate. The ultraviolet spectra suggest that above pH 7 the WO_8^{2-} ion is the complex-forming species. In this case the optical density of the complex ion is lower than that of the tetraperoxytungstate ion. The tartaric acid seems also to decompose the WO_8^{2-} group as without it hydrolysis starts around pH 10, giving possibly lower peroxides such as HWO_6^- that absorb around 287 mμ. In the presence of tartaric acid breakdown of the complex seems to result in complete hydrolysis of the peroxytungstate.

Further evidence of the nature of the complexes formed comes from the potentiometric measurements. Curve (b) of Fig. 2, corresponding to the formation of the $W_2O_{11}^{2-}$ and WO_8^{2-} ions, is altered on addition of tartaric acid. The region of constant pH given by $W_2O_{11}^{2-} + 2OH^- + 4H_2O_2 \rightleftharpoons 2WO_8^{2-} + 5H_2O$ is eliminated. The ultraviolet spectra, however, suggest that this reaction does take place: thus, to convert the tartratotetraperoxyditungstate into the tartratoperoxytungstate ion, addition of hydroxyl or hydrogen

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[10] Brown, unpublished work.

ions is not required. This can be explained by assuming that un-ionised tartaric acid is the ligand. To satisfy these experimental results, therefore, the equilibria involved, with increasing pH, might be:

$$\text{(a)}\ W_2O_{11}^{2-} + C_4H_6O_6 \rightleftharpoons [W_2O_{11},C_4H_6O_6]^{2-} \quad \text{at pH 2·8}$$

$$\text{(b)}\ [W_2O_{11},C_4H_6O_6]^{2-} + C_4H_4O_6^{2-} + 4H_2O_2 \rightleftharpoons 2[WO_8,C_4H_6O_6]^{2-} + 3H_2O$$

after one equivalent of sodium hydroxide had been added, *i.e.*, after the uncomplexed half of the tartaric acid present had been neutralised. Finally there is the reaction

$$\text{(c)}\ [WO_8,C_4H_6O_6]^{2-} + 4H_2O \rightleftharpoons WO_4^{2-} + 4H_2O_2 + C_6H_4O_6^{2-} + 2H^+$$

giving complete hydrolysis of the complexes.

Tartaric acid complexes with normal tungstate ion are most stable before ionisation of the tartaric acid.[9] The hydrogen ions are thought to be hydrogen-bonded to the oxygen ions of the tungstate group, thus preventing ionisation at the normal pH values. Hydrogen bonding with the peroxy-ions is also possible in both the peroxytungstates. The large increase in the optical rotations (Fig. 1) of the tartratoperoxytungstates, compared with those of tartaric acid, and the relatively slight difference between the optical rotations of the two tartratoperoxytungstates agree with the supposition that the ligands in the latter are the same, *viz.*, tartaric acid. Since the peroxytungstate and normal tungstate ions are probably similar in structure, with O_2^{2-} ions replacing O^{2-} ions, the tartaric acid is likely to be similarly bonded in each case, with the oxygen atoms of the carboxylic acid groups directly co-ordinated to the tungsten atoms and the hydrogen atoms of the hydroxyl groups hydrogen-bonded to the oxygen ions of the tungstate groups. There is some doubt whether the O_2^{2-} group should be considered as a bidentate or a monodentate ligand. If the structure of the ion WO_8^{2-} is similar to that of CrO_8^{3-} there would be a co-ordination number of 10 or 6 in the tartaric acid complex. However, discussion of the structure of the complex is speculative since there is no definite information about the structures of the peroxytungstates themselves.

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