Optically Active Co-ordination Compounds. Part XXXI.[1] Stereoselective Autoxidations of Dimeric Vanadium(IV) Tartrate Complexes

By **R. D. Gillard** * and **R. A. Wiggins**, The Chemical Laboratory, The University of Kent at Canterbury

The varying rates and products of uptake of dioxygen by solutions of vanadium(IV) tartrate complexes have been studied, using manometry and electronic spectra, as a function of the particular isomeric form (*i.e.* D, L, or *meso*) of tartaric acid which is present. Effects of pH are described.

In the systems containing D (or L) or a racemic mixture of D- and L-tartaric acid a deep orange complex is formed in the range pH 2·5—6·5, but not in that containing *meso*-tartaric acid. Circular dichroism and Raman spectra of the orange complex have been measured and a Job's plot made on the system in an attempt to determine the stoicheiometry. A possible structure for this complex is discussed.

FOLLOWING earlier work[2] on vanadium(IV) tartrate species, in which dimeric structures were postulated in order to account for the dependence of the properties of solutions made up from 1 : 1 molar ratios of tartaric acid and vanadium(IV) ion on the optical rotation of the acid, we initiated a study[3] of the uptake of dioxygen by vanadium(IV) tartrate species. Here the most striking finding was that the rate of oxygenation of racemic 1 : 1 solutions was very different from that for optically active solutions of the same stoicheiometry. We report, in this paper, studies on such systems, the products of oxygenation, and on complexes of vanadium(V) with tartrate ligands.

RESULTS AND DISCUSSION

In systems of stoicheiometry $[VO^{2+}]$: [tartaric acid] : $[OH^-] = 1 : 1 : x$, the electronic absorption bands formed when $3 < x < 4$ (*i.e.* at pH 6—7) in both the D- and DL-tartrate systems grew more intense[2] over a period of 1 h. The effect was stereoselective in that the increase in intensity was more pronounced in the former than in the latter system. This ' ageing ' effect is an autoxidation, the solutions reacting with atmospheric dioxygen.

For pH values in the range 6—7 it has been shown, by a wide variety of physical measurements, that the main species in the vanadium(IV)–D- or DL-tartrate systems are dimers.[4-7] These contain two vanadium(IV) cations, VO^{2+}, bridged by two quadridentate tartrate ligands (tart). In solutions containing only D-tartrate the bridges are obviously both of the D-configuration, whereas in the racemic tartrate solutions the dimers contain one D- and one L-tartrate bridge. This latter species must be more stable than that containing two D-tartrate bridges, otherwise dismutation of ligands would occur in solutions of these kinetically labile species to give DD- and LL-bridged molecules. Any dimer species formed in the *meso*-system is very unstable.[7]

When set aside solutions of $Na_4[(VO)_2(D\text{-tart})_2]$ changed from purple through green to orange and $Na_4[(VO)_2(D\text{-tart})(L\text{-tart})]$ altered from brown through green to orange. These changes could be either accelerated by bubbling dioxygen through the solutions or prevented by keeping the solutions under nitrogen. Manometry confirmed that solutions of the dimeric vanadium(IV) complexes absorb dioxygen. The final orange colour produced on oxygenation is due to a vanadium(V) tartrate complex, discussed later.

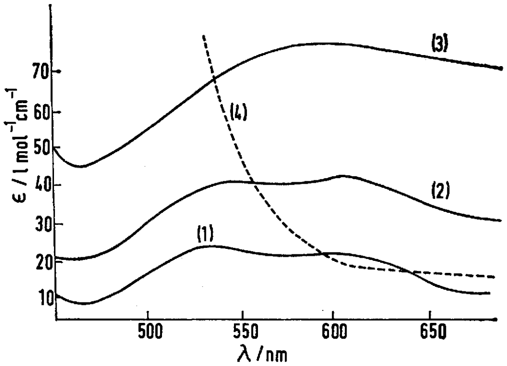

FIGURE 1 Change in electronic spectrum of an aqueous solution of $Na_4[(VO)_2(D\text{-tart})_2]$ on oxygenation at 25 °C. (1), Initial solution; (2), after 30 min; (3), after 145 min; (4) final orange solution. ε = Molar extinction coefficient based on $[VO^{2+}]_T$

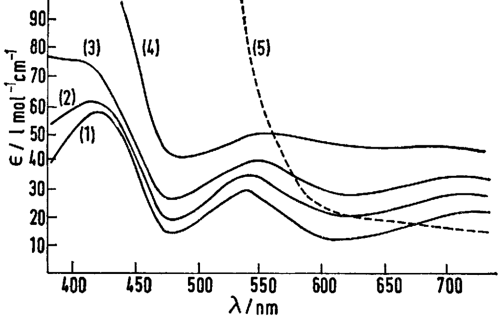

FIGURE 2 Change in electronic spectrum of an aqueous solution of $Na_4[(VO)_2(D\text{-tart})(L\text{-tart})]$ on oxygenation at 25 °C. (1), Initial solution; (2), after 30 min; (3) after 80 min; (4) after 6 h; (5) final orange solution. ε as in Figure 1

Solutions containing D- or DL-tartrate dimer both initially became green on oxygenation, the absorption maxima in the visible region occurring at *ca.* 600 nm (Figures 1 and 2). The increase of the absorbance to a

---

[1] Part XXX, I. G. Browning, R. D. Gillard, J. R. Lyons, P. R. Mitchell, and D. A. Phipps, *J.C.S. Dalton*, 1972, 1815.

[2] (*a*) J. H. Dunlop, D. F. Evans, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1260; J. H. Dunlop, Ph.D. Thesis, University of London, 1965.

[3] R. A. Wiggins, Ph.D. Thesis, University of Kent, 1970.

[4] R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, 1967, **6**, 735.

[5] J. G. Forrest and C. K. Prout, *J. Chem. Soc.* (*A*), 1967, 1312.

[6] R. E. Tapscott, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, 1968, **7**, 356.

[7] R. E. Tapscott, R. L. Belford, and I. C. Paul, *Co-ordination Chem. Rev.*, 1969, **4**, 323.

maximum and the subsequent decrease at this wavelength (Figure 3) indicate a reaction sequence:

$$\text{Dimeric tartrate} \xrightarrow{O_2} \underset{\text{(I)}}{\text{Intermediate}} \xrightarrow{O_2} \underset{\text{(II)}}{\underset{\text{species}}{\text{Orange vanadium(v)}}}$$

Dioxygen is necessary both for the formation of (I) and for the conversion of (I) into (II). Solutions of (I) kept under an inert atmosphere appear to be stable indefinitely. While the electronic spectra of the intermediates (I_D) and (I_{DL}) * differed ($\lambda_{max.}$ *ca.* 600 and 560 nm respectively), those of the orange solutions formed on prolonged oxygenation were the same for both systems.

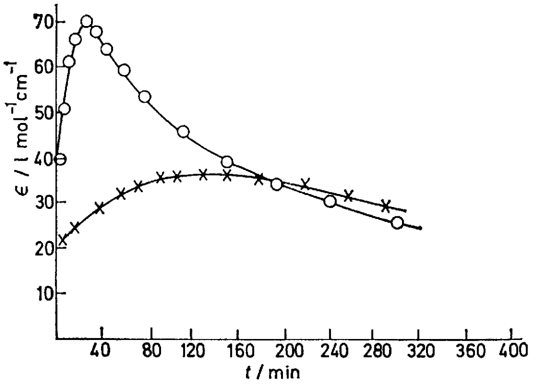

FIGURE 3 Comparison of changes in absorbance at 600 nm on oxygenation of 0·01M aqueous solutions of (○), $Na_4[(VO)_2(\text{D-tart})_2]$, (×), $Na_4[(VO)_2(\text{D-tart})(\text{L-tart})]$ at 25 °C. ε as in Figure 1

When solutions of stoicheiometry [VO^{2+}] : [*meso*-tartaric acid] : [OH^-] = 1 : 1 : 3·5 (pH 6·5) were oxygenated, a definite blue-green intermediate was formed. The electronic spectrum of (I_M) was again different from those of (I_D) and (I_{DL}) (Figure 4). Further, in this system, the electronic spectrum of the final vanadium(v) species was different from those of the D- and DL-systems.

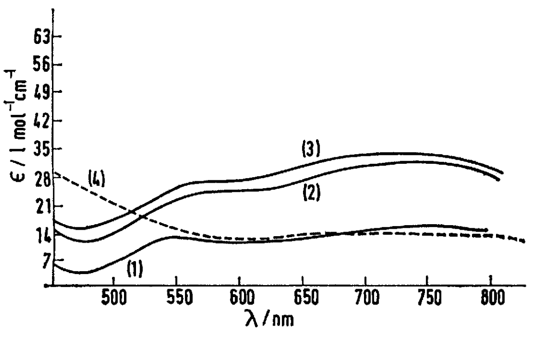

FIGURE 4 Change in electronic spectrum on oxygenation of a solution of stoicheiometry [VO^{2+}] : [*meso*-tartaric acid] : [OH^-] = 1 : 1 : 3·5 at 25 °C. (1), Initial solution; (2), after 15 min; (3), after 12 h; (4), final solution. ε as in Figure 1

The change in circular dichroism on oxygenation of solutions of $Na_4[(VO)_2(\text{D-tart})_2]$ has also been followed. There was a large initial drop in intensity during the first 30 min corresponding approximately to the time required to reach a maximum concentration of (I_D). During this initial period there was little change in the position of the chiroptical absorption bands. A very gradual decrease of the visible circular dichroism then occurred as the intermediary green colour faded and the solution became orange.

Solutions of (I) were sensitive to pH changes. Thus when solutions of (I_D) or (I_{DL}) were acidified (pH 4) the green colour disappeared and orange solutions formed. These possessed electronic spectra (and in the case of solutions containing optically active tartrate ions, circular dichroism) identical to those of the orange vanadium(v) species formed on prolonged oxygenation. The change was reversible, addition of base to the acidic orange solutions, resulting in reformation of the green solutions of (I_D) and (I_{DL}). On further addition of base (pH > 7) the green colour disappeared and the solutions exhibited the electronic spectrum of the dimeric vanadium(IV) tartrate complexes. The intensity of the absorption depended on the degree of oxygenation; the more the solutions were oxygenated the less dimeric complex was observed. These changes on variation of pH indicate that the partially oxygenated solutions contain at least three species: unchanged dimeric complex; the intermediate (I), which appears to be stable over the range pH 4—7; and the orange vanadium(v) tartrate species.

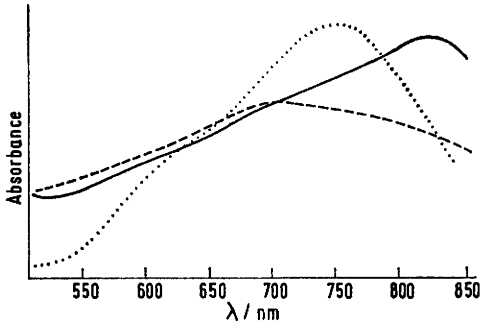

FIGURE 5 pH Dependence of electronic spectrum of (I_M). (——), pH 4·3; (– – – –), 7·0; (· · · ·), vanadium(IV) sulphate

The pH dependence of the electronic spectrum of solutions of (I_M) is shown in Figure 5. The electronic spectrum formed by oxygenation of solutions of composition [VO^{2+}] : [*meso*-tartaric acid] : [OH^-] = 1 : 1 : 3·5 had, at pH 4, an absorption maximum at 825 nm and a shoulder at *ca.* 700 nm. At pH 7 however, the maximum at 825 nm disappeared, suggesting that at pH 4 there are at least two species in solution, one of which becomes unstable at pH 7. The spectrum at pH 7 is not that of the starting solution. The species present at pH 2 was unstable at pH 10, autoxidation being very rapid. When acid was added to the solution at pH 7 the changes outlined above could be reversed. Thus as the pH was lowered below 4 the colour of the intermediate gradually

---

* The intermediate formed on oxygenation of the dimeric vanadium(IV) tartrate complexes is referred to generally in the text as (I), those in the D-, DL-, and *meso*-systems as (I_D), (I_{DL}), and (I_M) respectively.

faded; however, no orange colouration was formed, in contrast to the D- and DL-tartrate systems.

Nature of the Intermediate Species.—We consider that the increase in electronic absorption in the visible region on oxygenation of solutions of dimeric vanadium(IV) tartrate complexes is a result of the formation of a mixed-valence complex [8] containing vanadium-(IV) and -(V). The broadness of the absorption bands is probably due to a contribution from vanadium(IV) *d–d* transitions. Several examples of mixed-valence species are known containing vanadium-(IV) and -(V), most being based on the decavanadate ion $[V_{10}O_{28}]^{6-}$; Ostrowetsky [9] identified six polyanions in weakly acid solution corresponding to varying degrees of reduction of $[V_{10}O_{28}]^{6-}$.

Since (I) is an intermediate in oxygenation it might be thought to contain a peroxo-bridge. However, no evidence for such a bridge has been found. Tests with Luminol reagent [10] and with the enzyme catalase on solutions containing a maximum concentration of (I) proved negative.

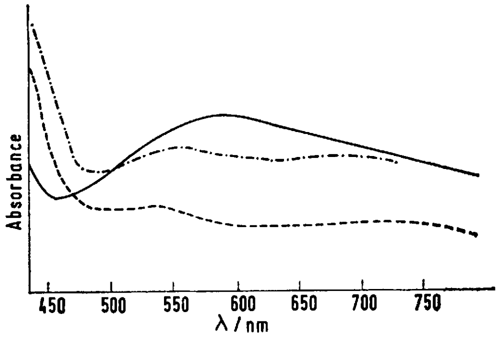

FIGURE 6 Change in electronic spectrum on addition of L-tartrate to a partially oxygenated solution of $Na_4[(VO)_2(D\text{-tart})_2]$. (——), ($I_D$); (—·—·—), ($I_{DL}$); (- - - -), mixture of L-tartrate and (I_D)

Since the electronic spectra of the three intermediates (I_D), (I_{DL}), and (I_M) are all different they either all contain different ratios of vanadium-(IV) to -(V) or some or all contain complexed tartrate ions. The fact that the electronic spectra of (I_D) and (I_{DL}) differ suggests that tartrate ion acts as a bridging ligand in the same way as it does in the dimeric vanadium(IV) tartrate complexes. It is possible that (I_D) contains D-tartrate bridges and (I_{DL}) has D- and L-tartrate bridges. If this is so then (I_{DL}) must be more stable than (I_D) otherwise it would undergo ligand dismutation into (I_D) and (I_L). It follows that the addition of L-tartrate to a solution containing (I_D) should cause rearrangement to the more stable (I_{DL}). A definite change in the electronic spectrum does occur (Figure 6),* the final spectrum being very similar to that of (I_{DL}). Addition of *meso*-tartrate to a solution of (I_D) resulted in little change in electronic spectrum. From studies on the vanadium(IV)–tartrate system it is clear that *meso*-tartrate bridges are unstable.[7] It is unlikely therefore that (I_M) will contain such bridges.

Oxygen Uptake.—The oxygen uptake by a series of D-, DL-, and *meso*-tartaric acid solutions of composition $[VO^{2+}]:[\text{tartaric acid}]:[OH^-] = 1:1:x$ was studied using Warburg manometry. There was no significant oxygen uptake at pH < 3 ($x < 3$). The colour of such solutions remained unchanged on exposure to air. However all the tartrate systems absorbed oxygen when $x \geqslant 3$.

Stoicheiometry. The oxygen : vanadium ratios found for the D-, DL-, and *meso*-tartrate systems are given in Table 1. From the values obtained using solutions where $x = 3$, 3·5, and 4·0, the overall reaction with molecular oxygen could be represented as in (1), where the ratio of *atoms* of oxygen : vanadium = 0·5 : 1. However the high values found for the ratio in alkaline solutions (when $x = 5$ or 6) would indicate that the stoicheiometry under these conditions was as in (2), for which the oxygen : vanadium ratio = 1·0 : 1. No concentration of peroxide ions was detected in any solution which absorbed dioxygen. Therefore, if equation (2) does represent the systems, then the peroxide ions must react further, very quickly, as in (3). The oxygen : vanadium ratio (*ca.* 1 : 1) actually observed at high pH requires that the two electrons come from a source other than vanadium, *e.g.* from the tartrate ions present in solution.

TABLE 1

Stoicheiometry of oxygen uptake for solutions of composition $[VO_2^+]:[\text{tartaric acid}]:[OH^-] = 1:1:x$

	Oxygen : Vanadium [a]			
x	DL	D	*meso*	Equation
3	0·41	0·35	0·43	(1)
3·5	0·52	0·44	0·44	(1)
4·0	0·55	0·46	0·52	(1)
5·0	0·76	0·77		(1) and (2)
6·0	0·75	0·81		(1) and (2)

[a] In atoms.

$$O_2 + 4V^{IV} + 4H^+ \rightleftharpoons 4V^V + 2H_2O \qquad (1)$$

$$O_2 + 2V^{IV} + 2H^+ \longrightarrow 2V^V + H_2O_2 \qquad (2)$$

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \qquad (3)$$

We believe that equation (1) represents the true stoicheiometry of the reaction and that the high oxygen : vanadium ratio found in alkaline solution is as a result of reduction of V^V by tartrate ion in these solutions. The latter reaction results in formation of V^{IV} and carbon dioxide, which remains in solution. The vanadium(IV), once formed, will autoxidize absorbing more oxygen, resulting in the observation of a high oxygen : vanadium ratio. We found no products of the oxidative degradation of tartaric acid (other than carbon dioxide).

Rate. The rate of uptake of oxygen by the vanadium-(IV)–tartrate system with different isomers of tartaric

---

* It is however difficult to assess the contribution of the dimeric vanadium(IV) DL-tartrate complex which will also be formed on the addition of L-tartrate ions.

[8] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.* 1967, **10**, 247.

[9] S. Ostrowetsky, *Bull. Soc. chim. France*, 1964, 1012.

[10] R. D. Gillard and A. Spencer, *J. Chem. Soc.* (*A*), 1970, 1761.

acid in the range pH 3—7 was in the order *meso* > D > DL [Figure 7(*a*)]. Also, within each of the D-, DL- and *meso*-tartrate systems, the rate of uptake increased with increasing pH [Figure 7(*b*)]. For solutions of stoicheiometry $[VO^{2+}] : [\text{tartaric acid}] : [OH] = 1 : 1 : 5$ and $1 : 1 : 6$, the initial uptake of oxygen was too rapid for accurate measurement with our manometers.

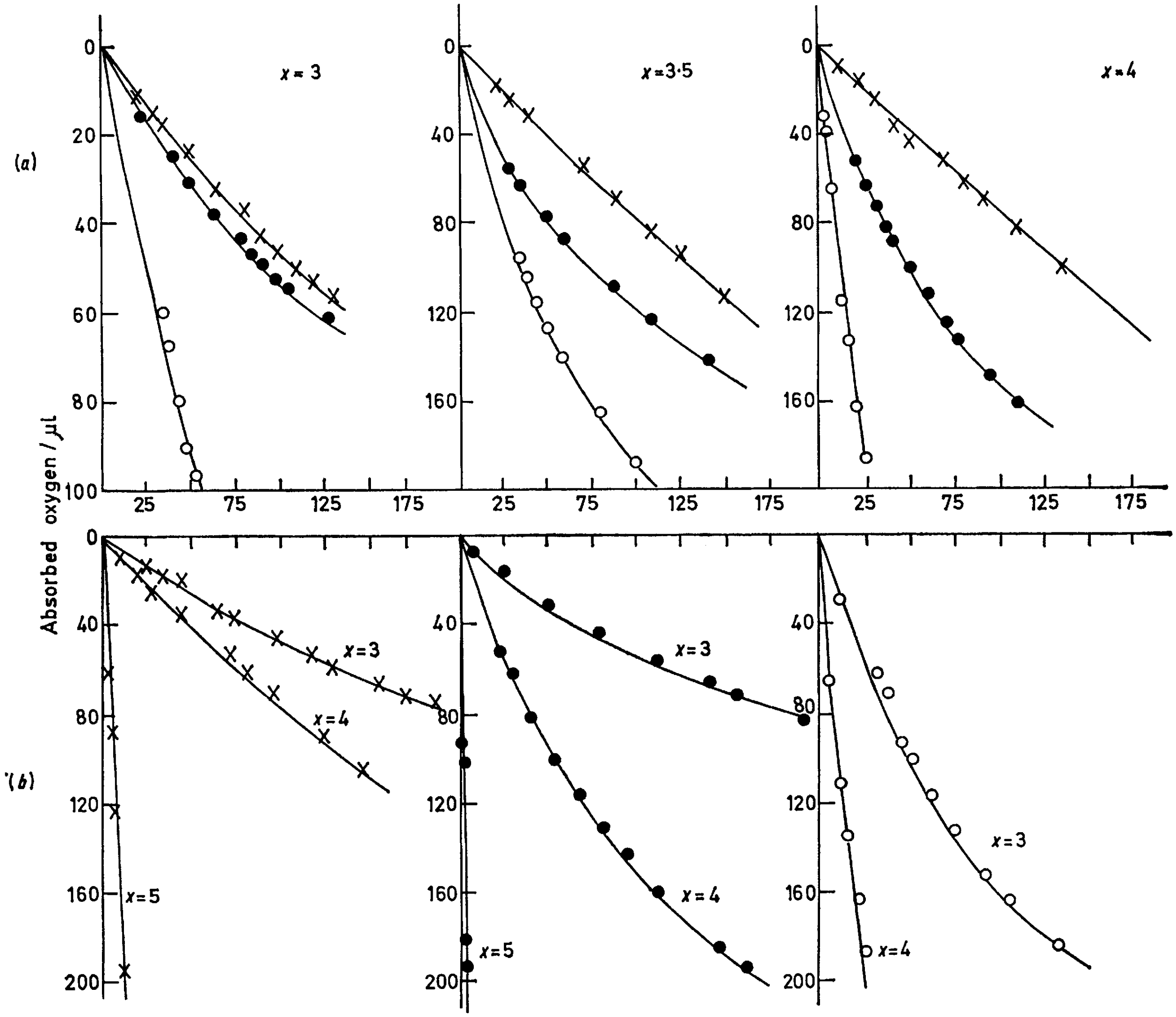

FIGURE 7 Oxygen uptake of solutions of stoicheiometry $[VO^{2+}] : [\text{tartaric acid}] : [OH^-] = 1 : 1 : x$. (×), DL-; (●), D-; (○), *meso*-tartaric acid

Complexes of Vanadium(V) *with Tartrate Ions.*—On oxygenation of solutions containing the dimeric vanadium(IV) tartrate complexes, $[(VO)_2(\text{D-tartrate})_2]^{4-}$ and $[(VO)_2(\text{D-tartrate})(\text{L-tartrate})]^{4-}$, an orange colour formed, accompanied by a decrease in the paramagnetic susceptibility of the solutions, indicative of the formation of vanadium(V) species, with the d^0 electronic configuration. We therefore studied the interaction of vanadium(V) with tartrate ions. Addition of D-, L-, or DL-tartaric acid to an aqueous solution of a metavanadate salt produced a deep orange solution, the charge-transfer bands (in the region 325—550 nm) of which were optically active (Figure 8) thus indicating complexing between the tartrate ions and the vanadium(V) chromophore. The orange solution formed with racemic tartrate ions had the same electronic spectrum as those containing only one enantiomer of tartaric acid. This behaviour differs from that of the vanadium(IV)-tartrate system, in which, as a result of dimer formation at pH 7, solutions containing DL- or D(or L-)-tartrate have[4] strikingly different electronic spectra.

A mixture of *meso*-tartaric acid and metavanadate ions or oxygenation of solutions of composition $[VO^{2+}] : [\textit{meso}\text{-tartaric acid}] = 1 : 1$ did not produce an orange colour. The electronic absorption bands of vanadium(V)-*meso*-tartrate solutions in the range 225—550 nm are at the same positions at the same pH as those observed for solutions containing decavanadate ions alone. The formation of an orange vanadium(V) tartrate complex with D- and L-, but not with *meso*-tartrate ions would suggest, by analogy with the dimeric vanadium(IV) tartrate complexes (where the *meso*-tartrate bridged species are very unstable), that the tartrate ion acts as a bridging ligand, just as it does for vanadium(IV).

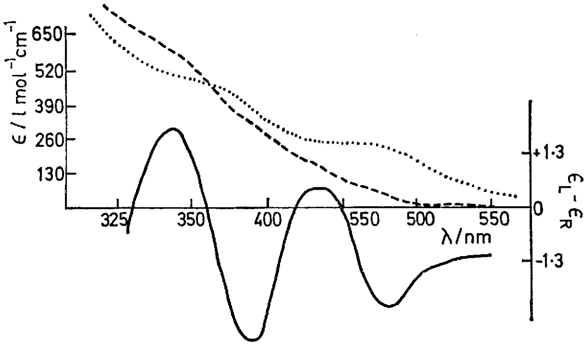

FIGURE 8 Electronic spectrum and circular dichroism of the orange vanadium(V) tartrates. (· · · ·), D- and DL-; (– – – –), *meso*-tartrate; (——), circular dichroism. Values of ε and ($\varepsilon_L - \varepsilon_R$) based on $[V^V]_T$

The orange vanadium(V) tartrate species exist in the range pH 6·5—2·5. Above pH 6·5 the orange colour disappeared and the solution became colourless; this change was reversible on lowering the pH. Below pH 2·5 the orange colour again disappeared with the formation in time of a blue solution. This contains the vanadium(IV) cation VO^{2+} as a result of reduction of the vanadium(V) by the tartrate ion species present. On addition of base to the blue solution a green colour formed which we consider to be a mixed-valence tartrate ion complex containing both vanadium-(IV) and -(V).

The positions of the absorption bands in the electronic spectrum of the vanadium(V) tartrate solutions did not change between pH 6·5 and 2·5. However, the absorption intensity did change (Figure 9), reaching a maximum at *ca.* pH 4·5. The circular dichroism of the optically active tartrate solutions paralleled the changes in the electronic spectrum. This indicates that the same tartrate complex is present throughout the pH range 6·5—2·5 with a maximum concentration of complex occurring at pH 4·5.

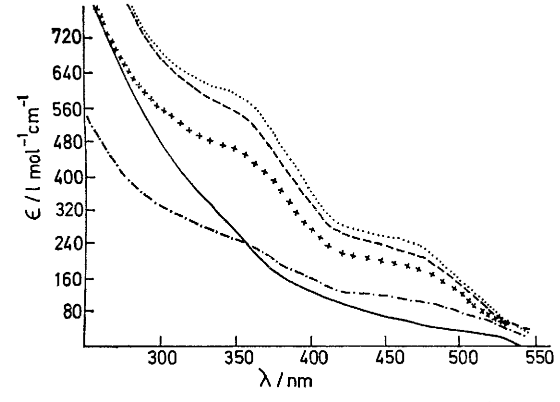

FIGURE 9 Variation of the electronic spectrum of the orange vanadium(V) tartrate with pH. (——), pH 6·4; (– – – –), 5·3; (· · · ·), 4·5; (×), 3·7; (— · — · —), 2·0. ε as in Figure 8

Several groups of workers have investigated the stoicheiometry of formation of the orange complex between vanadium(V) and tartaric acid, principally using the method of continuous variation. There have been claims for the formation of complexes with vanadium(V) : tartaric acid ratios of 2 : 1, 1 : 1, and 1 : 2 by Prasad and Pandey,[11] whereas Gosh *et al.*[12] report the formation of just one species of stoicheiometry 2 : 1. Jahr *et al.*,[13] in the most recent investigation, claim the existence of species of stoicheiometry 2 : 1 and 1 : 1. All these studies used either D- or DL-tartaric acid.

The stoicheiometry of the orange complex was reinvestigated, again using the method of continuous variation but measuring the circular dichroism absorption of the solution. The latter was measured for solutions containing various vanadium(V) : D-tartaric acid ratios of 1 : 4 to 4 : 1, the positions of the absorption maxima (−480, +434, −392, and +342 nm) being unchanged. No optical activity could be detected in solutions with vanadium(V) : D-tartaric acid ratios of <1 : 4 and >4 : 1. The intensity of the absorption reached a maximum at a ratio of *ca.* 2 : 1. Since the formation of the orange vanadium(V) tartrate is pH dependent the circular dichroism was measured of equimolar solutions containing various vanadium(V) : D-tartaric acid ratios at constant pH. The pH of each solution was adjusted to 4·5 as this appears to be the optimum for complex formation. An intensity maximum was again obtained at a ratio of *ca.* 2 : 1.

In the above studies the values found for the circular dichroism absorbance at a given vanadium(V) : D-tartaric acid ratio were not very reproducible. We believe that this is partly a result of the reduction of vanadium(V) by tartaric acid. Further, the values of the absorbance were very sensitive to small changes in pH and values found for the stoicheiometry of formation of the orange vanadium(V) tartrate complex must therefore be regarded as tentative. One significant result that does emerge from the above observations is that only one predominantly optically active species appears to be present in the orange vanadium(V) tartrate solutions in the pH range 2·5—6·5.

A further interesting observation on the vanadium(V) tartrate solutions is the effect of heat on the solutions. On heating the orange solution of the complex on a steam-bath it rapidly became colourless (Figure 10); the original colour returned on cooling. Solutions of the free decavanadate ion, which are also orange, are however stable to heat.

We have measured the Raman spectra of solutions containing the orange vanadium(V) tartrate at various values of pH and these are compared (Table 2) with measurements on the decavanadate ion carried out by

---

[11] S. Prasad and L. P. Pandey, *J. Proc. Inst. Chem.* (*India*), 1965, **37**, 125.

[12] B. N. Gosh, S. P. Moulik, K. K. Sengupta, and P. K. Pal, *J. Indian Chem. Soc.*, 1963, **40**, 509.

[13] K. F. Jahr, F. Preuss, and L. Rosenhahn, *J. Inorg. Nuclear Chem.*, 1969, **31**, 297.

Griffith and Lesniak.[14] The similarity of the spectra suggests that the tartrate complex contains V=O and $\mathrm{V}\overset{\mathrm{O}}{\diagup\;\diagdown}\mathrm{V}$ linkages similar to those in the decavanadate ion, the latter being[15] the predominant vanadate species in the pH range 7—2. The instability of the vanadium(V)–tartrate solutions became apparent during these measurements, decomposition after one scan (taking *ca.* 20 min) being sufficient to make further measurements (notably of polarization) difficult.

Conclusion.—The order of stability of the dimeric tartrate-bridged vanadium(IV) complexes is $K_{\mathrm{DL}} > K_{\mathrm{DD}} \gg K_{meso\text{-}meso}$, where $K = [(\mathrm{VO})_2(\mathrm{tart})_2{}^{4-}]/[(\mathrm{VO})(\mathrm{tart})^{2-}]^2$. This order is the converse of that found for rates of autoxidation, suggesting that the active species in the reaction with molecular oxygen are monomeric vanadium(IV) tartrate complexes. The observation that the rate of autoxidation also increases with increasing pH in all three tartrate systems further suggests that the active species in the reaction with dioxygen are monomeric hydroxo-complexes. Thus Kaden and Fallab,[16,17] in their studies on the autoxidation of bis(picolinato)vanadium(IV), have shown that the most readily autoxidized species are the partially hydrolysed metal ions $[\mathrm{V^{IV}(OH)_2Z}]$ (Z = the picolinate ion). The initial attack of dioxygen was said[18] to occur in a position *trans* to the vanadium(IV) oxygen atom.

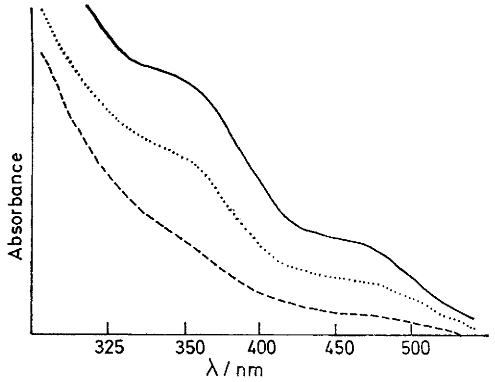

FIGURE 10 Effect of temperature on the orange solutions of the vanadium(V) tartrate. (——), original solution; (– – – –), after keeping at 80 °C for *ca.* 2 min; (· · · ·), after keeping at 80 °C for *ca.* 2 min and then cooling for *ca.* 30 min

Analysis of the overall kinetics of autoxidation of vanadium(IV) tartrate is difficult since the vanadium(V) species formed initially appears to combine with vanadium(IV) species still present to form a mixed vanadium(IV)–vanadium(V) complex (I). The detailed nature

TABLE 2

Comparison of Raman spectra of the decavanadate ion and the vanadium(V) tartrate complex

pH 2·5	Vanadate			*1004*s	980m		935w			840m	
	Vanadate + D-Tartaric acid		1072s		980s		971m			838w	
pH 3·3	Vanadate			*1001*s	970s		925w			840m	
	Vanadate + D-Tartaric acid		*1100*s	1005s			925m		855vw	832s	
pH 4·5	Vanadate			*992*s	960s	955w	920w			840w	
	Vanadate + D-Tartaric acid		1100s	1000s			925w		855w		
pH 10·9	Vanadate						*915*s	877s			810m
pH 0·8	Vanadate				940s		910w				
D-Tartaric acid (4M)		(1760)		1000			900				

pH 2·5	Vanadate		595m		550w	454m			320s			
	Vanadate + D-Tartaric acid			572s			400s	350m				
pH 3·3	Vanadate		597m		550w	458w			324s		251m	
	Vanadate + D-Tartaric acid	655w	590bs			442w	405s	352m		280bs		
pH 4·5	Vanadate		600w		543w	460w			322s		251w	
	Vanadate + D-Tartaric acid		600bs	570sh		470w	400s	350m				
pH 10·9	Vanadate				545m	500w		351m				228w
pH 0·8	Vanadate							348w	320vw			
D-Tartaric acid (4M)												

Absorption energies are given in wave numbers ($\mathrm{cm^{-1}}$); polarized bands are italicized; s = strong, m = medium, w = weak.

---

[14] W. P. Griffith and P. J. B. Lesniak, *J. Chem. Soc.* (*A*), 1969, 1066.

[15] M. J. Pope and B. W. Dale, *Quart. Rev.*, 1968, **22**, 527.

[16] Th. Kaden and S. Fallab, *Chimia*, 1965, **19**, 176.

[17] Th. Kaden and S. Fallab, *Chimia*, 1966, **20**, 51.

[18] S. Fallab, *Angew. Chem. Internat. Edn.*, 1967, **6**, 496.

of the latter is uncertain but available evidence suggests that it is polymeric and contains complexed tartrate which (at least in the D- and DL-systems) could be acting as a bridging ligand between the vanadium centres. The *meso*-tartrate system behaves differently probably as a result of the inability of this ligand to form stable bridges between metal centres.

Solutions containing the mixed-valence intermediate continue to react with oxygen, the final product in the D- and DL-tartrate systems being an orange solution containing vanadium(V) tartrate species. The nature of the fully oxidized solution in the *meso*-tartrate system is still not clear. The mixed-valence complex is in equilibrium with vanadium-(IV) and -(V) species but, in the presence of oxygen, this equilibrium is continually being disturbed by reaction of free vanadium-(IV) species with molecular oxygen, resulting in the concentration of the mixed-valence intermediate being continually diminished.

Both the Raman spectra of orange solutions containing the vanadium(V) tartrate and the pH range, 2·5—6·5, in which the orange species exist, suggest that the structure of the orange vanadium(V) tartrate species is like that [19] of the decavanadate ion $[V_{10}O_{28}]^{6-}$. Complexed tartrate must be present in the species responsible for the orange colour since the electronic absorption bands of the solutions containing resolved tartaric acid are optically active. The core of the orange tartrate complex appears to be less stable than that of the decavanadate ion, since solutions containing the tartrate complex become colourless when heated, a likely consequence of break-up of the polystructure of the complex.

A Job's plot on the vanadium(V)–tartrate system indicates that the orange species has an approximate molecular formula $[(V^{V})_2(\text{tartrate})]_n$. The electronic absorption spectra indicate that the same orange complex is formed in solutions containing D- (or L-) or DL-tartrate ions. Non-formation of this species in solutions containing *meso*-tartaric acid would indicate, by analogy with the vanadium(IV)–tartrate system, that the complex contains bridging tartrate ligands. A dimeric *meso*-tartrate-bridged vanadium(IV) complex is not formed because [7] such a structure would involve an eclipsed conformation for the bridging tartrates. Whatever the nature of the incorporation of tartrate in the orange vanadium(V) complex there must be some stereochemical restriction preventing formation of a *meso*-tartrate species.

EXPERIMENTAL

Electronic spectra were measured using a Unicam SP 800 spectrophotometer and circular dichroism spectra using a Roussel–Jouan Dichrographe model B.

Preparation of Dimeric Vanadium(IV) *Tartrate Complexes.*—$Na_4[(VO)_2(\text{D-tart})_2],6H_2O$ and $Na_4[(VO)_2(\text{D-tart})(\text{L-tart})],11H_2O$ complexes were prepared according to the method of Tapscott and Belford.[4] Samples were recrystallized three times from water. It was necessary to keep solutions under nitrogen during recrystallization (particularly the dimeric D–D-tartrate) to prevent oxidation. Concentrations of solutions of the dimeric complexes used for electronic and circular-dichroism measurements were checked by vanadium analysis using EDTA titration.[4]

Oxygenation.—Spectrophotometric measurements. The change in electronic spectrum on oxygenation of solutions of $Na_4[(VO)_2(\text{D-tart})_2]$ and $Na_4[(VO)_2(\text{D-tart})(\text{L-tart})]$ was measured using a 1-cm spectrophotometric flow cell coupled to a peristaltic pump (Watson and Marlow). The latter was used with P.V.C. tubing of 3 mm internal diameter. Before oxygenation the solutions were kept under an atmosphere of nitrogen. During oxygenation a vigorous stream of oxygen (saturated with water to minimize evaporation loses) was blown through the solution (*ca.* 10 l h^{-1}) so that oxygen was always in an excess. Solutions were also analysed for vanadium after oxygenation to check on any change of concentration as a result of evaporation. The flow cell was placed in a thermostatted cell-block at the same temperature (25 °C) as the oxygenation vessel, which was also kept in a thermostatted water bath. The absorbances of solutions were measured on a Unicam SP 800 spectrophotometer fitted with a constant-wavelength unit and automatic cell change (SP 825 Series 2); this enabled the absorbance to be measured at regular time intervals at one wavelength (*i.e.* 600 nm). Solutions of composition $[VO^{2+}] : [meso\text{-tartaric acid}] = 1 : 1$ ($[VO^{2+}]_T = 2 \times 10^{-3}$M) were adjusted to pH 4, 5, and 6, oxygenated for *ca.* 18 h, and their electronic spectra measured.

Magnetic measurements. The magnetic susceptibilities of the vanadium(IV) tartrate solutions were measured during oxygenation by the method of Evans.[20] Solutions used for measurements (using a 60 MHz Perkin-Elmer R10 spectrometer with a probe temperature of 33·4 °C) were 0·079M in vanadium and contained t-butyl alcohol (5%) as internal reference. These were contained in standard n.m.r. tubes and the external reference was a melting-point tube containing aqueous t-butyl alcohol (50%).

Oxygen uptake. The oxygen uptakes of solutions of stoicheiometry $[VO^{2+}](0{\cdot}15\text{M}) : [\text{tartaric acid}] : [OH^-] = 1 : 1 : x$ were followed using a Warburg manometer (Townson and Mercer). The purity of the D-tartaric acid was checked by measuring its optical rotatory dispersion and the composition of the vanadium(IV) sulphate (B.D.H.) was determined by titration with potassium permanganate. Sodium hydroxide solutions were prepared from concentrated volumetric solutions (B.D.H.). All aqueous solutions were prepared using deoxygenated distilled water.

For each measurement 0·15M-tartaric acid (0·25 cm^3) and the required amount of sodium hydroxide (*e.g.*, $x = 2$, 0·5 cm^3 of 0·15M-NaOH) were pipetted into the main body of the Warburg flask and 0·15M-vanadium(IV) sulphate (0·25 cm^3) placed in the side-arm of the flask. The total contents of the flask were made up to 2 cm^3 by addition of water. The flask was then filled with oxygen and allowed to equilibrate in a thermostatted water bath at 25 °C. The solutions were then mixed and the pressure changes measured at regular intervals; all measurements were made at least in triplicate. Changes in atmospheric pressure during the experiment were corrected for by placing a thermobarometer [*i.e.* a manometer with a flask containing water (2 cm^3)] in the thermostatted water bath with the experimental manometers.

Variation of Circular-dichroism and Electronic Spectra

---

[19] M. T. Evans, *Inorg. Chem.*, 1966, **5**, 967.
[20] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

with pH.—Solutions of the orange vanadium(V) tartrate were prepared by mixing aqueous solutions of sodium metavanadate (10^{-2}M, 5 cm^3) and D-tartaric acid (10^{-2}M, 5 cm^3), then diluting to 25 cm^3. The pH of the solutions was adjusted with hydrochloric acid or sodium hydroxide as required and measured on a Radiometer pH meter type 4d calibrated with 0·05M-potassium hydrogen phthalate. Measurements of the proton magnetic resonance of the vanadium(V) tartrate solutions were also attempted. However sufficient reduction of the vanadium took place during the measurements to broaden the resonance absorption so that no useful information could be obtained.

Stoicheiometry of Vanadium(V) *Tartrate*.—The method of continuous variation [21] was applied under the following conditions. (i) pH not constant: 10^{-2}M solutions of sodium metavanadate and D-tartaric acid were used as stock solutions. Solutions containing various vanadium(V) : D-tartaric acid ratios were prepared by mixing the required amounts of the stock solutions. (ii) pH constant: the same stock solutions were used as above, but each solution was adjusted to pH 4·5 by addition of acid or alkali as required. This adjustment was made using a Radiometer pH stat with titration equipment type SBR2C-BU1/TTA$_3$ and pH meter type 25.

Raman Spectra.—Solutions used for Raman measurements were prepared by dissolving $NaVO_3$ (0·249 g, 0·002 mol) and D-tartaric acid (0·30 g, 0·002 mol) in water (10 cm^3). The pH was then adjusted by addition of sodium hydroxide. The solutions were used immediately after preparation, Raman spectra being measured using a Coderg PH1 spectrometer with an O.I.P. (1·81E) He/Ne laser of 150 mW exciting line.

[1/1857 *Received*, 11*th October*, 1971]

---

[21] W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1941, **63**, 437.