Hydrolysis of the Oxovanadium(IV) Ion and the Stability of its Complexes with the 1,2-Dihydroxybenzenato(2−) Ion

By **R. Peter Henry, Philip C. H. Mitchell,*** and (the late) **John E. Prue**, Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

A technique which eliminates effects of changes in asymmetry potential has been adapted for use in pH titrations with high-resistance glass electrodes. A study, using cells without liquid junctions, has been made of the hydrolysis of the oxovanadium(IV) ion and of its complexes with the 1,2-dihydroxybenzenato(2−) ion. Equilibrium constants are reported.

THE oxovanadium(IV) ion, VO^{2+}, forms stable complexes with the 1,2-dihydroxybenzenato(2−) ion in aqueous solutions, but the results of earlier quantitative studies of the stabilities, and even the identities, of these complexes are discrepant and unsatisfactory. Potentiometric studies [1-3] were made on cells with liquid junctions and with uncertain control of ionic activity coefficients. Furthermore, the effects of hydrolysis of the oxovanadium(IV) ion or the formation of complexes with sulphate or chloride ions were ignored or inadequately considered. Spectrophotometric measurements [4] lead to stability-constant values which disagree with those reported from potentiometric measurements.

In the present study precise potentiometric measurements have been made on cells with glass and silver–silver chloride electrodes which avoid liquid junctions. A careful examination of the hydrolysis of the oxovanadium(IV) ion was necessary before the investigation of the complexes. The only satisfactory previous study [5] of this hydrolysis relates to measurements in 3M-sodium perchlorate. Another reason for this study of the 1,2-dihydroxybenzenato-complexes was the previous isolation [6] of thallium(I) salts of the anion $[V(C_6H_4O_2)_3]^{2-}$. The only evidence for the existence of such an anion in detectable amounts in solution was a report [7] of spectrophotometric evidence for the slow formation in solution at pH 4 of a 1 : 3 V^{IV} complex with the anion.

EXPERIMENTAL

Reagents.—For the preparation of oxovanadium(IV) perchlorate, a glass apparatus was used in which solutions could be manipulated in an atmosphere of nitrogen gas. Oxovanadium(IV) sulphate solution was deoxygenated and the oxide VO_2 precipitated by addition of concentrated ammonium carbonate. The oxide was then filtered off, by inversion of the apparatus, and washed (24 h) with oxygen-free demineralised water until no sulphate ions were detected in the washings. The minimum quantity of perchloric acid (AnalaR, 60%) necessary to dissolve the oxide was then added and the resulting solution diluted with oxygen-free

---

[1] R. Trujillo, F. Brito, and J. Cabrera, *Anales Real Soc. Espan. Fis. Quim.*, 1956, **52***B*, 589.

[2] T. Beltran and L. Mateo, *Anales Real Soc. Espan. Fis. Quim.*, 1965, **61***B*, **12**, 1219.

[3] K. Lal and R. P. Agarwal, *Bull. Chem. Soc. Japan*, 1967, **40**, 1148.

[4] S. Ya Schneiderman, *J. Chim. Ukraine*, 1959, **25**, 795.

[5] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, 1955, **9**, 1177.

[6] R. P. Henry, P. C. H. Mitchell, and J. E. Prue, *J. Chem. Soc.* (*A*), 1971, 3392.

[7] D. K. Bhatacharya and S. N. Baneiji, *Z. anorg. Chem.*, 1962, **118**, 315.

demineralised water to the required concentration. The vanadium(IV) concentration was determined by titration against standard potassium permanganate solution and the excess of perchloric acid concentration by titration against standard sodium hydroxide. The end-point of the latter titration was difficult to determine because of hydrolysis of the oxovanadium(IV) ion, but Gran's method,[8] for finding the end-point by extrapolation of points on the titration curve before the end-point is reached, overcame this problem.

Bromide-free sodium chloride was prepared by a standard method,[9] and the bromide content of hydrochloric acid was reduced to $<0{\cdot}002$ mole % by two distillations. A solution (0·01 mol kg^{-1}) of the latter was prepared and standardised conductimetrically.[10] Carbonate-free sodium hydroxide solution was standardised against the hydrochloric acid solution by weight titration. 1,2-Dihydroxybenzene (AnalaR) was sublimed in a nitrogen atmosphere under reduced pressure. The product melted sharply at 104 °C.

Apparatus.—The titration cell, which was immersed in a water thermostat at 25 °C, was a cylindrical flat-bottomed glass vessel of *ca*. 400 cm^3 capacity. It was fitted with a rubber stopper which gave an airtight seal and carried ground-glass sockets for the introduction of the electrodes, *etc*. Glass electrodes used were of type GHS 33/13 (Electronic Instruments, Ltd.), the stems of which were thinly coated with paraffin wax to reduce adhesion of liquid to the electrode when it was removed from solution (see below). Thermal-electrolytic silver–silver chloride electrodes were used. The potential was measured with a Cropico Vernier potentiometer type P10; the final 0·5 mV was displayed on a Hitachi 159 recording potentiometer and followed as a function of time. The null-point detector was a Vibron Electrometer model 62A. Careful attention to electrical shielding was necessary to prevent interference from the thermostat motor, operator movements, *etc*. The coaxial lead from the glass electrode was bound with aluminium foil, shielded cables being used elsewhere in the circuit; the thermostat-bath stirrer motor was shielded with a copper sheet, and the shielding was connected to an earthed ' equipotential surface ' of copper sheets on which the apparatus rested.

Procedure.—A technique previously used with low-resistance glass electrodes was adapted for the titrations.[11] A glass-electrode (g.e.) was transferred between the cells (A) and (B) [equations (1) and (2)]. Provided the transfer

$$\text{(A) g.e. }|\text{HCl } (0{\cdot}01 \text{ mol kg}^{-1})|\text{AgCl}|\text{Ag} \qquad (1)$$

$$\text{(B) g.e. }|\text{VO(ClO}_4)_2,\ \text{C}_6\text{H}_4(\text{OH})_2,\ \text{NaCl, NaOH}|\text{AgCl}|\text{Ag} \qquad (2)$$

technique eliminates any effect of changing asymmetry potential,[11] the potential difference $E(= E_{\text{B}} - E_{\text{A}})$ is given by (3) which on rearrangement gives (4), where m_{Cl} and m_{H}

$$E = 2k \log (m_1\gamma_1) - k \log m_{\text{Cl}}\gamma_{\pm}^2 - k \log m_{\text{H}} \qquad (3)$$

$$\log m_{\text{H}} = -E/k + 2 \log (m_1\gamma_1) - \log m_{\text{Cl}}\gamma_{\pm}^2 \qquad (4)$$

are the molalities of chloride and hydrogen ion respectively in cell (B), $\gamma_{\pm}$ is the mean ionic activity coefficient of HCl in cell (B), and m_1 and γ_1 are the molality and mean ionic activity coefficient, respectively, of the hydrochloric acid in reference cell (A). The value of γ for 0·01 mol kg^{-1} hydrochloric acid is accurately known.[12] There are no liquid junctions in the cells; the chloride ion concentration in cell (B) was kept sufficiently low for the degree of formation of VOCl$^+$ to be negligible.[13]

The solution in the titration vessel [cell (B)] was made up by weight. The two cells were immersed in the thermostat-bath, and two silver–silver chloride electrodes of small bias potential (usually $<40\ \mu$V) were inserted in each vessel. White Spot nitrogen was passed through the solutions, after passage through presaturators, and the solutions were set aside (1 h). In experiments involving 1,2-dihydroxybenzene, the latter was added at this stage and deoxygenation was continued (2 h). The glass electrode was then removed from a conditioning solution [a mixture of the solutions in vessels (A) and (B) at 25 °C], thoroughly washed with hydrochloric acid (0·01 mol kg^{-1}) from a Polythene washbottle kept in the thermostat-bath, and placed in cell (A). The e.m.f. of the cell was followed until any change was linear with time. Under normal conditions the changes were linear at the outset, and the glass electrode was removed from cell (A) after *ca*. 12 min, rinsed thoroughly with distilled water at 25 °C, inverted so that water adhering to the bulb ran down on to the stem where it was removed with filter paper (touching the bulb disturbs the potential), and finally inserted into cell (B). The e.m.f. was again followed until its change was linear with time. The linear portions of the e.m.f. against time curves, before and after transfer, were extrapolated to the time of transfer and the e.m.f. difference ΔE_E determined at that time.

The composition of the test solution was then changed by adding a small increment (*ca*. 0·01 cm^3) of sodium hydroxide with a previously calibrated Agla micrometer syringe. The change of e.m.f., ΔE_1, associated with this addition was obtained by extrapolating linear portions of the e.m.f. against time curves before and after the addition. This procedure was repeated for every addition of sodium hydroxide during the course of the titration and, in general, $E = \Delta E_t + \Delta E_1 + \Delta E_2 + \Delta E_n$ for n additions of alkali. A test of the procedure with acetic acid [14] established that a precision equal to that attained in the best work with hydrogen electrodes is attainable.

In the study of the hydrolysis of the oxovanadium(IV) ion, a cross-check on the concentrations was possible by extrapolation of the first few points of the titration curve by Gran's method [8] to determine the excess of perchloric acid. At the conclusion of each titration, the solution was acidified with perchloric acid and a spectrophotometric determination of the vanadium(IV) concentration established that no oxidation had occurred during the titration.

RESULTS AND DISCUSSION

Hydrolysis of the Oxovanadium(IV) *Ion*.—Satisfactory results were obtained with $m_{\text{H}} > 5 \times 10^{-4}$ mol kg^{-1}; below this concentration, e.m.f. against time curves were non-linear and only approached the usual shape after

---

[8] G. Gran, *Analyst.*, 1952, **77**, 661.

[9] G. Pinching and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 311.

[10] R. H. Stokes, *J. Phys. Chem.*, 1961, **65**, 1242.

[11] A. K. Covington and J. E. Prue, *J. Chem. Soc.*, 1955, 3696, 3701; see also H. L. Cleever and R. M. Reeves, *J. Phys. Chem.*, 1962, **66**, 2268.

[12] R. G. Bates, E. A. Guggenheim, H. S. Harned, D. J. G. Ives, G. J. Janz, C. B. Monk, R. A. Robinson, R. H. Stokes, W. F. K. Wynne-Jones, and J. E. Prue, *J. Chem. Phys.*, 1956, **25**, 361.

[13] S. Ahrland and B. Noren, *Acta Chem. Scand.*, 1958, **12**, 1595.

[14] R. P. Henry, J. E. Prue, F. J. C. Rossotti, and R. J. Whewell, *Chem. Comm.*, 1971, 868.

some hours. The conclusion that a hydrolytic reaction slowly approaching equilibrium was superimposing its effect on a changing asymmetry potential, was confirmed by the failure of back-titrations with perchloric acid to show reversibility in this region of the titration curve. It is presumably the slow formation of higher polymeric species, which may be insoluble, which is responsible for this complication.[5]

We postulate, following Rossotti and Rossotti,[5] that only two hydrolysed species exist in the range 2×10^{-3} mol kg^{-1} $> m_{\mathrm{H}} > 5 \times 10^{-4}$ mol kg^{-1} [equations (5) and (6)]. The equilibrium constants for the two species

$$\mathrm{VO^{2+} + H_2O \rightleftharpoons VO(OH)^+ + H^+} \qquad (5)$$

$$\mathrm{2VO^{2+} + 2H_2O \rightleftharpoons [VO(OH)]_2{}^{2+} + 2H^+} \qquad (6)$$

$\mathrm{VO(OH)^+}$ and $\mathrm{[VO(OH)]_2{}^+}$ are defined by $K_{\mathrm{h}} = m_{\mathrm{VO(OH)}} m_{\mathrm{H}} \gamma_+{}^2 / m_{\mathrm{VO}} \gamma_{2+}{}^2$ and $K_{\mathrm{h}}' = m_{\mathrm{[VO(OH)]_2}} m_{\mathrm{H}}{}^2 \gamma_{2+} \gamma_+{}^2 / m_{\mathrm{VO}}{}^2 \gamma_{2+}{}^2$. The solutions used throughout were judged to be sufficiently dilute for activity-coefficient values to be given by equation (7), where I is the ionic strength

$$-\log \gamma_i = Z_i{}^2 A I^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) \qquad (7)$$

and Z_i the charge number of ion i. Combination of K_{h} and K_{h}' with the material-balance equations for vanadium(IV) and hydrogen ions gives equation (8), where m_{V}

$$m_{\mathrm{H}}(m_{\mathrm{V}} - m_{\mathrm{VO}})\, \gamma_+{}^2 / m_{\mathrm{VO}} \gamma_{2+} = K_{\mathrm{h}} + (2K_{\mathrm{h}}' m_{\mathrm{VO}} / m_{\mathrm{H}}) \qquad (8)$$

is the total analytical concentration of vanadium(IV).

A suitable iterative computer program was used to calculate m_{Cl} from equation (4) and then values of $m_{\mathrm{VO}}/m_{\mathrm{H}}$ and the left-hand side of equation (8); in calculating the ionic strength values, it was assumed, with sufficient accuracy, that the vanadium(IV) was only present as $\mathrm{VO^{2+}}$. A least-squares program was then used to calculate the best-fit values of the constants. The average values from three titrations were $K_{\mathrm{h}} = 2{\cdot}16 \times 10^{-6}$ mol kg^{-1} and $K_{\mathrm{h}}' = 2{\cdot}13 \times 10^{-7}$ mol kg^{-1}. Differences δE between experimental e.m.f. values and those calculated from the values obtained from the constants are listed in Supplementary Publication No. SUP 20685 (11 pp., 1 microfiche).* The agreement, with a standard deviation of 0·08 mV, is satisfactory and confirms Rossotti and Rossotti's conclusion[5] that, over the concentration range investigated, the titration curves are adequately explained by two equilibria. Comparison with Rossotti and Rossotti's results gives values of 0·46 and 0·62 for the activity-coefficient quotients of the expressions for K_{h} and K_{h}' in 3M-sodium perchlorate. The values are reasonable, but could not of course have been theoretically predicted.

Equilibria between the Oxovanadium(IV) *Ion and* 1,2-*Dihydroxybenzene* ($\mathrm{H_2L}$).—A preliminary study with an automatic titrimeter showed that, with m_{V} *ca.* $1{\cdot}6 \times 10^{-3}$ mol kg^{-1} and a 1 : 1 $\mathrm{H_2L : V^{IV}}$ mole ratio, there was an end-point after the addition of 3 moles of alkali per mole of vanadium(IV) (subsequent to the neutralisation of the excess of perchloric acid). Presumably the formation of the chelate complex VO(L) is followed by its hydrolysis to $\mathrm{VO(L)(OH)^-}$. With the same vanadium(IV) concentration and $\mathrm{H_2L : V^{IV}}$ mole ratios $>2:1$, there was an inflexion after the addition of 1 mole of alkali and finally an end-point when 4 moles of alkali per mole of vanadium(IV) had been added, thereby indicating formation of $\mathrm{VO(L)_2{}^{2-}}$. In both cases a total titration time of at least 30 min was necessary to obtain reproducible titration curves. Earlier workers[1-3] make no mention of the time required to obtain stable potentials. In the precise measurements, at least 30 min were required after each addition of alkali before the normal e.m.f. against time variation appeared. This inevitably restricted the precision of the measurements; the longer the time required for the system to attain chemical equilibrium, the longer the extrapolation of the linear portion of the e.m.f. against time plots back to the addition of alkali, and the reliability of the extrapolation is thereby reduced. The vanadium(IV) ion molalities were kept within the range 10^{-3}—10^{-2} mol kg^{-1}; automatic titrimeter experiments showed that, with a concentration of 10^{-4} mol kg^{-1}, the end points, whatever the $\mathrm{H_2L : V^{IV}}$ mole ratio, always appeared at 3 moles of alkali per mole of vanadium(IV). At the higher pH values of the titration curves with the more dilute vanadium(IV) solutions, the reaction appears not to proceed beyond formation and hydrolysis of the 1 : 1 chelate complex VO(L).

The Complex VO(L). Solutions containing approximately 1 : 1 $\mathrm{H_2L : V^{IV}}$ mole ratios were used. Approximately 2 moles of alkali could be added before there were signs of increasing slowness of attainment of equilibrium (>30—40 min), probably due to formation of the hydrolysed species $\mathrm{VO(L)(OH)^-}$ and its subsequent polymerisation. Titrations were stopped at this point. In fitting the results, the equilibria taken into account were (5), (6), and (9). Combination of the material-balance

$$\mathrm{VO^{2+} + H_2L \rightleftharpoons VO(L) + 2H^+} \qquad (9)$$

relations for vanadium(IV) and hydrogen ions with the hydrolysis equilibrium constants gives equation (10).

$$a m_{\mathrm{VO}}{}^2 + b m_{\mathrm{VO}} + c = 0 \qquad (10)$$

where

$$a = 2K_{\mathrm{h}}' \gamma_{2+} / m_{\mathrm{H}}{}^2 \gamma_+{}^2$$

$$b = 2 + (K_{\mathrm{h}} \gamma_{2+} / m_{\mathrm{H}} \gamma_+{}^2)$$

$$c = 2m_{\mathrm{V}} - m_{\mathrm{H}} - m_{\mathrm{NaOH}} + m_{\mathrm{HClO_4}}$$

An iterative computer program was used to calculate m_{H} from equation (4) and then m_{VO} from equation (10). Equation (7) was again used for ionic activity coefficients, but all species were taken into account in calculating ionic-strength values. Knowing m_{VO}, the concentration of all other species could be calculated and the equilibrium constant $K_1 = m_{\mathrm{VO(L)}} m_{\mathrm{H}}{}^2 \gamma_{2+}{}^2 / m_{\mathrm{VO}} m_{\mathrm{H_2L}} \gamma_{2+}$ then obtained. The average value of K_1 was $6{\cdot}89 \times 10^{-6}$ mol kg^{-1}. The results, and values of the difference δE between experimental and calculated e.m.f. values,

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Index Issue.

are given in the Supplementary Publication. The standard deviation is 0·40 mV.

The complex $VO(L)_2^{2-}$. Solutions with $H_2L : V^{IV}$ mole ratios >2 were titrated against alkali. The results for the first half of the titration curve, up to the addition of 2 moles of alkali per mole of vanadium(IV), confirmed the value for K_1 reported above. The second part of the titration curve was used to obtain a value of the equilibrium constant for reaction (11). The

$$VO^{2+} + 2H_2L \rightleftharpoons VO(L)_2^{2-} + 4H^+ \qquad (11)$$

precision technique revealed that, over this point of the titration curve, 2—3 h were required after each addition of alkali before chemical equilibrium was reached. The precision of the extrapolations was therefore severely reduced. The equilibrium constant $K_2 = m_{VO(L)_2} m_H^4 \gamma_{2-} \gamma_+^4 / m_{VO} m_{H_2L}^2 \gamma_{2+}$. Combination of the material-balance relations for vanadium(IV), 1,2-dihydroxybenzene, and hydrogen ions with the equilibrium constants K_h, K_h', K_1, and K_2 gives equation (12).

$$am_{VO}^3 + bm_{VO}^2 + cm_{VO} + d = 0 \qquad (12)$$

where

$$a = 2K_h'K_1\gamma_{2+}^2/m_H^4\gamma_+^4$$

$$b = (6K_h'\gamma_{2+}^2/m_H^2\gamma_+^2\gamma_{2+}) + (K_hK_1\gamma_{2+}^2/m_H^3\gamma_+^4)$$

$$c = 4 + (3K_h\gamma_{2+}/m_H\gamma_+^2) - K_1\gamma_{2+}(2m_{H_2L} - m_H - m_{NaOH} + m_{HClO_4})/m_H^2\gamma_+^2$$

$$d = m_H + m_{NaOH} - m_{HClO_4} - 4m_V$$

With known values of K_h, K_h', and K_1, equation (12) was iteratively solved for m_{VO}. Knowing m_{VO}, the concentration of all other species could be calculated and thence K_2; the mean value was $1{\cdot}19 \times 10^{-13}$ mol² kg⁻². Values of δE calculated from our equilibrium constant values are given in the Supplementary Publication. The fit of the results can be improved by introducing a further equilibrium constant, K_{1h}, for reaction (13), where $K_{1h} = m_{VO(L)(OH)} m_H^3 \gamma_- \gamma_+^3 / m_{VO} m_{H_2O} \gamma_{2+}$. A

$$VO^{2+} + H_2L + H_2O \rightleftharpoons VO(L)(OH)^- + 3H^+ \qquad (13)$$

value of *ca.* 1×10^{-11} mol² kg⁻² for K_{1h} had been obtained from a preliminary automatic-titration study and this together with the other constants gives the $\delta E'$ values in the Supplementary Publication. Values of K_{1b} which were ten times greater or ten times less than this value, and also a dimer equilibrium were tried and rejected. The standard deviation of the $\delta E'$ values is 0·56 mV compared with that of 0·86 mV for δE values.

A meaningful comparison with earlier work is not possible. In addition to the points mentioned in the Introduction section, a titration curve reported by Lal and Agerwal[3] coincides with the results of Beltran and Mateo[2] in spite of a five-fold difference in the vanadium(IV) concentration! Earlier workers do not mention the time required to each equilibrium. Although this severely limited the precision of the present work, it is nevertheless believed that the results are incomparably more reliable than those reported earlier. Values of stability constants for VO(L) and $VO(L)_2^{2-}$ can be obtained by combining K_1 and K_2 values with the successive acidity constants of 1,2-dihydroxybenzene. The values in 0·1M-potassium nitrate determined by L'Heureux and Martell[15] were converted to values in water by the use of equation (7). The values so obtained are $pK_1 = 9{\cdot}44$ and $pK_2 = 12{\cdot}41$, and these give the successive stability constants $K_{VO(L)} = 10^{16{\cdot}69}$ mol kg⁻¹ and $K_{VO(L)_2^{2-}} = 10^{14{\cdot}09}$ mol kg⁻¹.

Finally, we note that the results provide no evidence for the presence of the complex VL_3^{2-} in the solutions

$$VO(L)_2^{2-} + H_2L \rightleftharpoons VL_3^{2-} + H_2O \qquad (14)$$

studied. Presumably equilibrium (14) lies far to the left and the ion VL_3^{2-}, which can be precipitated as the thallium(I) salt,[6] would be present in significant quantities only in much more concentrated solutions.

One of us (R. P. H.) thanks the University of Reading for a postgraduate studentship.

[2/2677 *Received, 27th November*, 1972]

---

[15] G. A. L'Heureux and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1966, **28**, 481.