ACID DISSOCIATION CONSTANTS OF TETRACYANOHYDROXOOXOMOLYBDATE(IV) ION

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Abstract

The third dissociation constant of tetracyanohydroxooxomolybdic acid, $H_3[MoO(OH)(CN)_4]$, has been obtained in the temperature range 25–50°C from the pH–titration curve of its tripotassium salt against hydrochloric acid. The values of pK_3 fitted an equation of Harned–Robinson type:

$$pK_3 = (1730 \cdot 72/T) - 6 \cdot 19 + 0 \cdot 0308T$$

obtained by the method of least squares.

Thermodynamic quantities ΔG°, ΔH°, ΔS°, and ΔC_p° for the process have been evaluated at 30°C.

The interaction of tetracyanohydroxooxomolybdate(IV) ion with simple as well as complex metal ions,[1,2] its oxidation–reduction properties,[3] and reduction at a dropping mercury electrode[4] have been reported earlier. This communication deals with the determination of thermodynamic dissociation constants of this anion and the related thermodynamic quantities.

Experimental

Blue $K_3[MoO(OH)(CN)_4]$ was prepared by Jakob's[5] method as modified and reported earlier.[1-3] Its solution strength was determined potentiometrically by titrating against potassium hexacyanoferrate(III).[3]

Determination of Dissociation Constants

The acid dissociation constants were determined from acidimetric titration curves. Aqueous solutions (0·02M) of tripotassium tetracyanohydroxooxomolybdate(IV) were titrated with 0·1M aqueous hydrochloric acid and the concomitant change in the pH was read with a Beckman G pH-meter using glass (Beckman 40485) and calomel (Beckman 39970) electrodes. The pH-meter was calibrated with reference to a 0·05M potassium hydrogen phthalate solution which has pH values known at several temperatures.[6] Ionic strengths were maintained by adding appropriate concentrations of potassium chloride.

A typical titration curve (at 30°C) is given in Figure 1. It shows two inflection points corresponding to the addition of 1 and approx. 3 equiv. of H^+ per mole of the complex. The apparent equilibrium constants (pK_3') were obtained from the half-equivalence points of the first segment.

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[3] Beg, M. A., Khan, A. A., and Kabir-ud-Din, *J. electroanal. Chem.*, 1968, **18**, 187.

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[5] Jakob, Z., *Roczn. Chem.*, 1957, **31**, 681.

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Materials

Reagent grade chemicals were used throughout. Doubly distilled water served as the solvent. To obviate oxidation, experiments were carried out in a nitrogen atmosphere. Prior to use nitrogen was purified by bubbling through chromous chloride and alkaline pyrogallol solutions and equilibrated with the solvent. Experiments were performed at constant temperature.
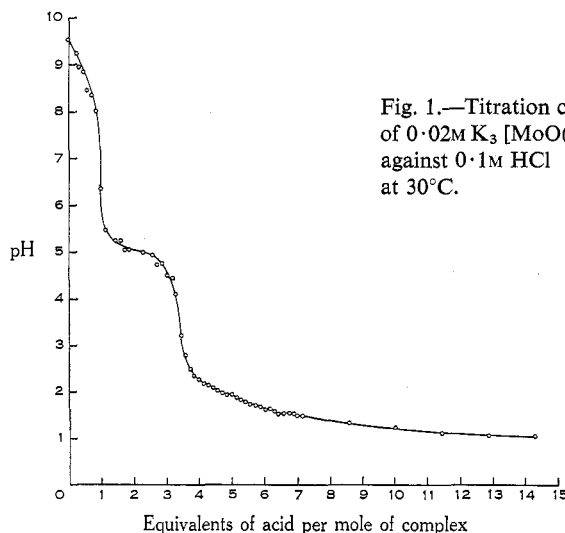

Fig. 1.—Titration curve of $0 \cdot 02M \ K_3 \ [MoO(OH)(CN)_4]$ against $0 \cdot 1M$ HCl at 30°C.

Equivalents of acid per mole of complex

Results and Discussion

Potentiometric titrations of tripotassium tetracyanohydroxooxomolybdate(IV) with hydrochloric acid showed two inflection points. The first inflection occurs at a pH between 6·65 to 7·5. This corresponds to the formation of dibasic complex $[Mo(OH)_2(CN)_4]^{2-}$ due to the addition of one proton (H^+) to the predominating species $[MoO(OH)(CN)_4]^{3-}$. The pH at the mid-point of first segment is taken to be equal to pK_3'.

The equivalence points were determined from the derivative plot $\Delta pH/\Delta V$. The half-equivalence points in the titrations were then calculated and the pH values were found at these points. The pK_3' values obtained from several independent measurements lie within $\pm 0 \cdot 15$ ($\pm 0 \cdot 25$ at 30° and $\mu = 0 \cdot 4$).

When 3 equiv. of H^+ were added a second inflection point was obtained. Addition of more acid followed the appearance of a green gel-like precipitate, which on the addition of more acid, disappeared. Thus, at the end of titration (*c.* 15 equiv. of H^+) the solution was clear and its colour was brownish-green.

These reactions may be explained on the basis of formation of a colloidal solution (green) of the basic molybdenum cyanide. Coagulation occurs after some time and a green precipitate separates out. This substance is a product of the breakdown of the dibasic complex in accordance with the reaction:

$$[Mo(OH)_2(CN)_4]^{2-} + 2H^+ \rightarrow 2HCN + Mo(OH)_2(CN)_2 \quad \text{(green precipitate)}$$

This basic cyanide dissolves slowly in excess of the acid:

$$Mo(OH)_2(CN)_2 + 2H^+ \rightarrow 2HCN + MoO^{2+} + H_2O$$
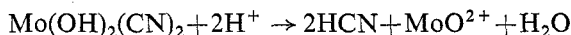
A similar sequence of reactions has been proposed for the analogous tungsten compound.[7] The compound $Mo(OH)_2(CN)_2$ had been prepared earlier[8] and its sulphur derivative, $MoS(CN)_2$, is also known.[9]

Fig. 2.—Extrapolation to zero ionic strength of pK_3' values observed at different temperatures.
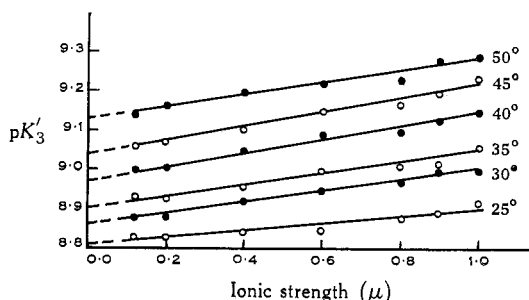
The acid pK_3' at 16° has been calculated from hydrolysis studies to be $8 \cdot 74$.[7] This value has been determined by us for a wide range of temperature and ionic strength, in good agreement with the value reported from hydrolysis data. We have also determined the thermodynamic constants at different temperatures from extrapolation of pK_3' values against the corresponding ionic strength, μ (Fig. 2). Values obtained from extrapolation are:

Temp. (°C)	25	30	35	40	45	50
pK_3	$8 \cdot 81$	$8 \cdot 86$	$8 \cdot 90$	$8 \cdot 97$	$9 \cdot 04$	$9 \cdot 13$

The variation of pK_3 with temperature is given by a Harned–Robinson equation:[10]

$$pK_3 = A^*/T - D^* + C^*T \tag{1}$$

The pK_3 data were treated (by use of a computer) by a least-squares method in which the fit of the data to a wide range of sets of possible values could be tested and the significance of any particular value assessed. The program was run on an IBM 1130 computer. The following equation was obtained:

$$pK_3 = (1730 \cdot 72/T) - 6 \cdot 19 + 0 \cdot 0308T \tag{2}$$

The maximum deviations in pK_3 values obtained from this equation, and those found experimentally, lie within $\pm 0 \cdot 02$ unit. Thermodynamic quantities at 30° derived from this equation[11] are ΔG° $+12264$ cal mol^{-1}, ΔH° -5016 cal mol^{-1}, ΔS° -57 cal K^{-1} mol^{-1}, ΔC_p° -85 cal K^{-1} mol^{-1}.

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[11] Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," 3rd Edn, p. 665 (Reinhold: New York 1958).