

### 134. The Dissociation Constant of the Ion-pair $\text{Co}(\text{NH}_3)_6^{3+}\text{OH}^-$ .

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The value of the dissociation constant of  $\text{Co}(\text{NH}_3)_6^{3+}\text{OH}^-$  has been obtained from the rate of decomposition of diacetone alcohol in solutions of hexamminocobalt trihydroxide. The physical significance of dissociation constants obtained in this way is discussed.

THE depolymerisation of diacetone alcohol is specifically catalysed by hydroxyl ions and measurement of the rates of this reaction in solutions of hydroxides has been used<sup>1</sup> to obtain values of the concentration of free hydroxyl ions and thereby the dissociation constants of such species as  $\text{CaOH}^+$  and  $\text{TlOH}$ . The values so obtained are in reasonable agreement with those derived by other methods.<sup>2</sup> As the extent to which covalent forces are responsible for the linking of ions such as  $\text{Ti}^+$  and  $\text{OH}^-$  is uncertain,<sup>3</sup> the association of the hydroxyl ion with the ion  $\text{Co}(\text{NH}_3)_6^{3+}$ , in which the first co-ordination sphere of the cobalt atom is fully occupied by attached ligands, is of interest, and we have studied the rate of decomposition of diacetone alcohol in solutions of hexamminocobalt trihydroxide.

#### EXPERIMENTAL

Hexamminocobalt trichloride was prepared and purified as suggested by Palmer.<sup>4</sup> An approximately 0.15N-solution of the hydroxide was prepared by treating a solution of the chloride with an excess of silver oxide, but the solution obtained was unstable and slowly deposited cobaltic oxide. A fresh sample (250 ml.) was prepared for each kinetic measurement by using a column of Amberlite I.R.A. 400 anion-exchange resin, prepared as recommended by Nachod.<sup>5</sup> The chloride was roughly weighed out and dissolved in 100–150 ml. of water and the solution passed through the column at a rate not exceeding 4 ml./min. into a 250 ml. volumetric flask protected by a soda-lime tube. Water was then passed through the column until the flask was full. The kinetic measurement was made immediately and a sample of the freshly prepared solution was standardised simultaneously by potentiometric titration, a glass electrode being used, against standard hydrochloric acid solution made from constant-boiling acid. Identical titration curves were obtained for freshly prepared solutions made by the ion-exchange or the silver oxide method, or by mixing the hexamminocobalt trichloride and potassium hydroxide. This shows that the complex cobalt cation is not attacked by the hydroxyl ion in its passage through the resin.

The kinetic measurements were made at  $25^\circ \pm 0.01^\circ$  in dilatometers similar to that described by Halberstadt, Hughes, and Ingold.<sup>6</sup> The concentration of diacetone alcohol was about 4%. Rate constants were calculated by Guggenheim's procedure. Some measurements on solutions of sodium and potassium hydroxides confirmed the results of Bell and Prue.<sup>1</sup>

#### RESULTS AND DISCUSSION

Table I gives the observed values of the first-order rate constant  $k$ ,  $[\text{OH}^-]^*$  being the stoichiometric concentration of hydroxyl ions. The results were analysed in the same way as those for calcium hydroxide.<sup>1</sup> Extrapolation of the catalytic constant for the cobalt base to infinite dilution confirmed the value of  $k/[\text{OH}^-] = 0.502_5 \text{ min.}^{-1} \text{ mole}^{-1} \text{ l.}$  previously found for the true catalytic constant. We therefore calculated the free hydroxyl-ion concentrations,  $[\text{OH}^-]$ , using this value. Now  $[\text{Co}(\text{NH}_3)_6\text{OH}^{2+}] = [\text{OH}^-]^* - [\text{OH}^-]$ , it being assumed that association beyond the first stage does not occur, and the values of the concentration dissociation quotient,  $Q$ , are given by

$$Q = [\text{Co}(\text{NH}_3)_6^{3+}][\text{OH}^-]/[\text{Co}(\text{NH}_3)_6\text{OH}^{2+}]$$

<sup>1</sup> Bell and Prue, *J.*, 1949, 362

<sup>2</sup> Bell and George, *Trans. Faraday Soc.*, 1953, **49**, 619.

<sup>3</sup> George, Rolfe, and Woodward, *ibid.*, p. 375.

<sup>4</sup> Palmer, "Experimental Inorganic Chemistry," Cambridge Univ. Press, 1954, p. 530.

<sup>5</sup> Nachod, *Analyt. Chem.*, 1952, **24**, 1027.

<sup>6</sup> Halberstadt, Hughes, and Ingold, *J.*, 1950, 2441.

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TABLE 1.

$10^2[\text{OH}^-] \cdot 10^3k/2.303$ (mole l. <sup>-1</sup> ) (min. <sup>-1</sup> )	$10^2[\text{OH}^-]$ (mole l. <sup>-1</sup> )	$10^3[\text{Co}(\text{NH}_3)_6\text{OH}^{2+}]$ (mole l. <sup>-1</sup> )	$10^3[\text{Co}(\text{NH}_3)_6^{3+}]$ (mole l. <sup>-1</sup> )	$10^2Q$ (mole l. <sup>-1</sup> )	$10^2I$ (mole l. <sup>-1</sup> )	$-\log_{10} K$
5.880	11.04	5.06	8.22	11.38	7.00	1.86
4.900	9.22	4.22	6.74	9.59	6.01	1.88
4.257	7.86	3.60	6.56	7.63	4.19	(1.99)
4.098	7.91	3.62	4.73	8.93	6.84	1.78
3.725	7.08	3.25	4.78	7.64	5.19	1.88
3.466	6.70	3.07	3.95	7.60	5.89	1.81
2.080	4.07	1.86	2.16	4.77	4.12	1.86
1.639	3.28	1.50	1.37	4.09	2.86	1.78
1.040	2.08	0.95	0.84	2.62	2.98	1.88

We assume that the activity coefficient of a  $z$ -valent ion at an ionic strength  $I$  is given by an expression of the form

$$-\log_{10} f_z = 0.50 z^2 I^{1/2} / (1 + I^{1/2}) + BI \quad . \quad . \quad . \quad (1)$$

and accordingly define a tentative thermodynamic dissociation constant  $K$  by

$$\log_{10} K = \log_{10} Q - 3.0 I^{1/2} / (1 + I^{1/2}) \quad . \quad . \quad . \quad (2)$$

With one exception the values of  $K$  are constant within the limits of experimental error and show no trend with concentration so the effect of the term linear in  $I$  in equation (1) is in this case negligible. An average value gives  $K = 0.014$  mole l.<sup>-1</sup>.

It is interesting to see whether the observed dissociation constant for the ion-pair corresponds to a reasonable value for the distance of closest approach of ions, assuming their interactions are adequately described by Bjerrum's model.<sup>7</sup> According to this model we regard pairs of ions of opposite charge approaching more closely than a distance  $q$  as single molecules and quantitatively the dissociation constant  $K$  of these ion pairs is given by

$$K^{-1} = 4\pi N_{\rho}(2q_1)^3 \int_{2q_1/q}^{2q_1/a} e^{vy-4y} dy \quad . \quad . \quad . \quad (3)$$

where  $\rho$  is the density of the solvent,  $q_1 = z_1 z_2 e^2 / 2DkT$  and  $a$  is the distance of closest approach of ions which are paired. Bjerrum only treated the case where  $q = q_1$ ; the effect of alternative choices of  $q$  has been examined recently by Brown and Prue.<sup>8</sup>

We now examine more closely the assumptions implicit in our calculation of  $K$  from the kinetic data. If the activity coefficient of the diacetone alcohol is effectively unity in dilute solution, the rate constant is given by

$$k = k_0 f_{\text{M,OH}} / f_{\text{M,X}} \quad . \quad . \quad . \quad (4)$$

where  $f_{\text{M,OH}}$  and  $f_{\text{M,X}}$  are stoichiometric activity coefficients relating to the hydroxide and the activated complex. We ascribe any deviation from unity of the stoichiometric activity coefficient factor to the incomplete dissociation of the metal hydroxide and thus relate the dissociation constants to deviations from a standard activity coefficient  $f_{\text{M,X}}$ . From Stuart models we estimate the radius of the activated complex ion as about 4 Å and if we assume a radius of 1.5 Å for the cation our standard activity coefficient will be, according to the Debye-Hückel theory

$$-\log_{10} f_{\text{M,X}} = AI^{1/2} / [1 + (qI^{1/2}/a^\circ)] \quad . \quad . \quad . \quad (5)$$

where  $A$  and  $a^\circ$  are constants and  $q = 4 \text{ Å} + 1.5 \text{ Å} = 5.5 \text{ Å}$ . Thus cation and hydroxyl ions approaching more closely than 5.5 Å are treated as associated, since this causes  $f_{\text{M,OH}}$  to be less than  $f_{\text{M,X}}$ . Now  $q_1$  has the values 3.6, 7.2, and 10.8 Å for 1-1, 2-1, and 3-1-valent electrolytes respectively. Therefore in the case of this particular reaction the kinetic method probably overestimates the association relevant to application of equation (3) with  $q = q_1$  for singly charged cations such as  $\text{Ti}^+$  and underestimates it in other cases. In Table 2 we compare values of  $a$  calculated from equation (1) for different values of the

<sup>7</sup> Bjerrum, *Kgl. danske Videnskab. Selskab*, 1926, **7**, No. 9.

<sup>8</sup> Brown and Prue, *Proc. Roy. Soc.*, 1955, *A*, **232**, 320.

integration limits, with crystallographic values. A value of  $2.5 \text{ \AA}$  was obtained for the crystallographic radius of the ion  $\text{Co}(\text{NH}_3)_6^{3+}$  by subtracting the radius of the iodide ion from the closest distance<sup>9</sup> of approach ( $4.7 \text{ \AA}$ ) of Co and I in the crystal of  $\text{Co}(\text{NH}_3)_6\text{I}_3$ .

TABLE 2.

Ion pair	$K$ (mole l. <sup>-1</sup> )	$a \text{ (\AA)}$			cryst.
		$q = \frac{1}{2}q_1$	$q = q_1$	$q = 2q_1$	
$\text{Tl}^+\text{OH}^-$ .....	0.38	—	1.2	4.1	2.8
$\text{Co}(\text{NH}_3)_6^{3+}\text{OH}^-$ .....	0.014	3.0	3.7	—	3.9

The values of  $a$  are markedly dependent on the integration limits; for  $q \simeq 5.5 \text{ \AA}$  ( $1\frac{1}{2}q_1$  for thallos hydroxide and  $\frac{1}{2}q_1$  for the cobalt base) they differ little from the crystallographic values. Bell and Prue's<sup>1</sup> previous conclusion concerning thallos hydroxide that, because the value of  $a$  calculated from Bjerrum's theory ( $q = q_1$ ) is considerably smaller than the crystallographic value, covalent forces must be involved in the linking of  $\text{Tl}^+$  and  $\text{OH}^-$  is probably unjustified. This explains George, Rolfe, and Woodward's<sup>3</sup> failure to detect any new Raman line due to associated thallos hydroxide.

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\* Meisel and Tiedje, *Z. anorg. Chem.*, 1927, **164**, 223.