594. *A Potentiometric Study of the Chloroiridate–Chloroiridite Couple.*

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When pure rhodium metal electrodes are used equilibrium is rapidly attained with the chloroiridate–chloroiridite couple, and satisfactory potentiometric titrations of potassium chloroiridate in hydrochloric acid solution with potassium ferrocyanide have been carried out to measure its oxidation–reduction potential.

At 20·3°, values obtained at several ionic strengths between 0·004 and 0·110 showed the variation of E_0' with $\sqrt{I}$ to approach linearity below $\sqrt{I}$ 0·15, in accord with the simple Debye–Hückel equation for a couple in which the oxidized and reduced forms carry charges of -2 and -3 respectively. From the extrapolated value at zero ionic strength and the temperature variation of E_0', which was found to be $-0{\cdot}00137 \pm 0{\cdot}00005$ v/°c, calculation gives $E_0 = 0{\cdot}8665$ at 25°. This value is about 0·14 v lower than those obtained by previous investigators using different electrodes with which equilibrium was established far more slowly.

Previous investigators [1, 2] showed that the oxidation–reduction potential of the chloroiridate–chloroiridite couple is about 1 v, and studied its variation with temperature and with ionic strength. Difficulty was encountered in getting stable potentials with platinum and especially gold electrodes which are attacked by chloroiridic acid. It was partially overcome by Woo [1] who used iridium-plated glass electrodes, and to a greater extent by Dwyer *et al.*[2] who used rhodium-plated glass electrodes. Nevertheless electrode equilibrium was only attained in about one hour.

Finding potassium chloroiridate to be an exceptionally useful oxidizing agent in our studies of the higher oxidation states of hæmoproteins [3] and requiring the thermodynamic data for the $IrCl_6^{2-}$–$IrCl_6^{3-}$ couple, we repeated the potential measurements. With pure rhodium electrodes stable potentials were set up almost immediately, and remained unchanged for hours. Unlike the previous workers we were able to carry out potentiometric titrations of potassium chloroiridate, using potassium ferrocyanide as the reducing agent. This electron-transfer reaction is extremely rapid in spite of the high charges of like sign on the two ions.[4] Our value of E_0 for the $IrCl_6^{2-}$–$IrCl_6^{3-}$ couple is lower than the previous values by about 140 mv; but we found the same value for two samples of potassium chloroiridate, and a determination of the equilibrium constant for the reaction between $IrCl_6^{2-}$ and $Fe(phen)_3^{2+}$ substantiated this lower value.

Results

The Titration of Potassium Chloroiridate with Potassium Ferrocyanide.—About 2×10^{-3}M-solutions of potassium chloroiridate containing initially 0·31N-hydrogen chloride were used, giving an ionic strength at the half titration point of 0·30. The advantage of working at this relatively high acid concentration was that errors that could otherwise arise from diffusion of potassium chloride from the bridge and hydrolysis of the chloroiridate and chloroiridite ions were minimized. E.M.F. measurements were made 15 sec. after the addition of ferrocyanide, and then after longer time intervals. Electrode equilibrium was found to be established within 30 sec. Fig. 1 shows the results of a typical titration at 20·3°. The linear slope, 0·0575, is within experimental error equal to that for a one-electron couple at this temperature, *viz.*, 0·0583.

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[1] Woo, *J. Amer. Chem. Soc.*, 1931, **53**, 469.
[2] Dwyer, McKenzie, and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 260.
[3] George, *Science*, 1953, **117**, 220; George and Irvine, *Biochem. J.*, 1954, **58**, 188; 1955, **60**, 596.
[4] George and Irvine, *J.*, 1954, 587.

The Variation of E_0' with Temperature.—Similar titrations were carried out at 15·0°, 25·0°, 31·4°, and 39·2°, and E_0', obtained from the half-titration point, is plotted against T in Fig. 2: $dE_0'/dt = -0{\cdot}00137 \pm 0{\cdot}00005$ v/°c. In all cases, the slopes of the lines corresponding to that in Fig. 1 were equal to $\boldsymbol{R}T/F$ within experimental error.

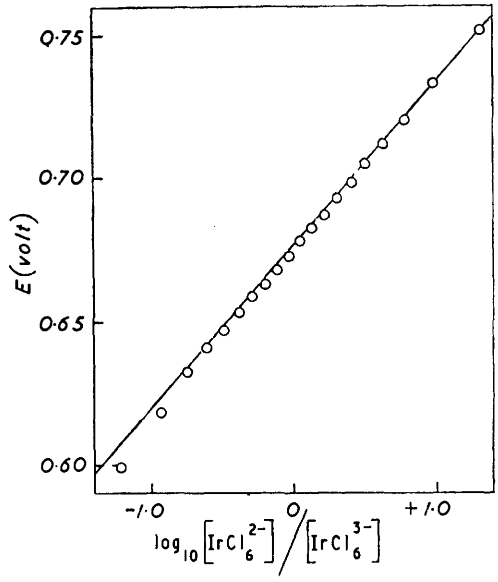


FIG. 1. *Plot of E.M.F. with respect to the saturated calomel electrode for the potentiometric titration of* $IrCl_6^{2-}$ *with* $Fe(CN)_6^{4-}$ *at* 20·3° *and* $I = 0{\cdot}30$.

FIG. 2. *Temperature variation of* E_0 *for the* $IrCl_6^{2-}$–$IrCl_6^{3-}$ *couple at* $I = 0{\cdot}30$.

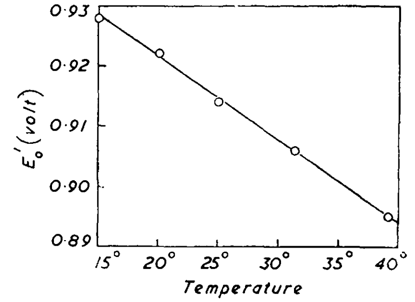
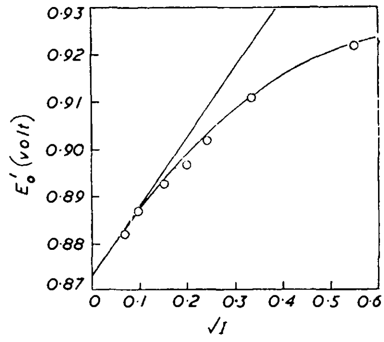


FIG. 3. *Plot of* E_0' *against* $\sqrt{I}$ *for the* $IrCl_6^{2-}$–$IrCl_6^{3-}$ *couple at* 20·3°.



The Variation of E_0' with Ionic Strength.—The results of these experiments are given in Table 1 and the plot of E_0' against $\sqrt{I}$ in Fig. 3. The lowest concentration of hydrochloric acid used was 6×10^{-3}M, but even in these dilute solutions the potentials were stable for a long time, indicating that no serious hydrolysis of the chloroiridate or chloroiridite ion occurred. Further, the titrations were reproducible to within 0·5 mv.

TABLE 1. *Variation of E_0' with ionic strength for the* $IrCl_6^{2-}$–$IrCl_6^{3-}$ *couple at* 20·3°.

I	0·0042	0·0084	0·0223	0·038	0·058	0·110
E_0' (v)	0·882	0·887	0·893	0·897	0·902	0·911

According to the simple Debye–Hückel theory, the mean activity coefficient of an ionic species of charge Z at low ionic strength is given by: $-\log f = AZ^2\sqrt{I}$. Hence, since $E_0' = E_0 + \log (f_{ox.}/f_{red.})$, where $f_{ox.}$ and $f_{red.}$ are the activity coefficients of the oxidized and reduced forms of a couple, the variation of E_0' with $\sqrt{I}$ for the $IrCl_6^{2-}$–$IrCl_6^{3-}$ couple should, in the limit, obey the equation

$$E_0' = E_0 + (\boldsymbol{RT/F}) \,.\, A[(-3)^2 - (-2)^2]\sqrt{I}$$

i.e.,

$$E_0' = E_0 + (5\boldsymbol{RTAF}) \,.\, \sqrt{I}$$

At 20·3° the value of A is 0·5048 (Manov *et al.*[5]) and so the limiting slope of the E_0'–$\sqrt{I}$ curve should be 0·147. The straight line in Fig. 3 has been drawn with this theoretical limiting slope, and it can be seen that the experimental values approach this line below $\sqrt{I} \approx 0{\cdot}15$ to give an extrapolated value at zero ionic strength of 0·873 v.

These E_0' values are much lower than those obtained by Woo [1] (1·031 v in 1·0*f*-HCl at 20°) and by Dwyer *et al.*[2] (1·017 v at zero ionic strength and 20°). The question therefore arises as to which values are the more reliable. Woo observed that gold, and to a small extent platinum, electrodes were attacked in the iridium solution, and chose iridium-plated glass electrodes for his measurements. Electrode equilibrium was reached in a few hours. E_0' values were calculated from E.M.F. measurements on approximately 1 : 1, 1 : 3, and 1 : 4 mixtures of chloroiridate and chloroiridite, but no actual titration was carried out. Dwyer *et al.* used rhodium-plated glass electrodes and approximately 1 : 1 mixtures: stirring was continued for many hours and a stable potential attained in about one hour. They also attempted a potentiometric titration of the chloroiridate with titanous chloride as the reducing agent, but, noting that the potential drop during the first 25% of reaction was much greater than expected, concluded that a false equilibrium was reached.

However, the slow attainment of electrode equilibrium with a simple inorganic couple suggests that additional reactions are intervening at the electrode surface, and that it is under these conditions that a false equilibrium is set up, namely, one in which the potential values are not directly determined by the activities of the two components of the couple and the free energy change for its reaction with the H^+–H_2 couple. Hence, since in the present experiments electrode equilibrium was attained as rapidly as with the ferricyanide ion–ferrocyanide ion couple, we believe these values to be the more reliable.

An Indirect Determination of E_0' *for the* $IrCl_6^{2-}$–$IrCl_6^{3-}$ *Couple.*—An experimental check on the E_0' value independent of any E.M.F. measurements involving the $IrCl_6^{2-}$–$IrCl_6^{3-}$ couple is clearly desirable. The determination of the equilibrium constant for the reaction, $Fe(phen)_3^{2+} + IrCl_6^{2-} \rightleftharpoons Fe(phen)_3^{3+} + IrCl_6^{3-}$, serves this purpose because E_0' for the $Fe(phen)_3^{3+}$–$Fe(phen)_3^{2+}$ couple is known with certainty to be a little greater than 1·0 v. Hume and Kolthoff [6] obtained a value of 1·06 v, thereby revising the original value of 1·14 volt at 24·8° obtained by Walden *et al.*[7] If E_0' for the $IrCl_6^{2-}$–$IrCl_6^{3-}$ couple is equal to that for the $Fe(phen)_3^{3+}$–$Fe(phen)_3^{2+}$ couple the equilibrium constant would be unity, whereas if the E_0' is lower, then, for each 50 mv, calculation shows that the equilibrium constant would fall by a factor of seven. By means of a spectrophotometric technique the equilibrium constant was measured for a series of initial concentrations of $IrCl_6^{2-}$ and $Fe(phen)_3^{2+}$ at 19·0° in 1·0N-hydrochloric acid, with the results listed in Table 2. The mean value of K, $3{\cdot}5 \pm 0{\cdot}5 \times 10^{-3}$, is very far from unity. Under identical conditions of temperature and acid concentration E_0' for the $Fe(phen)_3^{3+}$–$Fe(phen)_3^{2+}$ couple was determined by titration as 1·056 v, which compares very favourably with that obtained by Hume and Kolthoff.[6] From these data, E_0' for the

TABLE 2. *Determination of the equilibrium constant for the reaction:* $Fe(phen)_3^{2+} + IrCl_6^{2-} \rightleftharpoons Fe(phen)_3^{3+} + IrCl_6^{3-}$ *in* 1·0N-HCl *at* 19°.

Initial concn. (10^{-5} mole $l.^{-1}$)		Oxidn. (%) of	
$IrCl_6^{2-}$	$Fe(phen)_3^{2+}$	$Fe(phen)_3^{2+}$	10^3K
5·0	5·0	5·7	3·7
7·5	5·0	6·8	3·4
10·0	5·0	8·7	4·3
10·0	2·5	9·5	2·5
10·0	1·25	15·7	3·7

Mean $K = 3{\cdot}5 \pm 0{\cdot}5 \times 10^{-3}$.

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[5] Manov, Bates, Hamer, and Acree, *J. Amer. Chem. Soc.*, 1943, **65**, 1765.
[6] Hume and Kolthoff, *ibid.*, p. 1895.
[7] Walden, Hammett, and Chapman, *ibid.*, 1933, **55**, 2649.

$IrCl^{2-}$–$IrCl_3^{3-}$ couple is calculated to be 0·912 ± 0·005 v. At 20° and with 0·3M-hydrochloric acid the value obtained by direct ferrocyanide titration is 0·922 v. The very close agreement is a good reason for regarding the lower values as more reliable than the high values reported by the previous investigators.

This method for determining E_0' *via* the equilibrium constant may be criticized because of the possibility of complex formation, $IrCl_6^{2-} + Fe(phen)_3^{3+}$, $IrCl_6^{3-} + Fe(phen)_3^{2+}$, and $IrCl_6^{3-} + Fe(phen)_3^{3+}$, which would introduce additional free-energy terms besides that for the oxidation–reduction reaction. In the dilute solutions employed (10^{-4}M) it is, however, very unlikely that ion-pair complex formation of this kind would be significant. Furthermore, it is very improbable that E_0' values so very similar would be obtained if a false equilibrium were set up in the titration and complex formation occurred in the reaction with $Fe(phen)_3^{2+}$.

DISCUSSION

From the extrapolation giving $E_0 = 0{\cdot}873$ v at 20·3°, and $dE'_0/dt = -0{\cdot}00137 \pm 0{\cdot}00005$ v/°c, E_0 at 25° is calculated to be 0·8665 v, and hence the standard free-energy change for the reduction of chloroiridate by hydrogen, $IrCl_6^{2-} + \frac{1}{2}H_2 \rightleftharpoons IrCl_6^{3-} + H^+$, is −20·0 kcal./mole. Calculation also gives $\Delta H = -30{\cdot}5 \pm 0{\cdot}5$ kcal./mole and $\Delta S^\circ = -35{\cdot}2$ e.u. Taking $S_{H_2}{}^\circ = 31{\cdot}2$ e.u.[8] and following the convention that $\bar{S}_{H^+}{}^\circ = 0$, we calculate the difference between the partial molal entropies[9] of the chloroiridite and chloroiridate ions, $\bar{S}^\circ(IrCl_6^{3-}) - \bar{S}^\circ(IrCl_6^{2-})$, to be −19·6 e.u. A negative value is to be expected because of the higher charge on the chloroiridite ion, and the difference may be compared with the corresponding differences for the Fe^{2+} and Fe^{3+} aquo-ions (−43·0 e.u.), and the HPO_4^{2-} and PO_4^{3-} oxyanions (−43·4 e.u.).[8] Of the three pairs of ions, $IrCl_6^{2-}$ and $IrCl_6^{3-}$ are undoubtedly the largest, and a smaller partial molal entropy difference is to be expected. If Woo's values [1] for ΔG° and ΔH are used, namely, −23·54 and −30·4 kcal./mole respectively, $\Delta S^\circ = -23{\cdot}1$ e.u. and $\bar{S}^\circ(IrCl_6^{3-}) - \bar{S}^\circ(IrCl_6^{2-}) = -7{\cdot}5$ e.u. This value, which is so small compared with those for the other pairs of similarly charged ions, may be taken as a further indication that the potential values from which they are obtained are less reliable.

EXPERIMENTAL

Materials.—Two samples of potassium chloroiridate were used. One, from Johnson Matthey & Co., had no purity specification, but spectrophotometric titration with "AnalaR" potassium ferrocyanide (water distilled from dilute potassium permanganate) showed it to be at least 98% pure. The other sample, of 99% purity, was kindly lent to us by the Mond Nickel Co., in addition to the pure rhodium wire, about 1 mm. diameter, which was used for the electrodes.

The calomel electrode made up for these measurements was calibrated by comparison against a standard saturated calomel electrode using a separate potentiometer circuit and a Weston standard cell. At 25° its potential was $0{\cdot}244_0$ v.

Measurement of E.M.F.—The titration cell consisted of two compartments, one containing a saturated calomel electrode connected through an agar–potassium chloride bridge to the other containing the two rhodium electrodes and the potassium chloroiridate solution, approx. 2×10^{-3}M. "AnalaR" potassium ferrocyanide, about 10^{-2}M, was added three drops at a time from a small burette, and the chloroiridate solution was stirred by a magnetic stirrer. The two rhodium electrodes were cleaned before each titration by immersion in concentrated nitric acid, washing with distilled water, and burning in an alcohol flame. Throughout the potentiometric titrations, for which a Cambridge pH meter circuit was used, no detectable difference between them was noticed and the E.M.F. readings were reproducible to within 0·0005 v. Temperature was controlled throughout the titration by thermostat water circulating around the cell; at all temperatures the variation was 0·1° except at the highest, 39·2°, where it was 0·2°.

Determination of the Equilibrium Constant for the Reaction $IrCl_6^{2-} + Fe(phen)_3^{2+} \rightleftharpoons IrCl_6^{3-} + Fe(phen)_3^{3+}$.—Solutions were made up in 1·0N-hydrochloric acid at 19° containing

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[8] Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, 2nd edn., 1952.

[9] For definition of this term see Glasstone, "Physical Chemistry," Van Nostrand, New York, 1946, 2nd edn., p. 1011.

initial concentrations of $IrCl_6^{2-}$ and $Fe(phen)_3^{2+}$ as given in Table 2. The percentage oxidation of $Fe(phen)_3^{2+}$ and reduction of $IrCl_6^{2-}$ was measured with a Beckman DU spectrophotometer at 510 and 490 mμ, which are respectively wavelengths for peak absorption by the two reactants. Consistent values were obtained, and the equilibrium constant was evaluated:

$$K = [IrCl_6^{3-}][Fe(phen)_3^{3+}]/[IrCl_6^{2-}][Fe(phen)_3^{2+}]$$

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