V. I. KRAVTSOV, G. M. PETROVA

The recharging of chloride complexes of tri- and tetravalent iridium, described by the reaction

1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. I. KRAVTSOV, G. M. PETROVA

GALVANOSTATIC STUDY OF THE RECHARGING PROCESSES OF IRIDIUM CHLORIDE COMPLEXES

(Presented by Academician A. N. Frumkin, 12 VIII 1963)

The recharging of chloride complexes of tri- and tetravalent iridium, described by the reaction

$$\mathrm{IrCl}_6^{2-} + e \rightleftarrows \mathrm{IrCl}_6^{3-}, \tag{1}$$

proceeds without a change in the composition of the inner coordination sphere of the reacting complexes. In this respect system (1) is similar to the system $\mathrm{Fe(CN)}_6^{3-}/\mathrm{Fe(CN)}_6^{4-}$, in which the recharging of the ions is accompanied mainly by concentration polarization (see, for example, ([1])). However, N. K. Pshenitsyn, N. A. Ezerskaya, and V. D. Ratnikova ([2]) obtained polarographic waves on a platinum electrode that do not agree with the assumption of reversible reduction of IrCl_6^{2-} ions, which was explained by the authors as due to the complicating influence of hydrolysis of the reduction products.

In the present work reaction (1) was studied by analysis of galvanostatic curves with transition time ([3]). The work used twice-distilled HCl, water, and the salt $\mathrm{K_2IrCl_6}$, synthesized according to the described procedure ([4]). The indifferent electrolyte was $1\,M$ HCl, which before the start of each experiment was saturated with purified nitrogen ($\sim$ 2 hours) in a cell whose cathodic and anodic spaces were separated by a ground-glass joint. Then a weighed portion of $\mathrm{K_2IrCl_6}$ salt was introduced into $1\,M$ HCl (50 ml), and the solution was again saturated with nitrogen for one hour. Chloride complexes of Ir(III) were obtained directly in the cell by electrochemical reduction of part of the IrCl_6^{2-} ions on iridium and rhodium electrodes, carried out in an electrolyte stirred with a magnetic stirrer at $\varphi = 840$–900 mV*. Galvanostatic curves $\Delta\varphi$–t were photographed from the screen of an ENO-1 cathode oscillograph ([5]) when various current densities i were applied to a smooth platinum wire electrode ($d = 1$ mm, $s = 0.25$ cm^2), located in unstirred electrolyte. The values of the transition time τ (0.1–10 sec) were determined by extrapolating to their intersection the linear portions of the $\Delta\varphi$–t curves located before and after

Fig. 1

Figure 1: Fig. 1

attainment of the transition time (6). The experiments were carried out at a temperature of 25°.

The cathodic oscillograms *a* and *b* shown in Fig. 1 have one well-defined wave, corresponding to reduction of $IrCl_6^{2-}$ ions. In this case, in a solution containing only $IrCl_6^{2-}$ ions (Fig. 1, *a*), immediately after the current is switched on there is observed a sharp shift of the potential in the negative direction (~ 150 mV), absent from oscillogram *b*, recorded in a solution containing both $IrCl_6^{2-}$ ions and $IrCl_6^{3-}$ ions.

On anodic oscillogram *v* (Fig. 1), recorded immediately after preparation of the solution** $5 \cdot 10^{-3}\,M$ $IrCl_6^{2-}$, $5 \cdot 10^{-3}\,M$ $IrCl_6^{3-}$, $1\,M$ HCl, one wave is also observed. On anodic oscillogram *g*, recorded 2 hours 30 min after oscillogram *v*, two weakly expressed waves are already observed, and they become more clearly expressed upon further storage of the solution (oscillograms *d* and *e* in Fig. 1). At the same time, the length of the first wave decreases with time, while that of the second, located in the region of more positive potentials, increases. The shape of the cathodic oscillograms recorded simultaneously with the anodic oscillograms did not change with time. Thus, cathodic oscillogram *b* in Fig. 1, recorded 5 h after preparation of the solution, has only one wave.

Fig. 1. Cathodic (*a*, *b*) and anodic oscillograms $\Delta\varphi$—t, obtained with 1 M HCl containing $1 \cdot 10^{-2}\,M$ $IrCl_6^{2-}$ (a, $i = 800\ \mu A/cm^2$) and $5 \cdot 10^{-3}\,M$ $IrCl_6^{2-}$, $5 \cdot 10^{-3}\,M$ $IrCl_6^{3-}$ (b–e, $i = 400\ \mu A/cm^2$). Oscillogram *b* was recorded immediately after preparation of the solution, *c* after 2 h 30 min, *d* after 5 h, and *e* after 7 h 10 min.

The change in the shape of the anodic oscillograms indicates a change in the state of the trivalent iridium complexes in 1 M HCl. Simultaneously with the splitting of the anodic wave, a shift of the potential of the reversible electrode in the positive direction was observed, which was caused[7] by the aquation reaction:

$$IrCl_6^{3-} + H_2O \rightleftharpoons IrCl_5H_2O^{2-} + Cl^-, \qquad (2)$$

which was recently studied in detail in work[8]. The results obtained confirm the conclusion[2] that anodic oxidation of the activated ions $IrCl_5H_2O^{2-}$ proceeds

---

* Here, as below, potentials are given relative to zero of the hydrogen scale. Potential measurements in the work were made relative to the reference electrode $Hg\,|\,Hg_2Cl_2\,|\,NaCl$ (sat.).

** This solution was obtained from a solution of $1 \cdot 10^{-2}\,M$ K_2IrCl_6, $1\,M$ HCl in 37 min.

Fig. 2

Figure 2: Fig. 2

at more positive potentials than oxidation of the ions IrCl_6^{3-}. Figure 2 gives the values of $i\tau_k^{1/2}$ and $i\tau_a^{1/2}$, calculated respectively from anodic and cathodic oscillograms recorded in a "freshly prepared" solution containing $5 \cdot 10^{-3}\,M$ of each iridium form. The values of $i\tau^{1/2}$ do not depend on the current density i, which indicates the absence of slow preceding chemical reactions*[3].

Fig. 2. Dependence $i\tau^{1/2}$—i, obtained from cathodic (1) and anodic (2) oscillograms. Solution: $5 \cdot 10^{-3}\,M$ IrCl_6^{2-}, $5 \cdot 10^{-3}\,M$ IrCl_6^{3-}, 1 M HCl.

From the data of Table 1, which gives the results of one of the experiments, it is seen that, in accordance with equation (3),

$$i\tau_i^{1/2}/C_i = \frac{1}{2} F \pi^{1/2} D_i^{1/2} \tag{3}$$

the quantities $i\tau^{1/2}/C_i$ are practically independent of the concentration of the reactant C_i. In Table 1, n is the number of oscillograms from which the mean values of $i\tau_k^{1/2}$ and $i\tau_a^{1/2}$ were determined. The slight decrease in the quantity $i\tau_a^{1/2}/[\mathrm{IrCl}_6^{3-}]$ with increasing concentration of Ir(III) is apparently connected with an increase in the fraction of activated Ir(III) complexes, since the residence time in solution of IrCl_6^{3-} ions increased with increasing concentration, in particular because of preceding recordings of oscillograms. The value $i\tau_a^{1/2}/[\mathrm{IrCl}_6^{3-}]$ corresponding to a solution containing $7 \cdot 10^{-3}\,M$ Ir(III) is given in Table 1 in parentheses, since in this solution an appreciable fraction of Ir(III) was already present in the form of aquated complexes.

* Taking into account the considerable diameter of the platinum wire electrode used (1 mm), diffusion under the conditions of our experiments may, with sufficient accuracy, be regarded as semi-infinite diffusion to a planar electrode[10].

From 17 series of cathodic and 9 series of anodic* oscillograms, the following average values were determined: $i\tau_k^{1/2}/[\mathrm{IrCl}_6^{2-}] = 244 \pm 6\ \mathrm{A} \cdot \mathrm{sec}^{1/2} \cdot \mathrm{cm} \cdot \mathrm{M}^{-1}$ and $i\tau_a^{1/2}/[\mathrm{IrCl}_6^{3-}] = 239 \pm 5\ \mathrm{A} \cdot \mathrm{sec}^{1/2} \cdot \mathrm{cm} \cdot \mathrm{M}^{-1}$, from which, on the basis of equation

Table 1

Concentration of iridium complexes in 1 M HCl	$i\tau_k^{1/2}\cdot 10^3$, $\mathrm{A\cdot sec^{1/2}\cdot cm^{-2}}$	$i\tau_k^{1/2}/[\mathrm{IrCl_6^{2-}}]$, $\mathrm{A\cdot sec^{1/2}\cdot cm\cdot M^{-1}}$	n	$i\tau_a^{1/2}\cdot 10^4$, $\mathrm{A\cdot sec^{1/2}\cdot cm^{-2}}$	$i\tau_a^{1/2}/[\mathrm{IrCl_6^{3-}}]$, $\mathrm{A\cdot sec^{1/2}\cdot cm\cdot M^{-1}}$	n
$1\cdot 10^{-2}$ M $\mathrm{IrCl_6^{2-}}$	2.49 ± 0.03	249 ± 3	5	–	–	–
$9\cdot 10^{-3}$ M $\mathrm{IrCl_6^{2-}}$, $1\cdot 10^{-3}$ M $\mathrm{IrCl_6^{3-}}$	2.21 ± 0.03	246 ± 3	6	2.53 ± 0.04	253 ± 4	4
$8\cdot 10^{-3}$ M $\mathrm{IrCl_6^{2-}}$, $2\cdot 10^{-3}$ M $\mathrm{IrCl_6^{3-}}$	1.85 ± 0.03	232 ± 4	5	4.76 ± 0.06	238 ± 3	5
$6\cdot 10^{-3}$ M $\mathrm{IrCl_6^{2-}}$, $4\cdot 10^{-3}$ M $\mathrm{IrCl_6^{3-}}$	1.44 ± 0.02	240 ± 3	6	9.42 ± 0.17	236 ± 4	5
$3\cdot 10^{-3}$ M $\mathrm{IrCl_6^{2-}}$, $7\cdot 10^{-3}$ M $\mathrm{IrCl_6^{3-}}$	0.732 ± 0.013	244 ± 4	9	15.8 ± 0.30	(226 ± 4)	5

(3), the following values of the diffusion coefficients were established:

$$D_{\mathrm{IrCl6^{2-}}} = (8.2 \pm 0.4)\cdot 10^{-6}\ \mathrm{cm^2/sec}; \qquad D_{\mathrm{IrCl6^{3-}}} = (7.8 \pm 0.3)\cdot 10^{-6}\ \mathrm{cm^2/sec}.$$

Thus, within the limits of errors amounting to 4-5%, the values of the diffusion coefficients of the ions $\mathrm{IrCl_6^{2-}}$ and $\mathrm{IrCl_6^{3-}}$ coincide.

In Fig. 3, in the coordinates $\varphi - \lg \dfrac{\tau_k^{1/2} - t^{1/2}}{t^{1/2}}$, are presented cathodic oscillograms recorded in a solution containing $\mathrm{IrCl_6^{2-}}$ ions. In Fig. 4 are presented cathodic and anodic oscillograms obtained in a solution containing both $\mathrm{IrCl_6^{2-}}$ ions and $\mathrm{IrCl_6^{3-}}$ ions. The cathodic and a considerable part of the anodic oscillograms (at $\varphi \lesssim 1.0$ V) in Figs. 3 and 4 are straight lines with a slope coefficient of 62 mV, which indicates [3] the practically reversible course of the recharge processes of the complexes $\mathrm{IrCl_6^{2-}}$ and $\mathrm{IrCl_6^{3-}}$. In accordance with this conclusion, the potential determined from the cathodic and anodic oscillograms (Figs. 3, 4) at the value of the abscissa equal to zero ($\varphi = 930$ mV) does not depend on the density of the applied current, and its value is equal to the half-wave potential of the $\mathrm{IrCl_6^{2-}}/\mathrm{IrCl_6^{3-}}$ system.

Fig. 4

Figure 3: Fig. 4

Fig. 3. Cathodic oscillograms obtained with a solution of $1 \cdot 10^{-2}$ M $\mathrm{IrCl_6^{2-}}$, 1 M HCl:
1 –0.80 mA/cm^2 ($\tau = 9.72$ sec.); 2 –1.2 mA/cm^2 ($\tau = 4.2$ sec.); 3 –3.0 mA/cm^2 ($\tau = 0.65$ sec.).

* In the calculations only anodic oscillograms recorded in solutions in which the residence time of $\mathrm{IrCl_6^{3-}}$ ions did not exceed ~ 1.5 hours were used.

The deviation of the anodic oscillograms from the linear dependence

$$\varphi - \lg \frac{\tau_{\mathrm{k}}^{1/2} + t^{1/2}}{\tau_{\mathrm{a}}^{1/2} - t^{1/2}}$$

with slope $\sim 2.3RT/F$ (Fig. 4) was observed at $\varphi \gtrsim 1.0$ V also in solutions with the same concentration

Fig. 4. Oscillograms obtained for cathodic $(1, 2)$

$$\left(R = \frac{\tau_{\mathrm{k}}^{1/2} - t^{1/2}}{\tau_{\mathrm{a}}^{1/2} + t^{1/2}}\right)$$

and anodic $(3, 4)$

$$\left(R = \frac{\tau_{\mathrm{k}}^{1/2} + t^{1/2}}{\tau_{\mathrm{a}}^{1/2} - t^{1/2}}\right)$$

polarizations; solution—$2 \cdot 10^{-3}$ M $\mathrm{IrCl_6^{3-}}$, $8 \cdot 10^{-3}$ M $\mathrm{IrCl_6^{2-}}$, $1M$ HCl.
1—1.0 mA/cm^2; 2—2.4 mA/cm^2; 3—0.16 mA/cm^2; 4—0.60 mA/cm^2

of $\mathrm{IrCl_6^{2-}}$ and $\mathrm{IrCl_6^{3-}}$ ions ($5 \cdot 10^{-3}$ M). One of the possible reasons for these deviations may be oxidation at $\varphi \gtrsim 1.0$ V of small amounts of $\mathrm{IrCl_5H_2O^{2-}}$ ions present in the solution. At $\varphi \approx 1.0$ V it is also necessary to take into account the possible influence of the oxidation process of the platinum electrode. Thus, according to A. I. Shlygin and A. N. Frumkin ([10]), the oxidation of platinized platinum in $1M$ HCl proceeds at $\varphi = 0.95$ V.

The results obtained by us do not agree with the conclusion of N. K. Pshenitsyn et al. ([2]) concerning the irreversible course of reaction (1) on a platinum electrode. A possible reason for this discrepancy is that in work ([2]) lower concentrations of iridium chloride complexes were used than in our work. In this connection, the process of deposition (removal) of an oxychloride film on platinum ([11]) could have exerted a substantial influence on the form of the $i - \varphi$

curves in work (2). In favor of this explanation is the violation observed by us of the dependence $i\tau^{1/2}$ = const at low concentrations of the electrochemically active substance in solution ($< 10^{-3}\,M$).

Leningrad State University
named after A. A. Zhdanov

Received
7 VII 1963

REFERENCES

1. P. Delahay, C. C. Mattax, *J. Am. Chem. Soc.*, **76**, 874 (1954).
2. N. K. Pshenitsyn, N. A. Ezerskaya, V. D. Ratnikova, *ZhNKh*, **3**, 1791 (1958).
3. P. Delahay, *New Instruments and Methods in Electrochemistry*, IL, 1957.
4. F. Puche, *Ann. Chim.*, (11), **9**, 270, 278 (1938).
5. B. I. Kravtsov, *ZhFKh*, **35**, 1144 (1961).
6. W. H. Reinmuth, *Anal. Chem.*, **33**, 485 (1961).
7. A. A. Grinberg, A. Sh. Shamsiev, *ZhOKh*, **12**, 55 (1942).
8. J. A. Poulsen, C. G. Garner, *J. Am. Chem. Soc.*, **84**, 2032 (1962).
9. D. G. Peters, J. J. Lingane, *J. Electroanal. Chem.*, **2**, 1 (1961).
10. A. Slygin, A. Frumkin, *Acta Physicochim. URSS*, **3**, 791 (1935).
11. D. G. Peters, J. J. Lingane, *J. Electroanal. Chem.*, **4**, 193 (1962).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.