PHYSICAL CHEMISTRY

Ya. I. TUR' YAN

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Ya. I. TUR' YAN

POLAROGRAPHIC KINETIC CURRENTS CAUSED BY THE SLOW FORMATION OF PYRIDINE COMPLEXES OF NICKEL

STUDY OF THE KINETICS OF COMPLEX FORMATION

(Presented by Academician A. A. Grinberg, April 11, 1962)

The addition of small amounts of pyridine (Py) to a solution of $Ni(NO_3)_2$ + KNO_3 leads to the splitting of the polarographic wave of $Ni(H_2O)_q^{2+}$ (Fig. 1, $C_{Ni(NO_3)_2} = 7.7 \cdot 10^{-5}$ M, $m = 2.12$ mg/sec and $t = 3.7$ sec at $h_{Hg} = 60$ cm, 25°, n.c.e. reference)*.

The first wave, increasing with increasing C_{Py}, is kinetic: the height h_{Hg} has only a slight influence on i_k. The total i_d is always diffusion-controlled ($i_d = \text{const}\sqrt{h_{Hg}}$). Calculation of the equilibrium concentrations of the complexes on the basis of (1) showed that mainly $Ni(H_2O)_q^{2+}$ participates in diffusion, and only

Table 1

C_{Py}, mol/l	i_k, μa; 0.1 M KNO_3 (h_{Hg} = 45.5 cm)	i_k, μa; 0.1 M KNO_3 (h_{Hg} = 50 cm)	i_k, μa; 0.1 M KNO_3 (h_{Hg} = 55 cm)	i_k, μa; 0.1 M KNO_3 (h_{Hg} = 60 cm)	i_d, μa; 0.1 M KNO_3 (h_{Hg} = 45.5 cm)	i_d, μa; 0.1 M KNO_3 (h_{Hg} = 50 cm)	i_d, μa; 0.1 M KNO_3 (h_{Hg} = 55 cm)	i_d, μa; 0.1 M KNO_3 (h_{Hg} = 60 cm)	i_k, μa; 1 M KNO_3 (h_{Hg} = 50 cm)	i_d, μa; 1 M KNO_3 (h_{Hg} = 50 cm)	$[Ni(H_2O)_{q-1}Py^{2+}]$, %
0					0.51	0.54	0.56	0.59		0.40	
$5 \cdot 10^{-4}$	0.14	0.14	0.14	0.14	0.51	0.55	0.57	0.59	0.080	0.40	0.6
$7 \cdot 10^{-4}$	0.20	0.20	0.19	0.20	0.50	0.55	0.56	0.58	0.13	0.40	0.9
$1 \cdot 10^{-3}$	0.24	0.25	0.25	0.26	0.51	0.54	0.56	0.60	0.20	0.41	1.5

C_{Py}, mol/l	i_k, μa; 0.1 M KNO_3 (h_{Hg} = 45.5 cm)	i_k, μa; 0.1 M KNO_3 (h_{Hg} = 50 cm)	i_k, μa; 0.1 M KNO_3 (h_{Hg} = 55 cm)	i_k, μa; 0.1 M KNO_3 (h_{Hg} = 60 cm)	i_d, μa; 0.1 M KNO_3 (h_{Hg} = 45.5 cm)	i_d, μa; 0.1 M KNO_3 (h_{Hg} = 50 cm)	i_d, μa; 0.1 M KNO_3 (h_{Hg} = 55 cm)	i_d, μa; 0.1 M KNO_3 (h_{Hg} = 60 cm)	i_k, μa; 1 M KNO_3 (h_{Hg} = 50 cm)	i_d, μa; 1 M KNO_3 (h_{Hg} = 50 cm)	$[Ni(H_2O)_{q-1}Py^{2+}]$, %
$2.5 \cdot 10^{-3}$	0.39	0.40	0.42	0.44	0.50	0.53	0.56	0.58	0.34	0.42	3.5
$5 \cdot 10^{-3}$	0.47	0.49	0.51	0.54	0.50	0.54	0.57	0.59	0.40	0.43	6.9
Average					0.51	0.54	0.56	0.59			

to an insignificant extent $Ni(H_2O)_{q-1} \cdot Py^{2+}$ (Table 1). The total diffusion current is the result of reduction of $Ni(H_2O)_q^{2+}$ and, to an insignificant extent, $Ni(H_2O)_{q-1} \cdot Py^{2+}$. This is indicated both by the magnitude of the potential (Fig. 1) and by the independence of i_d from C_{Py} (Table 1; 0.1 M KNO_3).

The following scheme of the electrode process of the first wave is well confirmed by experiment:

$$Ni(H_2O)_q^{2+} + Py \xrightarrow{k_1} Ni(H_2O)_{q-1} \cdot Py^{2+} + Py \xrightarrow{k_2} Ni(H_2O)_{q-2} \cdot Py_2^{2+} \longrightarrow_{\text{red.}}$$

$$\begin{array}{cc} \uparrow \text{ diff. } k_s & \uparrow \text{ diff. } k_c \\ Ni(H_2O)_q^{2+} & Ni(H_2O)_{q-1} \cdot Py^{2+} \end{array} \qquad (1)$$

on the basis of the Brdička-Wiesner theory (^{3,4}). For an analogous electrode process we found (^{2}):

$$i_k = \frac{\frac{k_s}{a}(i_d - k_s C_M) + \mu_1 k_1 C_X i_d}{\frac{k_s}{a} + \frac{k_c}{a}\frac{\mu_1 k_1}{\mu_2 k_2} + \frac{k_s}{a}\frac{1}{\mu_2 k_2 C_X}\left(\frac{k_c}{a} + \mu_1 k_1 K_1\right) + \mu_1 k_1 C_X}; \qquad (2)$$

$C_X \gg C_M$, X is the addend.

* E. P. Zdorenko participated in the experimental part.

To check the applicability of equation (2), it is convenient, as a first approximation, to neglect diffusion of the complex (see Table 1). In this case equation (2)

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Fig. 1. 0.1 M KNO_3; C_{Py} (mol/l):
1—0; 2—$5 \cdot 10^{-4}$; 3—$7 \cdot 10^{-4}$;
4—$1 \cdot 10^{-3}$; 5—$2.5 \cdot 10^{-3}$; 6—$5 \cdot 10^{-3}$

Fig. 2. 1—4–0.1 M KNO_3, h_{Hg} (cm):
1—45.5; 2—50; 3—55; 4—60;
5—1 M KNO_3, $h_{Hg} = 50$ cm

can be simplified ($i_d = k_s C_M$ and $k_c = 0$):

$$i_k/(i_d - i_k) = C_X^2/(AC_X + B); \tag{3}$$

$$A = \frac{k_s}{a\mu_1 k_1}; \tag{4}$$

$$B = \frac{k_s K_1}{a\mu_2 k_2}. \tag{5}$$

In more accurate calculations by equation (2) for 0.1 M KNO_3 $k_c = k_s$

Table 2

Rate constants of ionic reactions

Reactions	Ionic strength	$\mu_1 k_1$, cm / (mol/l) · sec	k_1, 1/((mol/l) · sec)	$\mu_2 k_2$, cm / (mol/l) · sec	k_2, 1/((mol/l) · sec)
$Ni(H_2O)_q^{2+}$+ Py →→ $Ni(H_2O)_{q-1}Py^{2+}$+ H_2O	0.1	3.7	$2.0 \cdot 10^5$		
$Ni(H_2O)_q^{2+}$+ Py →→ $Ni(H_2O)_{q-1}Py^{2+}$+ H_2O	1	7.7	$8.1 \cdot 10^5$		

Reactions	Ionic strength	$\mu_1 k_1$, cm / (mol/l) · sec	k_1, 1/((mol/l) · sec)	$\mu_2 k_2$, cm / (mol/l) · sec	k_2, 1/((mol/l) · sec)
$Ni(H_2O)_{q-1}Py^{2+} + Py \rightarrow\rightarrow Ni(H_2O)_{q-2}Py_2^{2+} + H_2O$	0.1			$2.8 \cdot 10^2$	$2.7 \cdot 10^9$
$Ni(H_2O)_{q-1}Py^{2+} + Py \rightarrow\rightarrow Ni(H_2O)_{q-2}Py_2^{2+} + H_2O$	1			$2.1 \cdot 10^2$	$4.4 \cdot 10^8$
$Ni(H_2O)_q^{2+} + CNS^- \rightarrow\rightarrow Ni(H_2O)_{q-1} \cdot CNS^+ + H_2O^{(2)}$	1	0.23	$1.8 \cdot 10^2$		
$Ni(H_2O)_{q-1}CNS^+ + CNS^- \rightarrow\rightarrow Ni(H_2O)_{q-2}(CNS)_2 + H_2O^{(2)}$	1			1.3	$6.3 \cdot 10^4$*
$A^{2-} + H^+ \rightarrow HA^{-(5)}$**		$1.4 \cdot 10^6$	$5.0 \cdot 10^{12}$		
$HA^- + H^+ \rightarrow H_2A^{(5)}$**				$4.1 \cdot 10^8$	$5.5 \cdot 10^{10}$

* In [2], k_2 was found inaccurately, since in the Wiesner equation the value K_2 was substituted instead of $K = K_2/K_1$.

** A^{2-} and HA^- are the corresponding anions of maleic acid.

(Table 1), and for $1M$ KNO_3, k_c was found from the plot $i_d - \dfrac{1}{K_1 + C_X}$ (2). The instability constants were taken from (1). μ was found from the Wiesner equation (4). The calculated i_k (points in Fig. 2), using the values of the constants (Table 2), agreed with the experimental data (curves) within 5-7% rel.

In the polarographic study of the rate of recombination of maleic-acid anions (5), both with the aid of the approximate theory of Brdička—Wiesner (5) and with the aid of the more exact theory of Koutecký (6), the electrode process analogous to ours,

Fig. 3

Figure 3: Fig. 3

$$\mathrm{A}^{2-} + \mathrm{H}^{+} \xrightarrow{k_1} \mathrm{HA}^{-} + \mathrm{H}^{-} \xrightarrow{k_2} \mathrm{H}_2\mathrm{A}_{\text{reduc.}} \longrightarrow, \tag{6}$$

can be reduced to a simpler scheme:

$$\mathrm{A}^{2-} + \mathrm{H}^{+} \rightleftarrows \mathrm{HA}^{-} + \mathrm{H}^{+} \xrightarrow{k_2} \mathrm{H}_2\mathrm{A}_{\text{reduc.}} \longrightarrow, \tag{7}$$

since $\mu_1 k_1 \gg \mu_2 k_2$ (Table 2)*.

In the case of pyridine and thiocyanate (2) nickel complexes, this simplification cannot be made, since the rate of addition of the first addend particle is lower than the rate of addition of the second particle (Table 2). On the other hand, $\mu_1 k_1$ is not so much smaller than $\mu_2 k_2$ that the second recombination could be regarded as proceeding at equilibrium.

Fig. 3. 1—5—0.1M KNO$_3$, $h_{\mathrm{Hg}} = 50$ cm; C_{Py} (in M): 1—$5 \cdot 10^{-4}$; 2—$7 \cdot 10^{-4}$; 3—$1 \cdot 10^{-3}$; 4—$2.5 \cdot 10^{-3}$; 5—$5 \cdot 10^{-3}$; 1′—6′—1M KNO$_3$; $h_{\mathrm{Hg}} = 59$ cm; C_{CNS^-} (in M): 1′—$5.88 \cdot 10^{-3}$; 2′—$7.84 \cdot 10^{-3}$; 3′—$9.80 \cdot 10^{-3}$; 4′—$1.57 \cdot 10^{-2}$; 5′—$2.35 \cdot 10^{-2}$; 6′—$3.14 \cdot 10^{-2}$.

The obtained relation between k_1 and k_2 indicates that, as water molecules are displaced from the hydration shell of nickel, further addition of the addend is accelerated. This once again confirms the view that electroreduction of $\mathrm{Ni(H_2O)}_q^{2+}$ is hindered because of the stable hydration of this ion (8). Already when the first water molecule is replaced by the addend, the stability of the hydration shell is disrupted, and further addition of the addend requires a lower activation energy. It is interesting that the effect of electrostatic interaction only brings k_1 and k_2 closer together (thiocyanate nickel complexes), but $k_1 < k_2$ is preserved. Moreover, the rate constants for addition of Py are considerably larger than the corresponding rate constants for addition of CNS$^-$ (Table 2), i.e., the chemical nature of the addend in this case is of predominant importance. With increasing ionic strength, k_1 and k_2 become somewhat closer (Table 2).

As is known, the proton is also strongly hydrated, but since in both recombination reactions of maleic-acid anions the same—

---

* Taking account of the adsorption effect (7), apparently, further increases the difference in $\mu_1 k_1$ and $\mu_2 k_2$. It must be noted that it is impossible to determine the influence of pyridine adsorption on the kinetic currents studied by us, since any more adsorption-active substance likewise gives complexes with the nickel ion. However, it seems to us that we are dealing chiefly with a bulk process, which is convincingly confirmed by the applicability of equations (2) and (3).

hydroxonium in nature, the electrostatic effect comes to the fore, and therefore the rate (k_1) of the first recombination is greater than the rate (k_2) of the second recombination (Table 2).

By analogy with the discussion of the kinetics of the slow dissociation of the complex (^{9,10}), but using the Brdička–Wiesner theory, for the case of slow formation of complexes and irreversible electroreduction of MX_2 (scheme 1) we obtain:

$$\varphi = \text{const} + \frac{2RT}{\alpha nF} \ln \frac{C_X}{\sqrt{\frac{\mu_1 k_1}{\mu_1^b k_1 K_1 k_s/k_c \cdot k_s/a+1}}} - \frac{RT}{\alpha nF} \ln \frac{i}{i_d - mi + \frac{k_s}{a\mu_1 k_1 C_X} k_c C_{MX}}; \tag{8}$$

$$m = 1 + \frac{k_s}{a\mu_1 k_1 C_X} + \frac{\mu_1^b k_1 \frac{k_c}{a} C_X + \mu_1 k_1 K_1 \frac{k_s}{a} + \frac{k_c}{a}\frac{k_s}{a}}{\mu_1 k_1 \mu_2 k_2 C_X^2}. \tag{9}$$

Using $\mu_1 k_1$ and $\mu_2 k_2$ (Table 2), it is possible to demonstrate the applicability of equations (8) and (9) for describing the kinetic waves of pyridine and rhodanide (^{2}) complexes of nickel, i.e., this proves that the species undergoing electroreduction are, respectively: $\mathrm{Ni(H_2O)_{q-2}Py_2^{2+}}$ and $\mathrm{Ni(H_2O)_{q-2}(CNS)_2}$. Indeed, Fig. 3 shows the linearity of

$$\varphi - \lg \frac{i}{i_d - mi}$$

(equations (8), (9)) and the values of the slope coefficient, 0.042–0.048 (Py) and 0.040–0.042 ($\mathrm{CNS^-}$). In these calculations it was taken into account that

$$i_d \gg \frac{k_s}{a\mu_1 k_1 C_X} k_c C_{MX},$$

since the degree of participation of the complex ion in diffusion is insignificant, and

$$k_s \ll a\mu_1 k_1 C_X.$$

From Fig. 4, the dependence

$$\varphi' - \lg Z \left(Z = C_X \Big/ \sqrt{\frac{\mu_1 k_1 C_X}{\mu_1^b k_1 K_1 k_s/k_c + k_s/a} + 1}, \quad \varphi' = \varphi \text{ at } i = \frac{i_d}{m+1} \right)$$

is also linear (equation (8)), with slope coefficient 0.074 (Py) and 0.082 ($\mathrm{CNS^-}$).

Fig. 4. $\varphi' - \lg Z$

Figure 4: Fig. 4. $\varphi' - \lg Z$

Fig. 4. $\varphi' - \lg Z$

At larger C_{CNS^-}, when kinetic limitation is absent, Tanaka and Tamamushi ([9]) by another route also arrived at the conclusion of electroreduction of $\mathrm{Ni(H_2O)_{q-2}(CNS)_2}$. It is true, however, that it is not excluded that at still larger C_{CNS^-} a complex of the anionic type undergoes electroreduction ([11,12]).

Lisichansk Branch
of the State Institute
of the Nitrogen Industry and Products
of Organic Synthesis

Received
5 X 1961

REFERENCES

1. Ya. I. Tur' yan, G. Ya. Serova, *ZhFKh*, **31**, 2200 (1957).
2. Ya. I. Tur' yan, G. F. Serova, *DAN*, **125**, 595 (1959); *ZhFKh*, **34**, 1009 (1960).
3. R. Brdička, K. Wiesner, *Coll. Czech. Chem. Comm.*, **12**, 138 (1947).
4. K. Wiesner, *Chem. listy*, **41**, 6 (1947).
5. V. Ganuš, R. Brdička, *Khimiya*, **1**, 28 (1951).
6. J. Koutecky, *Coll. Czech. Chem. Comm.*, **19**, 1093 (1954).
7. S. G. Mairanovskii, L. I. Lishcheta, *Coll. Czech. Chem. Comm.*, **25**, 3025 (1960).
8. Ya. I. Tur' yan, *DAN*, **113**, 631 (1957).
9. N. Tanaka, R. Tamamushi, Proceedings of the 1st International Polarographic Congress, Prague, **1**, 1951, p. 486.
10. A. G. Stromberg, *ZhFKh*, **27**, 1287 (1953).
11. A. N. Frumkin, G. M. Florianovich, *DAN*, **80**, 907 (1951).
12. N. V. Nikolaeva-Fedorovich, Yu. M. Povarov, *ZhAKh*, **14**, 663 (1959).