Polish J. Chem., **75**, 293–298 (2001) **COMMUNICATION**

Kinetic Studies on Mechanism of Electron Transfer Between $Cr^{2+}_{(aq)}$ and $[Cr(bpy)_3]^{3+}$ – Ions*

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In our previous works we observed exceptionally fast electron transfer between $Cr^{2+}_{(aq)}$ ion and some chromium(III)–2,2′-bipyridine complexes [1,2], that contained at least two bipyridine (bpy) ligands. The electron transfer process leads to aquation of the chromium(III) species. Tris-bipyridine chromium complexes are known for 0, I, II and III oxidation states of the central atom [3]. The $[Cr(bpy)_3]^{2+}$ ion undergoes a slow disproportionation (dependent on initial concentration and pH) accompanied by a characteristic colour changes, according to [4]:

$$\underset{\text{wine-red}}{2[Cr(bpy)_3]^{2+}} \rightleftarrows \underset{\text{yellow}}{[Cr(bpy)_3]^{3+}} + \underset{\text{deep-blue}}{[Cr(bpy)_3]^{+}} \qquad (1)$$

The $[Cr(bpy)_3]^{3+}$ ion used in this work as an electron acceptor is a very inert complex. Its aquation was examined only in alkaline media [5,6], where time scale of kinetic experiments was few hours at elevated temperatures.

Injection of pale-blue chromium(II) perchlorate into deareated strongly acidic water solutions of pale-yellow $[Cr(bpy)_3]^{3+}$ ion leads to spectacular colour changes. In few seconds an immense increase of intensity of red colour is followed by fast decolorization to final pale-red or pale-blue, depending on the initial concentration of the chromium(III) reactant. Spectral changes are presented in Figure 1. The reaction products (200 μmol of Cr(III) and 100–300 μmol of Cr(II)) were separated chromatographically on a Sephadex SP C25 (20 × 3 cm) column. The reaction and the whole chromatographic process were performed under argon atmosphere. Chromium complexes were eluted with 0.1–1.0 M $HClO_4$; a substantial amount of a dark violet species remained on the top of the column. Distribution of the products was dependent on the concentration and the molar ratio of the reactants, but in all cases two chromium(III) complexes – $[Cr(bpy)(H_2O)_4]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ were identified, basing on their UV-VIS spectral characteristics. Rate of the reaction was followed spectro-

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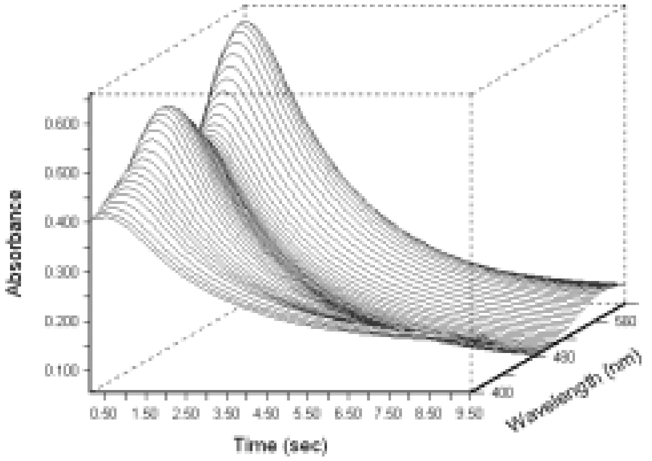

Figure 1. Spectral changes during the reaction course (eq. 2); [Cr(III)] = 2.7×10^{-4} M, [Cr(II)] = 1.15×10^{-2} M, $[H^+]$ = 5×10^{-2} M, I = 1.0 M, T = 298 K.

photometrically (400–600 nm), using a diode-array spectrophotometer HP 8453 equipped with a stopped-flow mixing system. Initial concentrations of the reactants were: [Cr(III)] = 2.7×10^{-4}M, [Cr(II)] = 6×10^{-3}–5×10^{-2}M, $[H^+]$ = 5×10^{-3}–5×10^{-1} M. The reaction was carried out at I = 1.0 M ($NaClO_4$) and constant temperature T = 298 K was maintained with a Julabo F25 refrigerated/heating circulator. The absorbance-time data were analyzed with the SPECFIT program [7], based on a factor analysis method. An isolation method – an excess of Cr(II) over Cr(III) – was applied and the consecutive first-order reaction scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{2}$$

was chosen for fitting. A typical fit generated by SPECFIT software is shown in Figure 2.

Course of the reaction can be deduced basing on spectroscopic observations *in situ* (Fig. 1), chromatographic separations and additional tests, in which $Cr^{2+}_{(aq)}$ was introduced into deareated bipyridine–$HClO_4$ solutions. Very intensive bands at 562 and 472 nm formed after mixing of the reactants are consistent with accumulation – in a few seconds – of an outersphere electron transfer direct product – the $[Cr(bpy)_3]^{2+}$ ion. The decomposition of this complex – probably *via* its aquation – leads to decrease of the absorbance within the whole examined spectral range. Total absorbance for the Cr(III) species and the $Cr^{2+}_{(aq)}$ ion is very low (< 0.05) at the used concentrations (d-d transitions), whereas a solution of the $[Cr(bpy)_3]^{2+}$ complex is characterized by very high absorbances at 562 and 472 nm, $\varepsilon = 4.3 \times 10^3$ and $3.8 \times 10^3 M^{-1}cm^{-1}$ respectively (CT M → L transitions) [8]. Presence of the $[Cr(bpy)_3]^{2+}$ cation in the reaction mix-

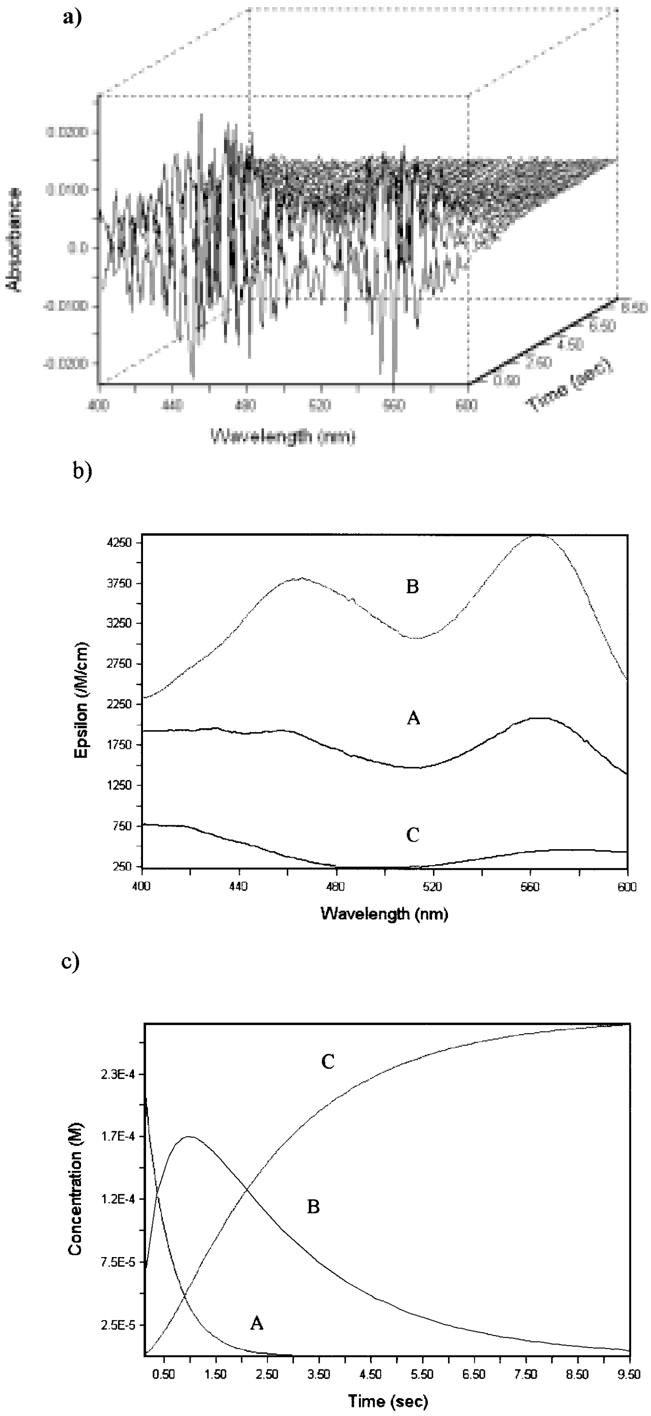

Figure 2. An example of fit results generated by SPECFIT software according to the model: A → B → C; a) residuals of fit; b) calculated spectra; c) change of concentrations with reaction time. Reaction conditions: $[\mathrm{Cr(III)}] = 2.7 \times 10^{-4}$ M, $[\mathrm{Cr(II)}] = 1.15 \times 10^{-2}$ M, $[\mathrm{H}^+] = 5 \times 10^{-2}$ M, $I = 1.0$ M, $T = 298$ K.

ture is additionally confirmed by chromatographic separations: the non-eluted dark-violet material is slowly air oxidized to yellow $[Cr(bpy)_3]^{3+}$ ion. A low solubility of $[Cr(bpy)_3](ClO_4)_2$ in perchlorates is well known [9]. Thus, in the first step of the reaction, an outersphere electron transfer converts $Cr^{2+}_{(aq)}$ ion into $Cr^{3+}_{(aq)}$ ion and $[Cr(bpy)_3]^{3+}$ complex into $[Cr(bpy)_3]^{2+}$ complex:

$$[Cr(H_2O)_6]^{2+} + [Cr(bpy)_3]^{3+} \longrightarrow [Cr(H_2O)_6]^{3+} + [Cr(bpy)_3]^{2+} \tag{3}$$

Probably the next step of the reaction, responsible for the decolorization of the solution, is aquation of the $[Cr(bpy)_3]^{2+}$ ion. Typical time scale for ligand substitution in chromium(II) species is within submicroseconds, however, the chromium(II)– tris-bipyridine complex is a low-spin species and its reactivity must be much lower. Stepwise aquation of the intermediate $[Cr(bpy)_3]^{2+}$ and possible electron transfer from the chromium(II) species to $[Cr(bpy)_3]^{3+}$ ion is shown in the Scheme:

Scheme

$$[Cr(bpy)_3]^{3+} + [Cr(H_2O)_6]^{2+} \longrightarrow [Cr(bpy)_3]^{2+} + [Cr(H_2O)_6]^{3+} \tag{4}$$

$$[Cr(bpy)_3]^{2+} + [Cr(bpy)_3]^{3+} \longrightarrow [Cr(bpy)_3]^{3+} + [Cr(bpy)_3]^{2+} \tag{5}$$

$$\updownarrow \begin{matrix} +H_2O \\ -bpy \end{matrix} \tag{5a}$$

$$[Cr(bpy)_{2(aq)}]^{2+} + [Cr(bpy)_3]^{3+} \longrightarrow [Cr(bpy)_2(H_2O)_2]^{3+} + [Cr(bpy)_3]^{2+} \tag{6}$$

$$\updownarrow \begin{matrix} +H_2O \\ -bpy \end{matrix} \tag{6a}$$

$$[Cr(bpy)_{(aq)}]^{2+} + [Cr(bpy)_3]^{3+} \longrightarrow [Cr(bpy)(H_2O)_4]^{3+} + [Cr(bpy)_3]^{2+} \tag{7}$$

$$\updownarrow \begin{matrix} +H_2O \\ -bpy \end{matrix} \tag{7a}$$

$$[Cr(H_2O)_6]^{2+} + [Cr(bpy)_3]^{3+} \longrightarrow [Cr(H_2O)_6]^{3+} + [Cr(bpy)_3]^{2+} \tag{8}$$

The $[Cr(bpy)_3]^{2+}$ complex formed in (4) is in the equilibrium with its aquation products – $[Cr(bpy)_{2(aq)}]^{2+}$, $[Cr(bpy)_{(aq)}]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ cations. Position of the equilibrium depends on pH and the total concentration of chromium(II). It seems that under conditions, applied in kinetic measurements (a very low concentration of the $[Cr(bpy)_3]^{3+}$ ion, 10^{-4} M and strongly acidic media), the $[Cr(H_2O)_6]^{2+}$ complex is the predominant form of chromium(II). However, in the case of experiments used for chromatographic separations of the products, (concentration of the chromium(III) reactant was two orders of magnitude higher than before) two chromium(II) species – $[Cr(bpy)(H_2O)_4]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ ions – are important. Electron transfer described by (6) is responsible for the observed (at higher concentrations of the Cr(III)) formation of the red $[Cr(bpy)(H_2O)_4]^{3+}$ complex and is equivalent to an apparent bipyridine transfer from chromium(III) to chromium(II).

If one assumes that the rate limiting step for the $[Cr(bpy)_3]^{2+}$ ion disappearance is the liberation of the first bipyridine ligand (5a), then the rate constants in the proposed kinetic scheme (2) have the following interpretation:

(i) The pseudo-first-order rate constant k_1 characterizes the rate of electron transfer from the $[Cr(H_2O)_6]^{2+}$ ion to the $[Cr(bpy)_3]^{3+}$ species (4) under applied excess of the $Cr^{2+}_{(aq)}$ ion and a very low concentration of the chromium(III) complex. For higher concentrations of the Cr(III) reactant, the k_1 would be a composite value connected with parallel electron transfer processes, in which $[Cr(bpy)(H_2O)_4]^{2+}$ and $[Cr(H_2O)_6]^{2+}$ species play the main role as the electron donors.

(ii) The first-order rate constant k_2 describes the rate of the first step of the $[Cr(bpy)_3]^{2+}$ ion aquation. This rate constant should be pH dependent, because an enhacement of the bipyridine complex aquation rate is expected with an increase of $[H^+]$ as is shown in equations (9, 10):

$$[Cr(bpy)_3]^{2+} + 2H_2O \qquad [Cr(bpy)_2(H_2O)_2]^{2+} + bpy \tag{9}$$

$$bpy + 2H_3O^+ \qquad H_2bpy^{2+} + 2H_2O \tag{10}$$

Kinetic results obtained, basing on the assumed consecutive reactions sequence (2), are presented in Table.

Table. The rate constants for the reaction (2) at T = 298 K, [Cr(III)] = 2.7 × 10^{-4} M, I = 1.0 M (Na^+, H^+, ClO_4^-).

$10^3\cdot[Cr^{2+}_{(aq)}]$, M	$[H_3O^+]$, M	k_1, s^{-1}	k_2, s^{-1}
5.7	0.05	1.22 ± 0.26	0.39 ± 0.02
11.5	0.005	1.77 ± 0.08	0.40 ± 0.02
11.5	0.05	1.89 ± 0.05	0.40 ± 0.02
11.5	0.5	1.86 ± 0.17	0.91 ± 0.03
46	0.05	6.20 ± 0.95	0.39 ± 0.02

As it is seen from the data shown in Table, the k_1 rate constant increases with an increase of $[Cr^{2+}_{(aq)}]$, whereas the rate constant k_2 increases with an increase of $[H^+]$. These facts are consistent with the proposed above interpretation of k_1 and k_2: k_1 – the electron transfer rate constant, k_2 – the aquation rate constant. The validity of the presented reaction sequence is additionally confirmed by two facts: (i) the spectrum of the B species generated by the SPECFIT program, basing on the calculated values of k_1 and k_2, is identical to that of the $[Cr(bpy)_3]^{2+}$ ion (practically the same λ_{max} and the molar absorption coefficients), (ii) injection of

A very high rate of electron transfer in the case of Cr(III)–bis- [2] and tris-bipyridine complexes can be rationalized in terms of the thermodynamic driving force [10] (important in the Marcus model for outersphere electron transfer) or kinetic reduction of activation barrier, because of interactions of the d_{z^2} Cr(II) orbital with π^* orbitals of the pyridine rings. In the former case – a stabile, low spin chromium(II) species is formed. In the latter – axially dehydrated $Cr^{2+}_{(aq)}$ ion is assumed to be located between two bipyridine ligands coordinated to Cr(III).

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