Calculation of activation-controlled reaction rate constants from parameters of electronic absorption spectra of ion pairs

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An equation relating the rate constants of a bimolecular activation-controlled redox reaction to the parameters directly determined from the electronic absorption spectra was obtained in the framework of the Marcus—Hush theory. Applicability of the equation for the prediction of redox reaction rate constants was shown.

Key words: ion pairs, electronic absorption spectra, outer-sphere charge transfer, activation-controlled reaction rate constants.

The formation of ion pairs due to the outer-sphere interaction of ions of coordination compounds is often accompanied by changes in the electronic absorption spectrum (EAS) related to charge phototransfer from the ion-donor to the ion-acceptor. The position, shape, and intensity of bands of the outer-sphere charge transfer provide information on the electron transfer between the ions. The concentration dependences of absorption make it possible to characterize the ion pairs that formed (to determine the concentration stability constants and molar absorption coefficients of associates[1—5]). In particular, intermediates that appear during redox reactions between ions can thus be characterized.

$[Fe(CN)_6]^{3-}$—$[Fe(CN)_6]^{4-}$ is an interesting system manifesting the outer-sphere interaction of the ions. Low-intensity broad absorption bands of the anionic pairs in this symmetrical system (the difference of the standard redox potentials of the ions is $\Delta E^0 = 0$) appear at the boundary of the visible and near-IR spectral regions.[6] The rate of electron transfer between the anions in this system has been determined by different physicochemical methods.[7—9] The application of the Marcus—Hush theory for the description of electron transfer[10—12] in symmetrical systems is more rigorous than that in nonsymmetrical systems. Hence, symmetrical systems are convenient objects for testing theoretical equations.

According to the theoretical concepts,[10—13] the rate of the bimolecular activation-controlled electron transfer reaction (v/L mol^{-1} s^{-1}) proceeding in excess of one of the ions (in this case, the reducing ion) can be written in the form

$$v = k_{et}K_{IP}[\text{red}][\text{ox}]/(1 + K_{IP}[\text{red}]), \qquad (1)$$

where $K_{IP} = K_{IP}{}^0 f$

$$K_{IP}{}^0 = \frac{4\pi N(d^*)^3}{3000}\exp\left(-\frac{z_1z_2e^2}{D_s d^* kT}\right), \qquad (2)$$

$$f = \exp\left(\frac{z_1z_2e^2K}{D_s kT(1 + Kd^*)}\right), \quad K = \left(\frac{8\pi Ne^2I}{1000D_s kT}\right)^{1/2}, \qquad (3)$$

$$k_{et} = \frac{2\pi}{\hbar}\frac{H_{d,a}^2}{(4\pi\chi RT)^{1/2}}\exp\left[-\frac{(\Delta E + \chi)^2}{4\chi RT}\right],$$

$$H_{d,a} = 2.06\cdot10^{-2}\frac{(\varepsilon_{max}\nu_{max}\nu_{1/2})^{1/2}}{d}, \qquad (4)$$

where k_{et} is the electron transfer rate constant; [red] and [ox] are the concentrations of the reductant and oxidant ions, respectively; $K_{IP}{}^0$/L mol^{-1} is the thermodynamic stability constant of the ion pair; f is the activity coefficient; d^*/Å is the contact distance between the ions; D_s is the dielectric constant of a solvent; I is the ionic strength of the solution; R is the universal gas constant; k is the Boltzmann constant; T/K is the absolute temperature; z_1 and z_2 are the ion charges; e is the electron charge; N is Avogadro's number; and $\hbar$ is the Planck constant.

Calculation of the rate constant requires data on the spectral parameters of the intermediate ion pair: the position of the maximum (ν_{max}/cm^{-1}), half-width ($\nu_{1/2}$/cm^{-1}), and molar absorption coefficient (ε_{max}/L mol^{-1} cm^{-1})); its stability (K_{IP}); the distance of electron transfer between the anions (d); and the reorga-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1007—1010, June, 2000.

nization energy of the system (χ/cm^{-1} or J mol^{-1}). The use of stability constants and molar absorption coefficients of ion pairs is especially difficult because separate determination of the latter is impeded by weak association of the ions and uncertainty of the contact distance between the nonspherical ions.[14] In addition, the dielectric constant and ionic strength of the solution are used for the recalculation of the stability constants on going from these experimental conditions to the others. Application of these parameters for the description of concentrated solutions of electrolytes is rather limited and can result in substantial distortions of the calculated values. An additional error appears due to the influence of the nature and concentration of alkali metal ions used as counterions on the absorption of the ion pair and position of the absorption maximum.[15]

These difficulties can be overcome by taking into account that the optical density of the ion pair in the absorption maximum (A_{max}) can be written in the form[16]:

$$A_{max} = \varepsilon_{max} l K_{IP}[red][ox]/(1 + K_{IP}[red]), \qquad (5)$$

where l/cm is the optical path length. Then

$$\upsilon = k_{et} A_{max}/\varepsilon_{max} l. \qquad (6)$$

After insertion of k_{et} from Eq. (4) into Eq. (6), we get rid of the barely determined stability constant and molar absorption coefficient of the ion pair and then, in the general case:

$$\upsilon = k_{calc}[ox][red] =$$

$$= \frac{1.69 \cdot 10^8 A_{max} \nu_{max} \nu_{1/2} \exp[-(\Delta E + \chi)^2/4\chi RT]}{l d^2 (\chi T)^{1/2}}, \qquad (7)$$

where k_{calc} is the calculated rate constant.

The reorganization energy of a system is related to the energy corresponding to the maximum of the charge-transfer band by the correlation

$$\chi = \nu_{max} - \Delta E^0. \qquad (8)$$

Thus, the calculation of the bimolecular reaction rate constant requires knowledge of the parameters of the charge-transfer band directly determined from the EAS, the contact distance between the ions, and the difference of the standard reduction potentials of the ions corrected to the work of their approach (ΔE_{corr}). For a symmetrical system, Eq. (7) can be written in the form

$$\upsilon = k_{calc}[ox][red] =$$

$$= \frac{1.69 \cdot 10^8 A_{max} \nu_{max}{}^{1/2} \nu_{1/2} \exp(-\chi/4RT)}{l d^2 T^{1/2}}. \qquad (9)$$

The calculated and experimental rate constants of the bimolecular electron transfer between the ions $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are presented in Table 1. We assumed that the calculation accuracy is mainly conditioned by the determination accuracy of A_{max}, $\nu_{1/2}$, and d. The latter has been calculated[14] from the stability constant of the ion pair[9] using the Fuoss equation.[17] The d value presented in Table 1 is close to the contact distances between the anions in the crystalline complexes $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6] \cdot 3H_2O$ and $K_4[Fe(CN)_6] \cdot 3D_2O$ (6.673, 7.051, and 7.099 Å, respectively).[18–20]

The k_{calc} values were calculated by two different methods. In the first case, we neglected the spin-orbital splitting of the absorption bands. In the second case, the spin-orbital coupling (λ_{so} = 460 cm^{-1}) was taken into account.[9] We assumed that for broad bands with nearby maxima with an intensity ratio of 1 : 2[4] the optical densities of individual bands were 1/3 and 2/3 of the absorption in the maximum of the observed band. The reaction rates were obtained by the summation of the rates of two reactions corresponding to two electron transitions.

For the presented symmetrical systems, taking into account the spin-orbital coupling, the experimental and calculated values virtually coincide, indicating the applicability of Eq. (9) for the prediction of the rate constants of activation-controlled reactions and correct estimation of the contact distance between the ions. For nonsymmetrical systems, the accuracy of prediction is mainly determined by the difference of the redox poten-

Table 1. Rate constants of electron transfer between the $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ ions and parameters used for calculation

Medium[a]	T/K	A_{max}/l[b,c] /cm^{-1}(±0.005)	ν_{max}[b]/cm^{-1} (±50)	$\nu_{1/2}$[b]/cm^{-1} (±300)	d/Å (±0.1)	$\Delta E^0 = \Delta E_{corr}$	logk_{calc} (±0.12)	logk_{exp}[b]
H_2O	299	0.075	12200	7900	6.9	0	5.05	4.98
H_2O	299	0.050	12430	6300	6.9	0	4.98	4.98
		0.025	11740	6200	—		—	
D_2O	299	0.075	12660	7900	6.9	0	4.82	4.70
D_2O	299	0.050	12890	6300	6.9	0	4.75	4.70
		0.025	12200	6200	—			
D_2O	348	0.063	12800	8500	6.9	0	5.61	5.57

[a] $[Fe(CN)_6]^{4-}$ = 0.5 mol L^{-1}, $[Fe(CN)_6]^{3-}$ = 0.1 mol L^{-1}.

[b] According to the published data.[9]

[c] Calculated by Eq. (5).

Table 2. Rate constants of electron transfer between the ions at 298 K and parameters used for calculation

Ion pair	A_{max}/l	ν_{max}	$\nu_{1/2}$	d/Å	[red]	[ox]	ΔE^0 [a] (ΔE_{corr})	$\log k_{calc}$	$\log k_{exp}$ [b]	$\log k_{therm}$ [c]
		cm^{-1}		(±0.1)	mol L^{-1}		/V (±0.05)		(±0.8)	(±0.8)
$[Fe(CN)_6]^{3-}$,NO_2^-	1.90 [d]	21900 [d]	6200 [d]	5.6	3.75	0.4	0.68 (0.60)	−3.1 ±0.3	−3.5	0.1
$[Ru(NH_3)_6]^{3+}$,I^-	0.32 [e]	24900 [e]	6380 [e]	4.6 [e]	0.35	0.0028	1.27 (1.32)	−8.5 ±0.6		−12.3
$[FeNO(CN)_5]^{2-}$,I^-	0.17 [f]	31000 [f]	7500 [f]	4.6 [f]	3	0.0005	1.40 (1.34)	−11.0 ±0.5		−12.6
$[Co\,edta]^-$,I^- [g]	0.41 [f]	33100 [f]	7000 [f]	5.0 [f]	3	0.0005	0.95 (0.92)	−8.2 ±0.4		−5.5

[a] According to the published data.[21,27]

[b] Calculated using the rate constant[28] of the reverse reaction $k_{-1} = 4.3 \cdot 10^6$ L mol^{-1} s^{-1}.

[c] The rate constant of the thermodynamically controlled reaction (k_{therm}) was calculated taking into account the rate constant[29] of the diffusion-controlled reverse reaction $k_{-1} = 1.2 \cdot 10^{10}$ L mol^{-1} s^{-1}.

[d] According to the published data.[24]

[e] According to the published data.[16]

[f] According to the published data.[25,26]

[g] H_4edta is ethylenediaminetetraacetic acid.

tials of the interacting ions. For example, the standard potential of the NO_2/NO_2^- pair was determined with an accuracy of ±0.04 V,[21] which substantially decreases the accuracy of calculation of the rate constants of reactions involving nitrite ions. In addition, on going from the standard to real potentials by the Fouss equation,[17] we assumed that the contact distance between the ions in pairs before and after their rearrangement remains unchanged. However, taking into account a low value of the calculated work of approach of the ions, the error of its determination can hardly affect the calculation of the values. The calculated and experimental rate constants of the bimolecular electron transfer between the $[Fe(CN)_6]^{3-}$ and NO_2^- ions are presented in Table 2. The contact distance between the anions was estimated from the character of the dependence of the reaction rate constant in the $[Ru(CN)_6]^{3-}$—NO_2^- system on the ionic strength of the solution.[22] The experimental and theoretical (the product of the ion charges is equal to 3) dependences coincide at $d = 5.6 \pm 0.1$ Å. The obtained distance is close to that between the anions (5.717 Å) in solid $(NH_4)_4[IrCl_6]NO_3$.[23] Comparison of these three systems seems reasonable because the sizes of the complex and nitrogen-containing anions entering the compared ion pairs are close.

Equation (7) can be fruitful for prediction of the type of bimolecular redox reaction. Comparison of the calculated constants of the activation- and thermodynamically controlled reactions of complex ions with iodide ions is presented in Table 2. It was assumed that the calculation error was mainly related to the inaccuracy in determination of the standard reduction potentials. The calculations were performed taking into account the spin-orbital splitting of the bands. According to calculation, the contribution to the reaction rate corresponding to the short-wave electron transition does not exceed 1% of the total value, which is much lower than the calculation accuracy. It follows from Table 2 that the interaction of the cobalt complex with iodide ions is activation-controlled, unlike two other processes of oxidation of iodide ions, because the calculated rate constants of the activation-controlled process are lower than that of the thermodynamically controlled reaction. In fact, it has previously been found[29] that the interaction of the $[Co\,edta]^-$ ions with iodide ions is much slower than the similar interaction of $[Fe(CN)_6]^{3-}$, despite a higher negative charge of the latter and a lower value of the standard reduction potential. The low reaction rate in the case of the $[Co\,edta]^-$ ions (more than two orders of magnitude lower than those of the thermodynamically controlled reactions) makes it possible to observe the absorption bands of outer-sphere charge transfer between the anions.

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Received November 17, 1999;
in revised form January 25, 2000