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Close contact distance between hexacyanometallate ions in the course of electron transfer

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On the basis of rate constants of redox reactions and stability constants of anion pairs, the contact distances between hexacyanometallate ions in the course of electron transfer were estimated as 6.7–7.1 Å, these values are comparable with the contact anion–anion distances in solids and subtantially lower than the sum of radii of nonhydrated ions.

The charge-transfer distance (d) is the most important model parameter in the quantitative examination of the kinetics of a wide range of redox reactions. For estimating it, the sum of the reactant radii is frequently used, which is considered as the closest possible contact distance (d^*) of the formation of intermediates (ion pairs). This work compares the contact distances between hexacyanometallate ions, which are calculated from the rates of bimolecular redox reactions (k_{obs}) and stability constants of anion pairs (K_{IP}). We consider anion pairs as the products of cooperative interactions of ions in bulk solution; these interactions are accompanied by the contact between anions participating in electron transfer.

When two ions interact, the value of k_{obs} is determined by the equation[1,2]

$$k_{obs} = K_{IP}k_{et} \tag{1}$$

where k_{et} is the rate constant of electron transfer, and K_{IP} can be estimated within an approximation of spherical particles from the Fuoss[3] equation

$$K_{IP} = K^0_{IP}f, \tag{2}$$

$$K^0_{IP} = \frac{4\;\;N(d^*)^3}{3000}\exp\left(-\frac{z_1z_2e^2}{D_sd^*kT}\right),$$

$$f = \exp\left[\frac{z_1z_2e^2K}{D_skT(1+Kd^*)}\right], \tag{3}$$

$$K = \left(\frac{8\;\;Ne^2I}{1000D_skT}\right)^{1/2},$$

where N is the Avogadro number, z_1 and z_2 are ionic charges, e is the elementary charge, D_s is the static dielectric constant, I is the solution ionic strength, T is the absolute temperature, and k is the Boltzmann constant.

As we have demonstrated earlier,[4] the Fuoss equation is also suitable for the quantitative description of associates containing two anions. According to the Marcus theory, k_{et} is determined by the equation[1]

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

where the preexponential factor $H_{d,a}$ (cm^{-1}) can be expressed in terms of charge-transfer spectral bands as follows:

$$H_{d,a} = 0.0206\frac{(\varepsilon_{max}\nu_{max}\nu_{1/2})^{1/2}}{d},$$

where $\hbar$ is Planck's constant, R is the molar gas constant, E is the standard free energy of the reaction and d is the charge-transfer distance (Å). The values of the optical transition energy (ν_{max}/cm^{-1}), the half-width of the absorption band ($\nu_{1/2}$/cm^{-1}), and the reorganization energy (χ) can be found from the experimental absorption spectra of ion pairs.[5,6] The reorganization energy can be either calculated from a particular model[7] or assessed by taking into account the additive nature of ion contributions to the sought values.[8] The molar absorption coefficients (ε_{max}/dm^3 mol^{-1} cm^{-1}) and the stability constants of ion pairs can be found from the concentration dependences of the absorption.[4–6]

It is possible to accurately determine the close-contact distances during the interaction of anions using equations (2) and (3) because of the fact that the dependence of K_{IP} on d^* at z_1, $z_2 < 0$ is clearly pronounced. The estimation of the contact distance in an ion pair from equation (4) presents the major problem because, in the general case, $d \neq d^*$. However, inasmuch as the electron transfer in hexacyanometallate ions proceeds between nonbinding t_{2g} orbitals localised predominantly at the transition-metal atoms, which, at the same time, are the charge centres of effective spheres, we can expect the distances obtained from equations (1)–(4) under comparable experimental conditions be equal. A comparison of the rate constants of bimolecular redox reactions between different hexacyanometallate ions (Table 1) shows that the experimental values[9,10] and those calculated using the data[5,6] and equation (1) are equal at a distance of 6.7 Å for the $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ pair and of 6.8±0.2 Å for the $[Fe(CN)_6]^{3-}$, $[Os(CN)_6]^{4-}$ pair.

An independent calculation of close-contact distances from the stability constants of the anion pairs $[Fe(CN)_6]^{3-}$, $[M(CN)_6]^{4-}$ (M = Fe or Os) was carried out by equation (2). In accordance with the spectroscopic data,[6] at a constant total concentration of potassium ions equal to 2.5 mol dm^{-3}, the stability constants of the $[Fe(CN)_6]^{3-}$, $[M(CN)_6]^{4-}$ (M = Fe or Os) ion pairs are equal to 0.055±0.006 dm^3 mol^{-1}. Inasmuch as Billing and Khostariya[6] determined the stability constants in solutions containing high concentration of multicharged ions, we found the ionic strengths of solutions in accordance with the equation[11] $I = 0.5\;\;C_i|z_i|$. In this case, the contact distance for hexacyanometallate ions is 6.9±0.1 Å. This value is consistent with the above results. The use of the classical equation $I = 0.5\;\;C_i|z_i|^2$ results in still lower values of d.

The third way to estimate the sought values is based on the use of the dependence of the rate constants of redox reactions

Table 1 Contact distances in $[Fe(CN)_6]^{3-}$, $[M(CN)_6]^{4-}$ anion pairs and parameters used in the calculations.

M	T/K	I/mol dm^{-3}	E/V	χ/V	ν_{max}/cm^{-1}	$\nu_{1/2}$/cm^{-1}	ε_{max}/dm^3 mol^{-1} cm^{-1}	k^a_{-1}/dm^3 mol^{-1} s^{-1}	k_{obs}/dm^3 mol^{-1} s^{-1}	D/Å
Fe	293	0.01 KOH	0	1.47	12200	7900	28	—	4.8×10^1	6.7
Os	298	0.03 KCl	0.25	1.47	16400	10100	45	4.7×10^4	2.8×10^0	6.6
Os	298	0.075 KCl	0.25	1.47	16400	10100	45	4.1×10^5	2.4×10^1	7.1
Os	298	0.24 KCl	0.25	1.47	16400	10100	45	1.5×10^6	8.8×10^1	6.8
Os	298	0.44 KCl	0.25	1.47	16400	10100	45	2.9×10^6	1.7×10^2	6.6

[a] k_{-1} is the rate constant of the reverse redox reaction.

on the ionic strength of solution in accordance with equation (3). The results of processing the data[9] (KCl, $I = 0.03$–0.44) by the least-squares technique agree with the theoretical dependence at a contact distance of 6.9 Å in the $[\mathrm{Os(CN)_6}]^{3-}$, $[\mathrm{Fe(CN)_6}]^{4-}$ and $[\mathrm{Ru(CN)_6}]^{3-}$, $[\mathrm{Fe(CN)_6}]^{4-}$ ion pairs and of 7.1 Å in the $[\mathrm{Ru(CN)_6}]^{3-}$, $[\mathrm{Os(CN)_6}]^{4-}$ ion pair.

Thus, the calculated contact distances agree with one another and with a contact distance of 6.673 Å between anions in solid $\mathrm{K_3[Fe(CN)_6]}$,[12] in which the contact between anions also takes place because of cooperative interactions of all ions. These distances are substantially lower as compared not only with the estimated value of 14 Å accepted in ref. 6 but also with the sum of ionic radii (according to different estimations,[13,14] about 8.6–9.4 Å). The relative positions of low-spin octahedral complexes with t_{2g}^5 and t_{2g}^6 electron configurations along the axes of the second order during the formation of an anion pair (like the positions of ions in a crystal) facilitate the most effective overlapping of the orbitals of complex ions participating in the electron transfer.

Undeniably, all of the *d* values obtained should be considered as effective, bearing in mind that approximations introduced in the derivation of equations (1)–(4) adequately correspond to the geometry and the charge distribution in real systems, and also that we are operating with parameters dependent on ionic strength. The agreement between contact distances determined by different methods can be partly caused by the fact that different approximations were used when we considered equilibrium [equations (2) and (3)] and kinetic [equation (4)] characteristics.

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