The Peroxodisulphate–Hexacyanoferrate(II) Reaction. Reactivity and Ionic Association in Isodielectric Water–Co-solvent Mixtures

Joaquin Baños and Francisco Sánchez-Burgos
Departamento de Química Física, Facultad de Química, Sevilla, Spain
M. Carmen Carmona-Guzmán *
Departamento de Fisicoquímica Aplicada, Facultad de Farmacia, Sevilla, Spain

The association constants of the potassium peroxodisulphate ion pair ($KS_2O_8^-$) and the potassium hexacyanoferrate(II) ion pair [$KFe(CN)_6^{3-}$] and the rate constant between peroxodisulphate and hexacyanoferrate(II) ions have been measured in several water–co-solvent mixtures. The assumption of ionic association does not provide a satisfactory interpretation of the experimental results.

The peroxodisulphate–hexacyanoferrate(II) reaction has been studied, in aqueous solutions, by a number of workers[1–6] and the results have been interpreted by postulating the formation of ion pairs.[2–5] When the reactants are present as potassium salts, the rate-determining step could involve the participation of the $KFe(CN)_6^{3-}$ and the $KS_2O_8^-$ ion pair as reactive species. This hypothesis was used by Chlebeck and Lister[2,3] but has been criticised by Kershaw and Prue[6] because 'one can always improve the fit of data by introducing more adjustable parameters to take account of additional reaction pathways and associated species, but unless independently obtained values of the association constants of the latter are available, the exercise is of doubtful value.' Similar ideas have been pointed out by other authors in different reactions.[7]

In order to observe the importance of ionic association in this reaction, isodielectric media ($D = 76$) have been used in the present work. In this fashion, the coulombic interactions between the reactants are approximately the same in the different media, and the association constants of the $KS_2O_8^-$ and $KFe(CN)_6^{3-}$ ion pairs would be similar in each case. On the other hand, owing to the high water content of the mixtures, a drastic change in the first solvation shell of the reactants is not likely in passing from pure water to the mixtures studied. For these reasons, the same association constant and consequently the same reactivity is to be expected in the different media.

Experimental

Reagents.—The reagents used were all AnalaR-grade chemicals from various sources, and were not purified further. The water used had a resistance >5 MΩ and was obtained by distilling from $KMnO_4$ and passing the distilled water through a mixed-bed ion-exchange column.

Kinetic Data.—Kinetic runs were carried out as described previously.[8] The Table gives the values of the molar absorption coefficient (ε) in water and in the water–co-solvent mixtures. The concentrations of the reactants were $[K_4Fe(CN)_6] = 4 \times 10^{-3}$ and $[K_2S_2O_8] = 2 \times 10^{-3}$ mol dm^{-3}. In every case we found that the co-solvents were inert in relation to the reactants and products. The Table gives the results of kinetic runs and the composition of each mixture. This composition was selected in order to have the same macroscopic dielectric constant for all the mixtures. Solvent mixtures were prepared by weight and the dielectric constant data are from the literature.[9–13]

Viscosity and Density Data.—The viscosities and densities of the water–co-solvent mixtures have been measured. The densities were determined with a picnometer and the viscosities from the flow time of solutions in an Ostwald-type viscosimeter. These data are also reported in the Table.

Conductance Measurements.—The conductance measurements were carried out as described previously.[8] The results are reported in the Table. The association constants have been calculated using a program which computes the fraction of $KS_2O_8^-$ and $KFe(CN)_6^{3-}$ ion pairs. The program has been checked using data for potassium sulphate[14] and potassium hexacyanoferrate(II).[15] The values of association constants of the $KS_2O_8^-$ ion pair in all the mixtures, except thf–water, were measured in previous work.[8]

Table. Viscosity (η/P), molar absorption coefficient of $Fe(CN)_6^{3-}$ (ε/dm^3 mol^{-1} cm^{-1}), observed rate constants (k/dm^3 mol^{-1} s^{-1}), association constants (K) of the $KFe(CN)_6^{3-}$ ion pair, and association constants (K) of the $KS_2O_8^-$ ion pair in different isodielectric water–co-solvent mixtures ($D = 76$)

Co-solvent	%(w/w)	$10^2\eta$	$10^{-3}\varepsilon$	10^3k	$K_{KFe(CN)_6^{3-}}$	$K_{KS_2O_8^-}$
Pure water			1.02	3.65	82	11[a]
Methanol	5.68	1.0786[a]	1.04	5.89	176	129[a]
Ethanol	4.39	1.0922[a]	1.02	5.28	316	147[a]
t-Butyl alcohol	2.94	1.1838[a]	1.04	6.64	238	119[a]
thf	3.62	1.0402	1.06	4.38	110	7.2
dmf	12.28	1.1770[a]	1.03	2.85	156	19[a]
Acetonitrile	6.02	0.9627[a]	1.03	5.02	276	140[a]
Sucrose	10.75	1.2120[a]	1.02	4.17	154	90[a]
Dextrose	10.52	1.1610[a]	1.02	3.67	496	217[a]

[a] Ref. 8.

Results and Discussion

Our results indicate that the rate constants in water–co-solvent mixtures follow the sequence for the co-solvent, *NN*-dimethylformamide (dmf) < pure water = dextrose < sucrose < tetrahydrofuran (thf) < acetonitrile < ethanol < methanol < t-butyl alcohol, and the association constants K follow the sequence for the co-solvent, thf < pure water < dmf < sucrose < t-butyl alcohol < methanol < acetonitrile < ethanol < dextrose for the $KS_2O_8^-$ ion pair and the sequence pure water < thf < sucrose < dmf < methanol < t-butyl alcohol < acetonitrile < ethanol < destrose for the $KFe(CN)_6^{3-}$ ion pair.

Reactivity in water cannot be compared with that in the mixtures because of the higher dielectric constant for water as compared to the other media. However, if the association were an important factor in this reaction, reactivity in, for example, the dextrose–water mixture would be greater than in the other media because of the greater association constant in this mixture. On the other hand, the rate constant sequence is not in agreement with the association constant sequences. It can therefore be concluded that the assumption of ionic association does not provide a satisfactory interpretation of the experimental results. The same conclusion is obtained for other reactions.[7,8,16]

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