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Kinetics of Reactions of Tris(2,2′-bipyridyl)iron(II) with Cyanide and with Hydroxide Ion in Binary Aqueous Solvent Mixtures †

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Rates of reaction of $[Fe(bipy)_3]^{2+}$ with cyanide ion in binary aqueous solvent mixtures containing ethylene glycol, glycerol, acetonitrile, dimethyl sulphoxide (dmso), or tris(dimethylamino)phosphine oxide (tdpo), and with hydroxide ion in binary aqueous solvent mixtures containing t-butyl alcohol, dmso, or tdpo, are reported. Reactivity trends in the various solvent mixtures are discussed and, in the case of the reaction with hydroxide in aqueous dmso, compared with reactivity trends for similar inorganic and organic reactions. Where the existence of the required thermodynamic data on Gibbs free energies of transfer of single ions permits, it is shown that the effect of solvation, and thence chemical-potential, changes for cyanide and hydroxide ions is dominant in determining reactivies in their reactions with $[Fe(bipy)_3]^{2+}$.

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We recently reported the results of a kinetic study of the reaction of the tris(2,2′-bipyridyl)iron(II) cation, $[Fe(bipy)_3]^{2+}$, with cyanide ion [equation (1)] in binary aqueous mixtures containing methanol, ethanol, dioxan, acetone, or t-butyl alcohol.[1] In each case the rate constant increased markedly as the proportion of organic co-solvent increased. The increase in the second-order

$$[Fe(bipy)_3]^{2+} + 2[CN]^- \longrightarrow [Fe(CN)_2(bipy)_2] + bipy \quad (1)$$

rate constant for this reaction with increasing proportion of organic co-solvent was ascribed to the increase in chemical potential of the cyanide ion. For the methanol–, t-butyl alcohol–, and acetone–water mixtures, for which it is possible to estimate changes in the chemical potential of cyanide ion with solvent composition, we compared those changes with changes in reactivity. In the cases of methanol– and t-butyl alcohol–water we found that the reactivity trends could be ascribed to a dominant effect of cyanide solvation in the initial state; the kinetic data for the reaction in acetone–water mixtures could not be accommodated in this pattern.

In the present paper, we report extensions in several directions of this study of solvent effects on reactivity for second-order reactions involving the $[Fe(bipy)_3]^{2+}$ cation. First, recent publication of Gibbs free-energy-of-transfer data for single ions in ethylene glycol–water mixtures [2] has enabled us to show that the reactivity trends for the $[Fe(bipy)_3]^{2+} + [CN]^-$ reaction in this mixture is also predominantly determined by changes in the chemical potential of the cyanide. Secondly, the similarity between the reaction of low-spin iron(III) complexes with cyanide and with hydroxide [3,4] prompted us to compare resulting trends for these two nucleophiles in several series of aqueous organic mixtures. Thirdly, we wished to extend the range of binary aqueous mixtures. All the co-solvents used in our previous study formed ' typically aqueous (t.a.) mixtures,' namely mixtures for which the excess molar Gibbs function, G^E, is positive, as a result of a dominant molar entropy of mixing, S^E.[5]

Here we report results for reactions in ' typically non-aqueous (t.n.a.) mixtures.' [5] In particular we have undertaken a study of reactions in dimethyl sulphoxide (dmso)–, tris(dimethylamino)phosphine oxide (tdpo)–, and acetonitrile–water mixtures. The last-named is a t.n.a.p. system, since both G^E and the molar enthalpy of mixing are positive.[6,7] In contrast, dmso– and tdpo–water mixtures belong to the class t.n.a.n., since both G^E and H^E are negative.[8–12] Further the co-solvents dmso and tdpo are reputedly poor solvators of anions,[9,13] with the possible exception of iodide and nitrate ions in dmso mixtures.[14] So in general we would expect a significant increase in the chemical potential of cyanide or hydroxide ions as the mol fraction of these co-solvents increases, with concomitant increase in rate constant. Such a trend in reactivity has already been reported for the alkaline hydrolysis of a range of substrates including methyl iodide,[15] benzyl chloride,[16] fluorodinitrobenzene (fdnb),[17] the trimethylamine–sulphur trioxide adduct,[18] and the cobalt(III) complexes $[CoCl(NH_3)_5]^{2+}$, $[CoBr(NH_3)_5]^{2+}$,[19] and [Co-

† No reprints available.

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TABLE 1

Observed first-order rate constants, $k_{obs.}$, and derived second-order rate constants, k_2 (*cf.* text), for the reaction of $[Fe(bipy)_3]^{2+}$ with hydroxide or cyanide ion in binary aqueous mixtures of mol fraction x_2 of the non-aqueous component. The ionic strength is 0.02 or 0.10 mol dm^{-3} as indicated, maintained with potassium chloride where necessary

Co-solvent	T/K	x_2	$10^3 k_{obs.}$/s^{-1}				k_2
		[KOH]/mol dm^{-3} =	0.005 [a]	0.010 [a]	0.015 [a]	0.020 [a]	dm^3 mol^{-1} s^{-1}
Dimethyl sulphoxide (dmso)	298.2	0.237	0.35	0.64	1.01	1.30	0.064
		0.276	0.79	1.33	2.1	2.8	0.14
		0.321	1.20	2.2	3.2	4.2	0.20
		0.373	2.7	4.0	6.8	7.7	0.35
Tris(dimethylamino)phosphine oxide (tdpo)	298.2	0.042	0.090	0.170	0.27	0.35	0.018
		0.094	0.34	0.66	1.10	1.30	0.066
		0.134	0.66	1.30	1.66	2.57	0.12
		0.194	2.2	4.6	7.0	9.1	0.46
t-Butyl alcohol	298.2	0.161	0.35	0.72	1.23	1.65	0.089
		0.224	0.80	1.55	2.1	3.0	0.15
		0.310	1.63	3.4	5.0	6.4	0.32
		[KOH]/mol dm^{-3} =	0.025 [b]	0.050 [b]	0.075 [b]	0.100 [b]	
dmso	308.2	0.028	1.26	2.3	3.2	4.1	0.038
		0.060	1.44	2.5	3.6	4.7	0.044
		0.98	2.2	4.4	6.1	8.5	0.082
		0.145	3.4	6.5	9.2	13.6	0.133
tdpo	308.2	0.011	1.22	2.4	3.4	4.3	0.041
		0.025	1.56	2.7	3.9	5.3	0.050
		0.042	2.2	3.6	5.8	7.3	0.070
		0.064	3.1	7.5	8.9	12.6	0.120
		[KCN]/mol dm^{-3} =	0.025 [b]	0.050 [b]	0.075 [b]	0.100 [b]	
Glycerol	308.2	0.198	1.77	3.5	5.4	6.2	0.061
Ethylene glycol	298.2	0.044				1.4	0.014
		0.094				1.7	0.017
		0.151				2.1	0.021
		0.217				3.4	0.034
Acetonitrile	298.2	0.037				1.6	0.016
		0.079				2.2	0.022
		0.129				2.9	0.029
dmso	298.2	0.028				1.4	0.014
		0.060				1.9	0.019
		0.098				3.4	0.034
		0.145				4.1	0.041
	308.2	0.028				3.5	0.035
		0.060				4.0	0.040
		0.098				5.4	0.054
		0.145	3.1	5.5	7.5	9.6	0.086
tdpo	308.2	0.011				3.2	0.032
		0.025				5.1	0.051
		0.042				6.6	0.066

[a] I = 0.02 mol dm^{-3}. [b] I = 0.10 mol dm^{-3}.

$(NH_3)_5(dmso)]^{3+}$,[20] in dmso–water mixtures. Indeed enhancement of reaction rates by added dmso has been said to merit attention in preparative chemistry.[21] In the present context, however, it is noteworthy that the Gibbs free energies of transfer for hydroxide ions from water to a limited range of dmso–water mixtures have been estimated [22] so that we can undertake an analysis, albeit restricted, of the kinetics of reaction between hydroxide ions and the $[Fe(bipy)_3]^{2+}$ cation in these mixtures, along the same lines as was successfully conducted for the reaction between cyanide ions and this iron(II) complex in alcohol–water mixtures.[1]

EXPERIMENTAL

The reagents and techniques used were the same as those described in our earlier paper [1] on the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide. The methods used for hydroxide runs were the same as those used for cyanide runs. Solutions of potassium hydroxide were made up from AnalaR material and standardised against standard acid.

RESULTS

Kinetics.—The reactions with cyanide and with hydroxide, which were always present in high concentration compared with that of the iron(II) complex, followed first-order kinetics over at least three half-lives. Observed first-order rate constants are reported in Table 1, in which each entry represents the mean of at least two acceptably consistent determinations. As in our earlier work on the reaction of $[Fe(bipy)_3]^{2+}$ with cyanide [4] or hydroxide [23] in water and in binary aqueous solvent mixtures,[1] the kinetic results conform to the pattern of equations (2) and (3). At the relatively high concentrations of cyanide and hydroxide used in our investigation, $k_1 \ll k_2[X^-]$. We have con-

$$-d[Fe(bipy)_3^{2+}]/dt = k_{obs.}[Fe(bipy)_3^{2+}] \quad (2)$$

$$k_{obs.} = k_1 + k_2[X^-] \quad (X = CN \text{ or } OH) \quad (3)$$

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[21] J. Murto, *Suomen Kem.*, 1961, **B34**, 92.
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firmed that the second-order process is dominant in a selection of our solvent mixtures. In these cases an unweighted least-mean-squares analysis gave a small value for k_1 and a value for k_2. In many instances, particularly at the higher mol fractions of organic co-solvent, k_1 was within its standard deviation of zero and thus negligible. In the solvent mixtures where we determined $k_{obs.}$ only at the highest cyanide or hydroxide concentration and simply divided $k_{obs.}$ by reagent concentration to obtain a value for k_2, the error introduced is 1—2%. This is slightly less than the uncertainties in k_2 values computed from the concentration dependence of $k_{obs.}$ values.

Analysis of Data.—At a fixed temperature and pressure, the second-order rate constant (k_2) for reaction between hydroxide or cyanide ion and the iron(II) complex can be expressed, using transition-state theory, in terms of the corresponding activation Gibbs function, $\Delta G^{\ddagger}$; $k_2 = (\boldsymbol{k}T/\boldsymbol{h}) \exp(-\Delta G^{\ddagger}/RT)$. This activation quantity can be related to the standard-state chemical potentials of the transition state, $\mu^{\ddagger}$, the iron(II) complex, $\mu^{\ominus}$(complex), and the incoming ionic nucleophile, $\mu^{\ominus}$(ion), in solution, by equation (4). The changes in each term of equation (4) on

$$\Delta G^{\ddagger} = \mu^{\ddagger} - \mu^{\ominus}(\text{complex}) - \mu^{\ominus}(\text{ion}) \qquad (4)$$

going from a solution in water to a mixture where the mol fraction of co-solvent is x_2 can be represented by the medium operator [24] δ_m [equation (5)]. It follows therefore

$$\delta_m \Delta G^{\ddagger} = \delta_m \mu^{\ddagger} - \delta_m \mu^{\ominus}(\text{complex}) - \delta_m \mu^{\ominus}(\text{ion}) \qquad (5)$$

that if the ion is destabilised as x_2 increases [$\delta_m \mu^{\ominus}(\text{ion}) > 0$] then $\delta_m \Delta G^{\ddagger}$ will tend to decrease and the rate constant increase. Thus the extent to which the effect of solvent on the anion, hydroxide or cyanide, determines the change in rate can be calculated if $\delta_m \mu^{\ominus}$(ion) is known from other experiments. In such comparisons, attention must be given to the definition of the standard states. Since we have expressed the rate constant in units of dm^3 mol^{-1} s^{-1}, then the standard state for the ion is the hypothetical solution where the ion has unit activity and molarity. If other solution standard states are used, consideration of the corresponding cratic and unitary contributions would be important.[25] In principal, $\delta_m \mu^{\ominus}$ values for ions can be obtained from corresponding values for salts, the latter being obtained, for example, from electrochemical measurements. However, this subdivision of salt values into ionic values cannot be made in any absolute sense and thus various extra-thermodynamic assumptions are made in such analyses. This is not the place to discuss the many methods available (*cf.* ref. 26). It is relevant however to note the bases of the methods used for the systems employed in our kinetic studies.

(a) *Hydroxide ions in dmso–water mixtures.* Das and Kundu [22] measured, using e.m.f. techniques, the autoprotolysis constant of water in dmso–water mixtures and calculated the sum [$\delta_m \mu^{\ominus}(H^+) + \delta_m \mu^{\ominus}(OH^-)$]. Khoo [27] had previously obtained $\delta_m \mu^{\ominus}(H^+)$ from the dependence of $\mu^{\ominus}$(HX) (X = halogen) on x_2. The single-ion quantity $\delta_m \mu^{\ominus}(H^+)$ was obtained using the method proposed by Feakins and Watson.[28] The latter workers suggested that the solvation energy of HX, $\Delta G_s^{\ominus}$(HX), is related to the solvation energy of H^+, $\Delta G_s^{\ominus}(H^+)$, by equation (6) where r_i is the radius of the counter anion X^- and α is a

$$\Delta G_s^{\ominus}(\text{HX}) = \Delta G_s^{\ominus}(\text{H}^+) + \alpha r_i^{-1} \qquad (6)$$

constant of proportionality for a series of singly charged anions. Hence combination of the single-ion value for transfer of H^+ with that for H^+ and OH^- yields [22] the required value for $\delta_m \mu^{\ominus}(OH^-)$. Over the range $0 \leqslant x_2 \leqslant 0.257$, $\delta_m \mu^{\ominus}(OH^-)$ values are a linear function of x_2 and using a small computer program the required values at other mol fractions were obtained by simple interpolation and short extrapolation. The values obtained were used in the analysis of the kinetic results as described in the next section. The most notable feature is a marked destabilisation of $[OH]^-$ by added dmso, *e.g.* at $x_2 = 0.257$, $\delta_m \mu^{\ominus}(OH^-) = 68.4$ kJ mol^{-1}. Indeed, in a footnote to their paper concerned with an analysis of the rate of alkaline hydrolysis of ethyl acetate in dmso–water mixtures, Fuchs *et al.*[29] seem to question whether this conclusion is correct and say that use of these $\delta_m \mu^{\ominus}(OH^-)$ values would not provide meaningful conclusions in their case. Certainly the method [*cf.* equation (6)] suggested by Feakins and Watson,[28] and used by Khoo,[27] may be too simple according to more recent work by Feakins and his co-workers.[30] For the time being, however, the data given by Das and Kundu [22] remain the only set available.

(b) *Cyanide ions in ethylene glycol–water mixtures.* In a number of publications, Wells has explored another solution to the problem of calculating transfer quantities for ions in a range of solvent mixtures. In the first application of this method, Wells [31] calculated $\delta_m \mu^{\ominus}(H^+)$ for methanol–water mixtures. The transfer was treated in two stages. First the Born expression was used to calculate the change in chemical potential for the transfer of a tetrahedral species $[H(OH_2)_5]^+$ having a radius equal to three times that of a water molecule. Secondly, the change in chemical potential was calculated for the equilibrium replacement of one of the five water molecules by a molecule of methanol. From the calculated value of $\delta_m \mu^{\ominus}(H^+)$ and values of $\delta_m \mu^{\ominus}$(HX), the single-ion value $\delta_m \mu^{\ominus}(X^-)$ was obtained. Wells [2] applied this method to the analysis of single-ion transfer values for chloride ion in ethylene glycol–water mixtures. For such mixtures, chloride is destabilised as x_2 increases, with, for example, $\delta_m \mu^{\ominus}(Cl^-) = 3.53$ kJ mol^{-1} when $x_2 = 0.404$. We have previously argued that $\delta_m \mu^{\ominus}(CN^-) \simeq \delta_m \mu^{\ominus}(Cl^-)$, and thus cyanide ions will be similarly destabilised. The effect of the co-solvent here is predicted to be less marked than when dmso is added.

(c) *Cyanide ions in glycerol–water mixtures.* Wells also extended his treatment to a consideration of ions in glycerol–water mixtures, and obtained [32] $\delta_m \mu^{\ominus}(Cl^-)$ values for mixtures over the range $0 \leqslant x_2 \leqslant 0.164$. Cyanide ions in water are expected to be slightly destabilised when glycerol is added; for instance when $x_2 = 0.164$, $\delta_m \mu^{\ominus}(CN^-) \simeq \delta_m \mu^{\ominus}(Cl^-) = 1.30$ kJ mol^{-1}.

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[25] R. W. Gurney, 'Ionic Processes in Solution,' McGraw-Hill, New York, 1953.
[26] M. J. Blandamer, *Quart. Rev.*, 1970, **24**, 169.
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DISCUSSION

For the reaction of $[Fe(bipy)_3]^{2+}$ with cyanide or with hydroxide the k_2 term in the rate law [equations (2) and (3)] is dominant under the conditions used in our experiments and is assigned to a bimolecular process. In both cases, however, there are alternative positions of attack by the ion at the iron complex: (*i*) at the iron atom, or (*ii*) at the co-ordinated ligand, presumably at the 6 or 6′ position.[3,4,33] Both reaction paths seem equally acceptable for cyanide attack; attack of the hydroxide ion at the ligand is a more attractive hypothesis than direct attack at the iron atom. Insofar as the site of attack is concerned, our subsequent discussions are fortunately not affected because the analysis is simply based on the fact that the reaction is bimolecular.

The effects of various co-solvents on the second-order rate constant, k_2, are illustrated in Figure 1. At low mol fractions, organic co-solvents such as ethylene glycol and dmso had little effect on the rate constant. This indicates that the solvation shells of hydroxide and

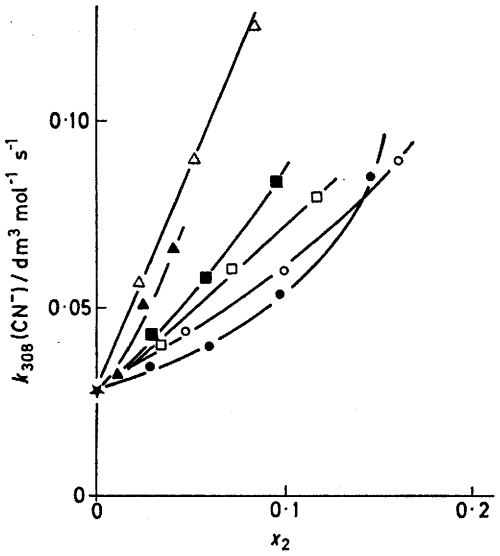

FIGURE 1 Variation of second-order rate constants for the reaction of $[Fe(bipy)_3]^{2+}$ with cyanide at 308.2 K. Rate constants are taken from Table 1 and from ref. 1. Co-solvents: dioxan (△), tdpo (▲), acetonitrile (■), EtOH (□), MeOH (○), and dmso (●)

cyanide ions are almost unaffected in these water-rich mixtures, there being a marked preferential solvation by water. As the mol fraction increased, so the rate constant increased more rapidly. There appears to be no simple correlation between the relative effects of co-solvents on $\delta_m\Delta G^{\ddagger}$ [*cf.* equation (5)] and the type of co-solvent as indicated by the 'typically aqueous' and 'typically non-aqueous' classification referred to above.[34] This contrasts with the data for the aquation of $[Fe(5NO_2\text{-phen})_3]^{2+}$ and the solvolysis of t-butyl chloride where plots of $\delta_m\Delta G^{\ddagger}$ against G^E for the mixture provide a valuable method of presenting the data and show remarkably good correlation for the t.a. (and some t.n.a.n.) mixtures.[35] It appears that this pattern is only observed for unimolecular first-order reactions where the activation process requires considerable reorganisation of the surrounding solvent molecules. This idea is certainly in accord with the conclusions drawn by Robertson [36] from trends in heat capacity of activation, $\Delta C_p^{\ddagger}$, for solvolytic reactions. In addition, in the present reactions we have the additional complication of a bimolecular transition state and attacking reagents that are strongly solvated.

The effect on the rate constant of changing from

TABLE 2

Ratios ($k_2 : k_0$) of rate constants for cyanide or hydroxide attack at $[Fe(bipy)_3]^{2+}$ in binary aqueous mixtures (mol fraction x_2 of organic component), k_2, to those in water, k_0, as calculated from estimated values for Gibbs free energies of transfer of cyanide or hydroxide ion from water into the binary mixture [$\delta_m\mu^{\ominus}(CN^-)$ or $\delta_m\mu^{\ominus}(OH^-)$] and as determined experimentally

Co-solvent	x_2	T/K	$\delta_m\mu^{\ominus}(CN^-)$ / J mol^{-1}	$k_2 : k_0$ calc.	$k_2 : k_0$ expt.
Glycerol	0.198	308.2	695	1.3	2.2
Ethylene glycol	0.044	298.2	535	1.2	1.8
	0.094		1 155	1.6	2.2
	0.151		1 845	2.1	2.7
			$\delta_m\mu^{\ominus}(OH^-)$ / J mol^{-1}		
dmso	0.237	298.2	6 290	13	8
	0.276		7 330	19	18
	0.321		8 530	31	25
	0.373		9 940	55	44

hydroxide to cyanide in the reaction with the $[Fe(bipy)_3]^{2+}$ complex is evident from Table 1. The ions $[CN]^-$ and $[OH]^-$ are of similar size, with thermochemical radii [37] of 1.82 and 1.40 or 1.53 Å. Thus on simple electrostatic arguments, differences in solvation and thus chemical potentials could well be small. If anything, one would expect the effect of solvent variation on reactivity to be somewhat greater for the slightly smaller hydroxide ion. Such direct comparison between rate constants, at the same temperature, pressure, and co-solvent mol fraction, as is possible from the data at hand does give some slender support for this forecast.

The rate of the changes in solvation of the anion as x_2 increases is further highlighted by the comparisons given in Table 2. The calculated ratio $k_2 : k_0$ has been obtained from the values of $\delta_m\mu^{\ominus}(CN^-)$ and $\delta_m\mu^{\ominus}(OH^-)$ discussed above. Thus we assumed that as the composition of the mixture changes so the difference $\delta_m\mu$ — $\delta_m\mu^{\ominus}$(complex) remains zero and hence $\delta_m\Delta G^{\ddagger} = -\delta_m\mu^{\ominus}(CN^-)$. As in the case of methanol– and t-butyl alcohol–water mixtures, the calculated and experimental rate ratios are similar. We conclude that, at least in

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the water-rich mixtures, the change in the solvation of the small $[CN]^-$ ion is more important than analogous changes for the complex and transition states. A similar conclusion follows from the analysis of the rate data [38] for the reaction between cyanide and the Schiff-base complex tris[α-(2-pyridyl)benzylideneaniline]iron(II) in aqueous mixtures containing either methanol or ethanol.

As explained above, the foregoing conclusions depend on the validity of our assumption that $\delta_m\mu^\ominus(CN^-) = \delta_m\mu^\ominus(Cl^-)$. A similar analysis based on the rate data

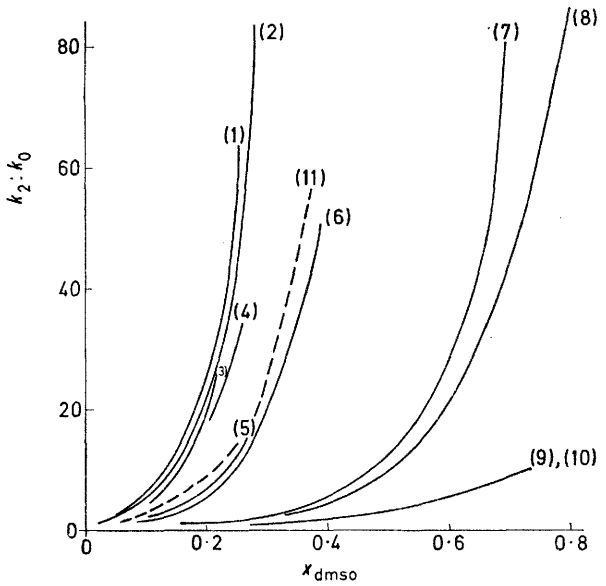

FIGURE 2 Variation of the ratio ($k_2 : k_0$) of the second-order rate constant for reaction of substrates with hydroxide ion in aqueous dmso (mol fraction x_{dmso}) to that in water. Substrates: (1) $[Co(NH_3)_5(dmso)]^{3+}$, (2) MeI, (3) fdnb, (4) $[CoBr(NH_3)_5]^{2+}$, (5) $[CoCl(NH_3)_5]^{2+}$, (6) $[Fe(bipy)_3]^{2+}$, (7) $PhCH_2Cl$, (8) $NMe_3{\cdot}SO_3$, (9) ethyl acetate, (10) ethyl benzoate. The broken line (11) shows the variation of $k_2 : k_0$ predicted from the $\delta_m\mu^\ominus(OH^-)$ values used in this paper. All the points are at 298.2 K

for the reaction between $[Fe(bipy)_3]^{2+}$ and hydroxide does not suffer from this drawback in that values of $\delta_m\mu^\ominus(OH^-)$ for dmso–water mixtures are available. The outcome of this analysis is also summarised in Table 2, which shows a correlation between predicted and calculated rate ratios based on the same assumption, *viz.* $\delta_m\Delta G^\ddagger = -\delta_m\mu^\ominus(OH^-)$, as that discussed above. It is unfortunate that $\delta_m\mu^\ominus(OH^-)$ values are only available over the range $0 \leqslant x_2 \leqslant 0.257$, where the effect of added dmso on rate constants is small compared with the dramatic change in rate constants as x_2 increases further. Over the small mol-fraction range where the two sets of data overlap the curvature in the plots of k_2/k_0 against x_2 is small and the divergence between this trend and the approximately linear dependence of $\delta_m\mu^\ominus(OH^-)$ is small.

The agreement between predicted and calculated rate constants (Table 2) is fair, with the experimental values being *ca.* 20% less than predicted values. Thus we conclude that, in equation (5), $\delta_m\mu^\ddagger - \delta_m\mu^\ominus$(complex) is close to zero while $\delta_m\mu^\ominus(OH^-)$ is the key factor determining the changes in the rate ($\delta_m\Delta G^\ddagger$) of alkaline hydrolysis (*cf.* cyanide attack above). Although $\delta_m\mu^\ddagger - \delta_m\mu^\ominus$(complex) is close to zero, each term is unlikely to be so. Recently, values of $\delta_m\mu^\ominus[Fe(phen)_3^{2+}]$ have been estimated, using Born calculations and naphthalene as a model for the ligands, for transfer from water to aqueous mixtures containing mol fractions of 0.2, 0.4, 0.6, 0.8, and 1.0 of methanol, acetone, or *NN*-dimethylformamide.[39] From these results it seems highly likely that both $\delta_m\mu^\ddagger$ and $\delta_m\mu^\ominus[Fe(bipy)_3^{2+}]$ in our system are negative and comparable in magnitude to $\delta_m\mu^\ominus(OH^-)$.

The rapid increase in rate constant for the reaction between $[OH]^-$ and $[Fe(bipy)_3]^{2+}$ when dmso is added at $x_2 \geqslant 0.3$ is not unexpected when set against kinetic data for other similar reactions in this range of solvent mixtures. We compare the rate ratio $k_2 : k_0$ for a variety of reactions, both organic and inorganic, in Figure 2. The majority of these reactions are thought to proceed by a simple one-step mechanism. The exceptions are the reactions of the cobalt(III) complexes. Here the mechanism is of a rate-determining dissociative reaction subsequent to a rapidly established pre-equilibrium [the $S_N1(CB)$ mechanism of equations (7)

$$[Co(NH_3)_5(dmso)]^{3+} + [OH]^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4(NH_2)(dmso)]^{2+} + H_2O \quad (7)$$

and (8)].[40] In these cases an increase in the chemical

$$[Co(NH_3)_4(NH_2)(dmso)]^{2+} \xrightarrow{\text{slow}} \text{products} \quad (8)$$

potential of the hydroxide ion will lead to an increase in the overall observed rate constant *via* its effect on the equilibrium (7).

The shapes of the plots in Figure 2 are all remarkably similar, but the magnitudes of the rate accelerations observed on increasing the mol fraction of dmso vary greatly according to the reaction. Thus, for example, the ratio of the rate constant for reaction with hydroxide in a mol fraction of 0.5 of dmso to that in water ranges from several thousand for methyl iodide [15] down to about five for ethyl acetate [41] and less than four for ethyl benzoate.[42] It is therefore apparent that the variation of $\delta_m\mu^\ominus(OH^-)$ is not the dominant factor determining reactivity in most cases, other factors also being involved. We can point to two variables which may be of importance. One possible variable is the extent of substrate–hydroxide interaction in the transition state. The more developed this interaction the

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more the rate dependence on x_2 will reflect the change in $\delta_m\mu^\ominus(OH^-)$. The degree of interaction is expected to

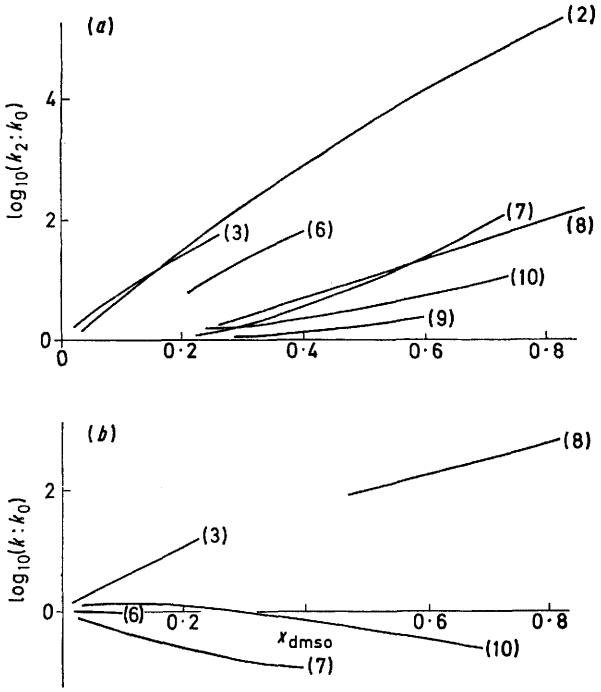

FIGURE 3 Comparison of the kinetic patterns for (*a*) alkaline hydrolysis and (*b*) neutral (acid) hydrolysis of various substrates, numbered as in Figure 2, in aqueous dmso (mol fraction x_{dmso}). The ratio $k_2 : k_0$ is as defined in Figure 2

follow the order fdnb > MeI > $PhCH_2Cl$ > $NMe_3{\cdot}SO_3$. The interaction between $[OH]^-$ and fdnb is expected to be strong with considerable charge-transfer stabilisation, while the attack of $[OH]^-$ at MeI has more S_N2 character than attack at benzyl chloride, the solvolysis of the latter being generally regarded as having a borderline S_N2 or S_N1 mechanism. At the other extreme, the hydrolysis of $NMe_3{\cdot}SO_3$ in neutral solution appears to be essentially S_N1.[43] The order of the curves in Figure 2 is consistent with such an explanation, although we cannot predict *a priori* the positions of the curves for the reactions involving $[OH]^- + [Fe(bipy)_3]^{2+}$ and the cobalt complexes, the latter reactions being S_N1(CB) rather than S_N2. However, the rate increases for the fdnb and MeI systems are significantly larger than predicted by the values for $\delta_m\mu^\ominus(OH^-)$.

Reactivity trends for alkaline and neutral (acid) hydrolysis are compared, using logarithmic scales, in Figure 3. The very different trend for example between the behaviour of fdnb and $PhCH_2Cl$ undergoing neutral hydrolysis goes some way towards rationalising the behaviour of their alkaline hydrolysis with respect to the reaction between $[OH]^-$ and $[Fe(bipy)_3]^{2+}$. Irrespective of the inconsistencies between the various reactions detailed above, the interpretation of the reactivity trends for $[Fe(bipy)_3]^{2+} + OH^-$ and CN^- in terms of variation in chemical potential is gratifyingly successful.

We thank the Royal Society for a Grant-in-aid for the purchase of the spectrophotometer, and the S.R.C. for support.

[6/1335 *Received*, 8*th July*, 1976]

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