Reactivity Studies on the Hydrolysis of Iron(II) Complexes of Substituted Phenanthrolines in Dioxane–Water Solvents

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The kinetics of the hydrolysis of tris(4,7-diphenyl-1,10-phenanthroline)iron(II), tris(5-phenyl-1,10-phenanthroline)iron(II), and tris(5-nitro-1,10-phenanthroline)iron(II) has been studied in a wide range of dioxane–water mixtures with different acid catalysts (HCl, H_2SO_4, or p-$MeC_6H_4SO_3H$) at different temperatures. The effect of the solvent, the substituent on the ligand, and the nature of the conjugate base on the kinetics and the activation parameters is discussed in terms of the solvation of the species and the transition state.

The kinetics of the hydrolysis of iron(II) complexes of substituted phenanthrolines have been studied in several aqueous mixtures.[1–6] These studies point mainly to elucidation of the reaction mechanism and to understanding the reactivity changes due to variation in the solvent composition. The hydrolysis has also been carried out in different acid solutions and a specific effect of the conjugate base on the reaction rate has been found.[5,7,8]

Recently,[4] we described the hydrolysis kinetics of tris(1,10-phenanthroline)iron(II) in a wide concentration range of water–1,4-dioxane mixtures. The reactivity changes found were explained in terms of the polarity of the mixture and solvation of the transition and initial states. Burgess *et al.*[5] have also studied the kinetics of iron(II) complexes with substituted phenanthrolines in dioxane–water mixtures, but that study was limited to three compositions and one temperature. The effect of the ligand substituent on the rate constant has been discussed in terms of ion-pair formation.[5]

We have performed a detailed investigation of the effect of the solvent on the hydrolysis of tris(4,7-diphenyl-1,10-phenanthroline)iron(II) (**1**), tris(5-phenyl-1,10-phenanthroline)iron(II) (**2**), and tris(5-nitro-1,10-phenanthroline)iron(II) (**3**) in a wide range of dioxane compositions, with different acid catalysts, and temperatures ranging from 15 to 45 °C.

Experimental

Materials.—The phenanthroline complexes were prepared by mixing a solution of ammonium iron(II) sulphate (AnalaR) with a solution of the corresponding ligand (Sigma). 1,4-Dioxane (Merck p.a.) was purified prior to use, following a standard procedure,[9a] in order to prevent peroxide formation.

Hydrochloric and sulphuric acids (Merck p.a.), and toluene-p-sulphonic acid monohydrate (Aldrich) were used as purchased.

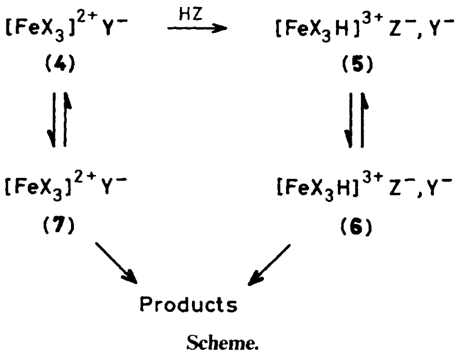
Kinetic Measurements.—Aliquots (3 cm^3) of the solvent mixture were poured into 1-cm cells and placed in the thermostatted cell holder of a Perkin-Elmer Lambda 3 spectrophotometer. After thermal equilibration the complex was added and the absorbance decrease monitored at 510 nm [540 nm for (**1**)]. Plots of ln (absorbance) *versus* time always remained linear. First-order rate constants ($k_{obs.}$) were obtained in all cases. All the kinetic runs were performed in duplicate and plots giving correlation coefficients worse than 0.999 were discarded. The activation parameters were determined from the Eyring equation.

Results and Discussion

The observed rate constants ($k_{obs.}$) for the different reactions are shown in Tables 1 and 2. In all cases the rate constants increase with decreasing water content. It is expected that the complex cation and the conjugate base form ion pairs and that the reaction is assisted more effectively by the anion when the dioxane content increases.

A very conspicuous feature of the hydrolysis reaction of the complexes, in dioxane–water solvents, is that it occurs even in the absence of added acid and, surprisingly, is faster than in the presence of the acid catalyst. For example, with complex (**2**) the rate constant is 13 times greater at a composition of 50% dioxane and 130 times greater at 70% dioxane, compared with the values of $k_{obs.}$ for the reaction in H_2SO_4 media. This highlights the important role of the hydrophobicity of the medium.

Taking into account the above results and the findings discussed below, we propose the following reaction Scheme, where (**4**) and (**5**) are solvent-separated ion pairs and (**6**) and (**7**) are contact ion pairs. In acid media the step (**4**)→(**5**) is very rapid and irreversible, so that all the reaction occurs through (**6**). On the other hand, in the absence of added acid the reaction occurs through the equilibrium (**4**)⇌(**7**).



Scheme.

It is noteworthy, that for the hydrolysis of complex (**1**) in different acids at all temperatures, and also in some cases for (**2**), maxima in $k_{obs.}$ are attained in poor water media. This was also observed[9b] in the reaction of tris(1,10-phenanthroline)iron(II) (**8**). The appearance of the maximum could be understood by the greater hydrophobic solvation of the complex cation with increasing dioxane content of the mixture.

Table 1. Pseudo first-order rate constants for the reaction of complex (**1**) in dioxane–water mixtures, HCl-catalysed under different experimental conditions

% Dioxane (v/v)	HCl/mol dm^{-3}	$10^2 k_{obs.}/s^{-1}$ 0.1				0.05	0.2
	Temperature/°C	25	30	38	45	25	25
30			2.13	7.55	19.2	0.97	
35				8.93			
40				10.2			
45		1.19	2.92	10.6	29.5	1.22	1.20
60		2.12	5.61	18.7	49.6	2.52	2.43
65							4.00
70		4.95	11.9	36.6	114	5.92	5.12
75		7.25					6.97
80		10.6	30.4	84.9	248	11.6	10.1
85		16.1	35.0	123	314	18.1	12.3
90		17.9	38.5	128	323	19.8	15.8
95		13.5	33.2	115	253	15.3	13.1

Table 2. First-order rate constants ($10^2 k_{obs.}/s^{-1}$) for the hydrolysis reactions of complexes (**1**)—(**3**) under different conditions of temperature, acid, and solvent

Substrate	Acid	Temp. (°C)	% Dioxane (v/v) 30	40	45	50	60	65	70	75	80	85	90	95
(**1**)	H_2SO_4	25	0.90			1.02	1.18		1.50	1.57	1.67	1.35	1.10	
		30	2.07			2.35	2.63		3.42	3.78	3.87	3.32	2.78	
		35	5.07			5.47	5.77		7.93	8.48	8.82	7.95	6.90	
		40	9.78			11.2	12.5		16.0	18.1	19.2	17.3	12.4	
		45	20.0			22.2	25.5		32.8	37.4	36.0	34.6	25.6	
	p-$MeC_6H_4SO_3H$	25			0.97		1.35		1.61	1.77	2.00	1.82		
		30			2.25	2.48	3.10	3.42	3.72	4.03	4.52	4.13	3.09	
		38			8.48		11.8		14.3	15.4	15.4	15.5	10.0	
		45	19.2		23.7		32.3		39.4	41.1	42.7	41.6	33.6	
(**2**)	H_2SO_4	25	1.14	1.29		1.30	1.67		2.28		2.64	2.89	2.87	
		30	2.83	2.89		2.98	3.86		4.84	5.21	6.16	6.53	6.55	
		35	5.90	6.27		6.94	7.70		9.54	11.3	13.2	15.3	14.7	
		40	12.7	13.7		15.3	17.7		19.6	23.2	27.8	30.6	31.4	
	HCl	25	1.20	1.50		1.87	3.08		11.3		2.65	49.9	58.2	66.4
		30	3.50	4.04		4.78	8.73		24.3		59.9	106	121	120
		40		16.5		22.2	43.4		127		336	448	565	
	p-$MeC_6H_4SO_3H$	25	1.72		1.73		2.09		2.77		4.33	4.86	4.50	4.15
		35	6.65		8.72		14.3		17.6		26.9	29.5	28.2	22.3
		40	16.9		22.4		32.3		40.1		55.8	59.7	64.8	60.2
		45	29.3		32.5		46.2		60.4			89.0	95.4	108
(**3**)	H_2SO_4	25	11.6	12.1		15.0	22.6		37.0		47.1	55.3	52.8	
		30	28.3	30.7		34.8	50.3		66.6		89.0	95.2		
		40	96.3	117		155	217		279		378	408	434	
		45	184	232		276	414		478		787	895	932	
	HCl	15			5.53	6.29	13.3	19.4	31.3	45.5	72.8	111	120	109
		20			12.0	13.6	23.6	40.2	69.7	90.0	150	216	306	336
		25		16.9			55.1	103	138	242	380	655	918	1 057
		30	23.7	36.6	44.3	55.1	157	191	287	391		1 535	2 590	
	p-$MeC_6H_4SO_3H$	25	13.7		23.4		36.0		59.1		84.2	108	134	126
		35	66.2		98.0	92.2	142	174	251	280	349	438	459	501
		40	123		189	228	310	421	456	548	742	913	981	1 044

The influence on reaction rate of the substituent on the ligand in a given reaction medium is given by the sequence 5-NO_2 > 5-Ph > 4,7-Ph_2. However, the ratio of the reaction constants $k(\mathbf{3}):k(\mathbf{2})$ shows an increase when the water content decreases, if the conjugate base is hydrophilic. On the other hand, an inverse order is observed for the more hydrophobic toluene-p-sulphonic acid. The same regularity appears in the comparison of $k(\mathbf{3})$ with $k(\mathbf{1})$. Therefore, we conclude that the hydrophobicity of the ligand and conjugate base plays a very important role in the reactivity of the complex.

The effect of the hydrochloric acid concentration on the hydrolysis rate of complex (**1**) (Table 1) shows that increasing acid content only has a significant effect at concentrations greater than 70% dioxane. A similar effect was described by Burgess *et al.*[5] for (**8**) in water–dioxane mixtures catalysed by $HClO_4$ and H_2SO_4. With HCl they observed, for (**8**) and also

Table 3. Activation parameters* for the hydrolysis reactions of the complexes (**1**)—(**3**) with H_2SO_4, HCl, and p-$MeC_6H_4SO_3H$ catalysts in different dioxane–water mixtures

Complex	% Dioxane	H_2SO_4		HCl		p-$MeC_6H_4SO_3H$	
		$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
(**1**)	30	119 ± 3	118 ± 12	118 ± 4	159 ± 13		
	45			124 ± 2	96 ± 7	124 ± 1	132 ± 4
	50	119 ± 2	117 ± 7				
	60	118.7 ± 0.5	117 ± 2	121 ± 4	90 ± 14	123 ± 2	132 ± 5
	70	119 ± 2	120 ± 6	119 ± 3	92 ± 11	124 ± 2	137 ± 6
	75	122 ± 1	130 ± 5			122 ± 2	132 ± 7
	80	119 ± 3	122 ± 8	118 ± 7	95 ± 22	117.8 ± 0.4	118 ± 1
	85	126 ± 3	141 ± 8	115 ± 2	89 ± 6	121 ± 2	129 ± 6
	90	120 ± 5	122 ± 17	112 ± 1	78 ± 5	121 ± 4	127 ± 14
	95			113 ± 6	81 ± 20		
(**2**)	30	121 ± 3	86 ± 10			111 ± 6	56 ± 20
	40	119 ± 1	81 ± 3	122 ± 10	179 ± 32		
	45					117 ± 10	76 ± 31
	50	125 ± 1	101 ± 3	127 ± 5	200 ± 17		
	60	118 ± 3	79 ± 11	136 ± 8	230 ± 25	123 ± 13	99 ± 42
	70	108 ± 1	48 ± 4	126 ± 4	206 ± 13	122 ± 11	98 ± 35
	80	119 ± 2	86 ± 5	132 ± 3	235 ± 11	119 ± 9	93 ± 30
	85	120 ± 3	91 ± 9	113.8 ± 0.1	178.7 ± 0.2	115 ± 11	78 ± 36
	90	121 ± 1	94 ± 1	118 ± 3	195 ± 9	121 ± 11	92 ± 36
	95			118 ± 17	195 ± 56	128 ± 6	121 ± 20
(**3**)	30	104 ± 5	48 ± 15			115 ± 5	172 ± 17
	40	112 ± 4	75 ± 14				
	45					109 ± 1	155 ± 4
	50	113 ± 4	80 ± 11				
	60	112 ± 1	81 ± 5	117 ± 12	106 ± 42	111 ± 5	166 ± 15
	65			111 ± 6	88 ± 19		
	70	101 ± 3	46 ± 11	104 ± 2	69 ± 6	107 ± 4	155 ± 13
	75			106 ± 9	77 ± 31		
	80	109 ± 3	76 ± 10	118 ± 10	209 ± 34	112 ± 3	178 ± 8
	85	108 ± 6	74 ± 18	127 ± 9	161 ± 31	110 ± 2	173 ± 7
	90	113 ± 3	175 ± 11	147 ± 5	229 ± 15	102 ± 6	147 ± 18
	95			162 ± 3	365 ± 9	109 ± 3	170 ± 9

* $\Delta H^\ddagger$ are in kJ mol^{-1} and $\Delta S^\ddagger$ in J K^{-1} mol^{-1}; errors are standard errors.

for (**3**), an increase in the rate constant with increasing HCl content. For the 4,7-dimethyl-1,10-phenanthroline complex they did not observe changes in k by increasing [HCl] in the same concentration range. The effect that we observe at dioxane concentrations greater than 80% is probably due to the greater hydrophobic character of complex (**1**) compared with the three complexes studied by Burgess *et al.*,[5] and also to the greater dioxane content of the mixture.

In Table 3 the activation parameters are shown for the hydrolysis reaction of the complexes in different solvents and with different acid catalysts. For the hydrolysis of (**3**) in sulphuric and toluene-*p*-sulphonic acid $\Delta H^\ddagger$ is smaller than that for (**1**) and (**2**) under the same conditions. This is interpreted as greater solvation of the transition state for the reaction of (**3**). On the other hand, the hydrolysis of (**3**) in HCl shows a large $\Delta H^\ddagger$ increase at dioxane concentrations over 75% (Table 3). This can be understood by assuming that, for the more hydrophilic ligand, an increase in the dioxane concentration is accompanied by a considerable destabilisation of the transition state.

In some cases minima in the $\Delta H^\ddagger$ *vs.* composition plots (not shown) are observed. These can be explained, in general, by a more effective solvation of the transition state. Obviously, as the rate-determining step in the hydrolysis of these complexes[10] is release of the first phenanthroline, the transition state which we refer to, corresponds to this process.

In the reactions of the three complexes in toluene-*p*-sulphonic acid a small $\Delta H^\ddagger$ variation with solvent composition was observed. However, for the more hydrophobic ligands (4,7-diphenyl-1,10-phenanthroline and 5-phenyl-1,10-phenanthroline) a minimum appears around 80% dioxane concentration.

The behaviour of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ in this case is such as to smooth the $\Delta G^\ddagger$ changes when the composition of the mixtures varies. In fact, when a minimum in $\Delta H^\ddagger$ appears a minimum in $\Delta S^\ddagger$ can also be observed.[11]

The observed $\Delta S^\ddagger$ values are very large, and this can be understood in terms of the formation of contact ion pairs from separated ion pairs. Marcus,[12] in a recent study of the entropy changes in the formation of contact ion pairs, showed that the entropy loss due to the translational contribution of the ions is overcompensated by rotational entropy gain, electrostatic entropy gain, and translational entropy gain due to solvent release. This could explain why, for the more hydrophilic ligand [in (**3**)], the entropy effect in HCl and H_2SO_4 media is greater (probably due to the formation of contact ion pairs) just as is found in the more hydrophobic media. The effect is more important for HCl suggesting that the reactivity order obtained by Burgess *et al.* for the different anions could be mainly an entropy effect.

On the other hand, for complex (**1**) in HCl $\Delta S^\ddagger$ shows a pronounced decrease when the concentration changes from 30 to 45% dioxane, and thereafter is practically constant. This shows that the more favourable medium for the formation of contact ion pair for complex (**1**) is the water-rich solvent. For the complex with the ligand of hydrophobicity between the two described extremes [complex (**2**)] in HCl, $\Delta S^{\ddagger}$ is relatively constant, within experimental error. The entropy changes for the other reactions do not show a clear trend, perhaps due to considerable experimental error.

The difference in $\Delta G^{\ddagger}$ for a reaction in two solvents[13] is given by $\delta\Delta G^{\ddagger} = \Delta G_t^{\circ}$ (transition state) $- \Delta G_t^{\circ}$ (reactants). Recently, Abraham *et al.*[14] have developed a linear relationship to estimate the ΔG for transfer of hydrophobic solutes from water to different solvents, $\Delta G_t^{\circ} = MR_T + D$. From this $\delta\Delta G^{\ddagger} = M[R_T$ (transition state) $- R_T$ (reactants)], and for a given mixture $\delta\Delta G^{\ddagger}$ is a function of M only, because R_T is a characteristic constant of the solute. The values given by Abraham *et al.* for M in dioxane–water solvents show a minimum for a 90% dioxane mixture. We observed a maximum in the reactivity for the reaction of (**1**) in a solvent mixture with a similar dioxane content. As the reaction is faster in dioxane–water mixtures than in water, and M is always negative, it implies that R_T (transition state) $>$ R_T (reactants) and therefore the transition state is more hydrophobic than the reactants.

Finally, a word of caution must be expressed with respect to the R_T value for the transition state, because the transition state normally includes solvent molecules and cannot be separated from the medium in which the reaction takes place.[15]

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