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Ligand-Oxidation in Iron Diimine Complexes.
VI. The Importance of Solvation on Ligand-Reactivity

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Introduction

It has long been suggested that iron(II) complexes of the aromatic diimine ligands 2,2′-bipyrine (bipy) and 1,10-phenanthroline (phen) in aqueous solutions are strongly solvated, the water molecules being attached firmly in the pockets formed by the ligands [1, 2]. Kurucsev, Sargeson and West [2] measured the diffusion coefficients (D) of these two complexes in water and compared the solvodynamic mean radii (r_{solv}) obtained by the application of the Stokes-Einstein equation, $r_{solv} = kT/(6\pi\eta D)$ [η = kinematic viscosity; k = Boltzman constant; T = absolute temperature], with the structural mean radii (r_{st}) obtained by means of molecular models. The larger solvodynamic radii [2] 11.9 and 13.0 Å compared to the structural radii 7.1 ± 0.5 and 7.9 ± 0.5 Å for the bipy and phen compounds, respectively, prompted the authors to suggest that these complex molecules are strongly solvated by water molecules. The presence of the solvating molecules was further confirmed in analogous aromatic diimine complexes by solvent extraction methods [3, 4]. For the iron(II) complex derived from 4,7-diphenyl-1,10-phenanthroline, 57 ± 6 water molecules per complex molecule were found [3, 4].

In 1974, some of us [5] demonstrated that solvation is also important for the iron(II) complexes of aliphatic diimine complexes, FeL_3^{2+}, L = $H_3CN{=}C(R){-}C(R'){=}NCH_3$, R, R′ = H, H; H, CH_3; CH_3, CH_3; $-CH_2CH_2CH_2CH_2-$, first synthesized by Krumholz [6] in 1953. The technique employed was cyclic voltammetry and the medium 10.5 *M* H_2SO_4. This medium was chosen because reversible electrochemical [5] or chemical [7, 8] oxidation to the corresponding iron(III) complexes can only be observed if the acidity is ⩾10 *M* H_2SO_4. At lower acid concentration, chemical and electrochemical reactions follow up the primary reversible one-electron transfer yielding new complexes in which some of the ligand molecules are oxidized, *e.g.*, to $H_3CN{=}C(OH){-}CH{=}CH{=}NCH_3$ [8, 9]. The solvodynamic mean radii for the above-mentioned aliphatic diimine complexes in 10.5 *M* H_2SO_4 and the aqueous data for the bipy and phen complexes correlated linearly with the structural mean radii, thus suggesting that solvation is important in 10.5 *M* H_2SO_4 for the aliphatic diimine complexes.

In 1975, the complex, R, R′ = H, H and CH_3, CH_3 were investigated by means of cyclic voltammetry and pulse techniques [10] in a room temperature molten salt, composed of aluminum chloride and ethylpyridinium bromide in a 2:1 mole ratio [11]. Reversible one-electron electrochemical oxidations were found [10] in this medium of high Lewis acidity, which consists of ethylpyridinium dialuminum heptachloride [12]. The solvodynamic mean radii were found to be identical, within the experimental error, to the structural mean radii, indicating that solvation is not important in this medium. Ligand oxidation reactions do not take place in this totally anhydrous medium [10].

In 1976, the electrochemical oxidations of iron(II) diimine complexes were investigated in acetonitrile [13]. Aliphatic and mixed ($C_5H_4N{-}C(R_1){=}NR_2$) diimine ligands were employed and the oxidations were found to be reversible one-electron processes, without chemical reactions following up the electrochemical step R, R′ = H, H; H, CH_3; CH_3, CH_3; R_1R_2 = H, CH_3; CH_3, CH_3). More recently, these investigations were expanded to nineteen complexes, and for the R, R′ = H, C_6H_5; CH_3, C_6H_5, ligand oxidation reactions were found to occur at potential scan rates up to 5 V s^{-1}. Above 10 V s^{-1}, reversible one-electron oxidation processes occur [14].

This paper extends the solvation studies in aqueous sulphuric acid and presents new data for acetonitrile solutions comprising iron(II) complexes of aliphatic, mixed and aromatic diimine ligands. The importance of solvation is discussed in connection with the ligand-reactivity found in these complexes.

Experimental

The syntheses and purification procedures of the complex compounds are described in the literature [15, 16]. The experimental techniques employed in measurements in H_2SO_4 solutions are described in reference 5 (10.5 *M* H_2SO_4). The experimental part in acetonitrile solutions is described in reference 13.

The structural mean radii were obtained by measurements of scale molecular models (Framework

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TABLE I. Diffusion Coefficients, D, of the FeL_3^{2+} Complexes and Corresponding Solvodynamic Mean Radii in Aqueous Acid Solutions and Acetonitrile, 0.2 *M* Tetraethylammonium Perchlorate, Solutions at 25.0 °C. Errors in D and r_{solv} of 10%.

No.	*Aliphatic Diimine* L = $H_3CN{=}C(R){-}C(R'){=}NCH_3$		Acetonitrile		10.5 *M* H_2SO_4	
	R	R'	D, $cm^2\ s^{-1}$ × 10^5	r_{solv}, Å	D, $cm^2\ s^{-1}$ × 10^7	r_{solv}, A
1	H	H	1.2	4.7	5.3^5	6.0^5
2	H	CH_3	0.93	6.0	4.2^5	7.5^5
3	CH_3	CH_3	0.99	5.6	3.5^5	9.0^5
4	CH_3	C_2H_5	0.75	7.4	3.9	8.2
5	$-CH_2CH_2CH_2CH_2-$		0.73	7.6	3.2^5	10.2^5
6	$-CH_2CH(CH_3)CH_2CH_2-$		0.73	7.6	2.7	11.7
7	H	C_6H_5	0.31	18.	1.8	18
8	CH_3	C_6H_5	0.29	19	1.6	20
	Aromatic Diimine		Acetonitrile		Water	
9	bipy		0.88	6.3		11.8^2
10	phen		–	–		13.0^2
	Mixed Diimine L = $C_5H_4N{-}C(R_1){=}NR_2$		Acetonitrile		4.0 *M* H_2SO_4	
			D, $cm^2\ s^{-1}$ × 10^5	r_{solv}, A	D, $cm^2\ s^{-1}$ × 10^6	r_{solv}, A
	R_1	R_2				
11	H	CH_3	1.0	5.4	1.4	8.8
12	H	C_2H_5	0.91	6.1	–	–
13	CH_3	CH_3	1.0	5.5	–	–
14	CH_3	C_2H_5	0.72	7.7	1.3	9.1
15	CH_3	C_6H_5	0.76	7.3	–	–
16	C_6H_5	CH_3	0.72	7.7	1.1	11
17	C_6H_5	C_6H_5	0.60	9.2	–	–
18	CH_3	*p*-$NH_2C_6H_4$	0.55	10	–	

Molecular Models, Prentice Hall Inc., Englewood Cliffs, N.J.). The kinematic viscosity fo the acetonitrile solutions containing 0.2 *M* tetraethylammonium perchlorate and m*M* amounts of water is 0.398 cP, as determined with a calibrated Ostwald viscosimeter.

Results and Discussion

Table I lists the compounds studied in acetonitrile and sulfuric acid solutions. The electrochemical oxidation of these complexes on disk platinum electrodes is a reversible one-electron process [5, 13, 17]. Therefore, application of the Randles-Sevcik equation [18] to the cyclic voltammograms allows us to obtain the diffusion coefficients of the electroactive species listed on Table I. These coefficients applied to the Stokes–Einstein equation, yield the solvodynamic mean radii, r_{solv}, of the diffusing species (see Table I), provided that the molecules can be described as spheres. Such a description is a good approximation ot the structure of these complexes, principally when the pockets between the ligands are filled up with solvent molecules.

Plots of solvodynamic mean radii as a function of the structural mean radii are shown in Fig. 1 for aqueous acid and acetonitrile solutions. The upper straight line, with a slope of 2.4 ± 0.1, comprises data for aqueous solutions of [bipy(9) and phen(10)], of two mixed diimine compounds in 4.0

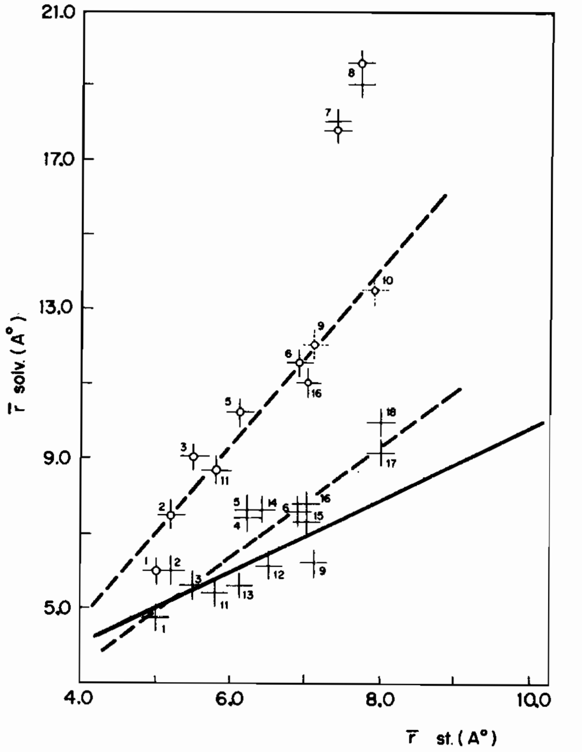


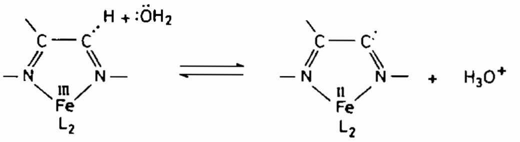
Fig. 1. Solvodynamic mean radii (r_{solv}) as a function of the structural mean radii (r_{st}) of the iron(II) complexes in —ϕ— 10.5 *M* H_2SO_4, 4 *M* H_2SO_4 and ---ϕ--- H_2O and + in acetonitrile, 0.2 *M* tetraethylammonium perchlorate, at 25.0 °C. The numbers refer to the compounds given in Table I.

M H_2SO_4 [R_1, R_2 = H, CH_3 (11); C_6H_5, CH_3 (16)] and five aliphatic diimine complexes in 10.5 *M* H_2SO_4. [R,R′ = H,H (1); CH_3, CH_3 (3); $-CH_2CH_2CH_2CH_2-$ (15) [5] and $-CH_2CH(CH_3)CH_2CH_2-$] [5]. The observed solvodynamic radii are 1.2–1.7 times larger than the structural ones. Two additional aliphatic diimine complexes with bulkier phenyl groups as substituents, R, R′ = H, C_6H_5 (7); CH_3, C_6H_5 (8), do not fit this line, but present solvodynamic radii which are 2.5 times larger than the structural ones. The phenyl groups provide larger pockets between ligands for these compounds.

Acetonitrile data for seventeen complexes of aliphatic, mixed and aromatic ligands are also shown in Table I and Fig. 1. From Fig. 1 it is easily seen that for the majority of the studied complexes, solvation in acetonitrile is not as important as in aqueous acid solutions. In fact, if one considers compounds, 1, 2, 3, 11, 12, 13, 6, 9, 15, and 16, a straight line with a unity slope within the experimental error (full line) is obtained. The compounds 4, 5, 6, 14, 15, 16, 17 and 18, which have bulky substituents on the diimine chromophore [19], determine a straight line with a slope of about 40% (intermediate broken line on Fig. 1) bigger than unity, but yet about half of the slope observed for aqueous acid solutions. The aliphatic diimine complexes with phenyl substituents (7, 8) in acetonitrile follow the same behavior observed in aqueous acid solutions, *i.e.*, solvodynamic radii *ca.* 2.5 times larger than structural radii.

The Nature of the Solvating Species and Ligand-Reactivity

The fact that r_{solv} and r_{st} correlate linearly for iron diimine complexes in solvents ranging from water to 10.5 *M* H_2SO_4 indicates that the solvating entities must have approximately the same size. As the acid concentration increases the water activity decreases but the activity of H_3O^+ ions increases [20]. Since the structural mean radius of H_2O is very similar to that of H_3O^+ ions, one can suggest that as the acid concentration increases the solvating species are H_3O^+ ions. The presence of these two solvating species is very important in understanding the ligand-oxidation reactions which occur for all the aliphatic diimine complexes reported here [21] and also for the mixed diimine complexes [22]. The ligand-oxidation reactions are favored in media of low acid activity and high water activity, and retarded if the situation is reversed. The postulated mechanism for ligand-oxidation reactions involves as rate determining step the following equilibrium [8]



(1)

assisted by a nucleophilic attack of solvent water. At high acid concentration the above equilibrium is displaced to the left. The solvation by H_3O^+ ions can explain the higher stability of ferric complexes towards this internal redox reaction. The participation of the above equilibrium in the R, R′ = H, H case has been confirmed by means of the dependence of the overall rate constant for the ligand-oxidation reactions on the acid and water activities [23]. The aliphatic diimine complexes with phenyl substituents have the highest rates of ligand-oxidation at a fixed acid concentration [21]

In going from acid solutions to acetonitrile solutions (containing millimolar amounts of water), one observes that the ligand-oxidation reactions are slowed down. In the time scale of cyclic voltammetry in the 0.05–1.0 V s^{-1} potential scan rate range, over 1 V potential range, all of the reported compounds, except R, R′ = H, C_6H_5 (7); CH_3, C_6H_5 (8) are reversibly oxidized in one-electron processes. For the phenyl derivatives (7, 8) such behavior is only observed at potential scan rates higher than 10 V s^{-1}, and at lower scan rates chemical and electrochemical reactions which lead to ligand-oxidized products occur [13]. It is important to notice that these compounds are, in acetonitrile, probably largely solvated by water molecules much as in 10 *M* H_2SO_4.

The only medium so far in which ligand-oxidation processes in aliphatic or mixed diimine complexes of iron(III) were found not to occur [10, 24] is the ethylpyridinium dialuminum heptachloride molten salt [11, 12], which is totally anhydrous. This medium favors strongly the thermodynamic formation of the iron(III) complexes and the absence of nucleophilic agents precludes ligand-oxidation reactions to take place. It is to be expected that in a 'totally anhydrous' acetonitrile ligand-oxidation reactions would not take place.

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