Russian Journal of General Chemistry, Vol. 73, No. 8, 2003, pp. 1303–1308. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 8, 2003, pp. 1377–1382.

Effect of the Composition of the H_2SO_4–AcOH Binary Solvent on the Dissociation Kinetics of Metal Porphyrins

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Received October 1, 2001

Abstract—The kinetics and mechanism of dissociation of copper(II) complexes with octaethylporphyrin and of manganese(III) with tetraphenylporphyrin were studied in relation to the composition of an H_2SO_4–AcOH binary solvent. Concentration ranges of H_2SO_4 in the composition of the binary solvent, where the kinetics of dissociation of metal porphyrins obeys common kinetic regularities, were found using data for porphyrin complexes of transition metals and indium. The reaction order with respect to proton and the nature of the active form of this latter change in the range of solvent compositions, where the H_0–$c^0_{H_2SO_4}$ dependence is nonlinear.

In aprotic solvents, porphyrin complexes with *p*- and *d*-metal cations behave as nonelectrolytes. In solutions containing a proton-donor component, they dissociate into a solvated metal cation (or a solvated salt) and a free or protonated porphyrin [1, 2]. The different location of strong absorption bands in the electronic absorption spectra of porphyrins and their metal complexes makes possible the kinetics of dissociation of metal porphyrins to be studied by spectrophotometry [3]. As a rule, dissociation of complexes is impossible to study kinetically in pure proton-donor solvents. When using mixed solvents, one can vary their composition and component concentrations to obtain a solvent with necessary acidity and solution power.

The H_2SO_4–AcOH system has most commonly been used for studying dissociation of stable complexes [1, 4–7]. However, as a rule, kinetic measurements were carried out within narrow ranges of H_2SO_4 concentrations in AcOH. In this work we have studied the kinetics of dissociation of copper(II) complexes of octaethylporphirin (CuOEP) and of manganese(III) with tetraphenylporphyrin [(Cl)MnTPP], which differ greatly in their stability. The study was carried out within various ranges of H_2SO_4 concentrations in the H_2SO_4–AcOH binary solvent. We have also summarized dissociation kinetics data for a series of metal porphyrins over a wide range of concentrations of the binary solvent.

The electronic absorption spectra of the synthesized metal porphyrins are consistent with published data [8, 9].

The location of bands in the spectrum of CuOEP in glacial acetic acid (λ_{max} 564 and 529 nm) and in chloroform almost coincide; the spectrum in AcOH does not change on heating. The spectra of CuOEP in the AcOH–0.1–0.25 M H_2SO_4 system vary with time, passing into the spectrum of H_4OEP^{2+} with isosbestic points preserved (Fig. 1), which corresponds to reaction (1).

$$CuOEP + 4H^+_{solv} \longrightarrow H_4OEP^{2+} + Cu^{2+}_{solv}. \quad (1)$$

Reaction (1) is first-order with respect to metal porphyrin concentration (Fig. 2). As seen from the apparent parameters of CuOEP dissociation at 298–353 K (Table 1, Fig. 3), the reaction rate is proportional to the concentration of H_2SO_4. This points to a first order of the reaction with respect to sulfuric acid concentration. However, sulfuric acid behaves as a weak electrolyte in AcOH. With regard to pK_a 4.3 [10], we can ascertain the equation $c^0_{H_2SO_4} = c^2_{AcOH_2^+}/K_a$ ($c^0_{H_2SO_4}$ is the initial concentration of H_2SO_4 in AcOH, $c^2_{AcOH_2^+}$ is the equilibrium concentration of protonated acetic acid, and K_a is the acidic dissociation constant of sulfuric acid in acetic acid) at low concentrations of H_2SO_4 in AcOH. Then we can write the overall CuOEP dissociation kinetic equation in form (2).

$$-\frac{dc_{CuOEP}}{d\tau} = k(1/K_a)c_{CuOEP}\,c^2_{AcOH_2^+}. \quad (2)$$

Here τ is time and *k* is the true dissociation rate constant.

A linear dependence of apparent dissociation rate constant (k_{app}) on initial concentration of sulfuric acid in acetic acid was found previously for the complexes

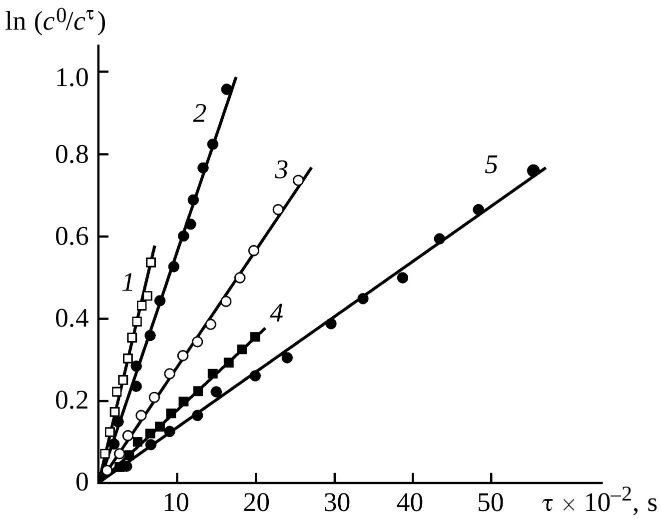

Fig. 1. Plot of $\ln(c^0/c^\tau)$ vs. τ for dissociation of (*1, 4*) (Cl)MnTPP and (*2, 3, 5*) CuOEP in the H_2SO_4–AcOH binary solvent [$c^0_{H_2SO_4}$, M: (*5*) 0.15, (*2, 3*) 0.2, (*4*) 7.18, and (*1*) 7.85]. Temperature, K: (*1*) 308, (*2*) 343, (*3*) 333, (*4*) 298, and (*5*) 323.

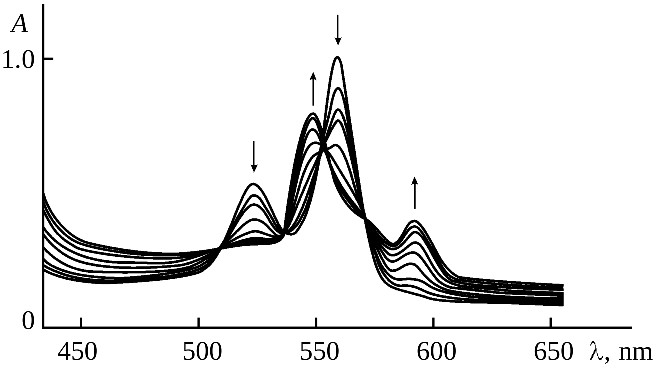

Fig. 2. Changes in the electronic absorption spectrum of CuOEP upon thermostating in the H_2SO_4–AcOH binary solvent ($c^0_{H_2SO_4}$ 0.15 M, 323 K).

(Ac)FeChl [Chl is the dianion of pheophytin (a)] and (Cl)PtDP and (Cl)PtMP (DP and MP are the dianions of proto- and mesoporphyrin) at H_2SO_4 concentrations 0.2–1.0 and 0.4–2 M, respectively [11, 12].

The second order with respect to solvated proton, moderate activation energies, and negative $\Delta S^{\neq}$ values make it possible to define the stage of protonation of two nitrogen atoms of the coordinated porphyrin as a limiting stage, which results in destruction of the complex in the second, fast stage [scheme (3)].

$$CuOEP + 2AcOH_2^+ \xrightarrow{\text{slowly}} (AcOH)_2CuH_2OEP$$

$$\xrightarrow{\text{fast}} Cu^{2+}_{solv} + H_2OEP. \qquad (3)$$

It is seen from Fig. 1 that H_2OEP is not accumulated in the reaction mixture, i.e. the formation of the H_4OEP^{2+} dication, too, occurs very fast.

In the case of (Cl)MnTPP, a hypsochromic shift of the absorption bands in the electronic spectrum takes place on passing from chloroform to proton-donor solvents: λ_{max} of the first absorption band is 616, 606, and 602 in chloroform, glacial AcOH, and AcOH–H_2SO_4 ($c^0_{H_2SO_4}$ 5 M), respectively. In AcOH–H_2SO_4 ($c^0_{H_2SO_4}$ 0–5 M), the spectrum is time invariant.

At the H_2SO_4 concentrations in AcOH higher than 5.0 M, the electronic spectrum of the complex gradually transforms into the spectrum of the doubly protonated tetraphenylporphyrin H_4TPP^{2+} upon thermostating at 298 K (Fig. 4). The kinetic characteristics of (Cl)MnTPP dissociation [Eq. (4)] in the AcOH–H_2SO_4 binary solvent ($c^0_{H_2SO_4}$ 3–8 M) at 288–318 K are given in Table 2 and Fig. 5. At H_2SO_4 concentrations of 8.5–10 M, the complex dissociates instantaneously to give the doubly protonated ligand [scheme (4)].

$$(Cl)MnTPP + 4H^+_{solv} \longrightarrow H_4TPP^{2+} + ClMn^{2+}_{solv}. \quad (4)$$

The absence of ionization or substitution of the Cl^- ligand replacement in the coordination sphere of manganese tetraphenylporphyrin was experimentally confirmed by the invariance of the absorption spectrum of (Cl)MnTPP in $CHCl_3$ after isolation of the

Table 1. Apparent kinetic parameters of CuOEP dissociation in the H_2SO_4–AcOH binary solvent

$c^0_{H_2SO_4}$, M	$k_{app} \times 10^4$, s^{-1}					$k^{298}_{app} \times 10^5$, s^{-1} [a]	E_a, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
	313 K	323 K	333 K	343 K	353 K			
0.10				1.8±0.1	3.2±0.3	0.85±0.05	58±1	64±4
0.15		0.74±0.03	1.3±0.1	2.1±0.1		1.6±0.2	59±12	60±41
0.20		1.60±0.09	2.9±0.2	5.0±0.6		3.1±0.1	52±1	83±3
0.25	1.3±0.1	2.2±0.1	4.0±0.5	7.6±0.7		5.6±0.3	44±3	110±9

[a] Found by extrapolation of the k_{app}–$1/T$ plot.

complex from the reaction mixture at instant $\tau_{1/2}$ ($\tau_{1/2}$ is the half-life period of the metal porphyrin). Moreover, the kinetic studies of dissociation of Mn(III)TPP with a series of acido ligands (Cl^-, Br^-, AcO^-, and HSO_4^-) in the AcOH–H_2SO_4 binary solvent ($c^0_{H_2SO_4}$ 3–5 M) [13, 14] showed that quantitative parameters of dissociation of different extra complexes are different. This means that the manganese(III) complexes dissociate by metal–nitrogen bonds without initial ionization of metal–acido ligand bonds. The absence of an appreciable concentration of $[MnTPP]^+$ ions in the solution is confirmed by the high dissociation activation energy and entropy of (Cl)MnTPP [Eq. (4)] compared to H_2TPP complexes with doubly charged metal ions (Table 2) [1, 3].

Using the above results, we can examine the dissociation rate constants of (Cl)MnTPP as a function of solvent composition over a wide range of H_2SO_4 concentrations. The value of $\log k^{298}_{app}$ for dissociation of (Cl)MnTPP in 4–8 M H_2SO_4 are linearly related to the initial H_2SO_4 concentration in AcOH and with the acidity function H_0 [15] (Fig. 5). The correlations seem to be associated with the fact that H_0 is proportional to $c^0_{H_2SO_4}$ in this very range of compositions of the binary solvent [15]. The slope of the straight line in the $\log k^{298}_{app}$–H_0 coordinates is close to two (1.74), i.e. the kinetic equations includes the total acidity h_0, rather than the concentration of any active form of proton in the solution [Eq. (5)]. The total acidity of the medium is determined by the presence of the species $AcOH_2^+$, $H_3SO_4^+$, H_2SO_4, and AcOH and of ion pairs [15]. In the range of compositions of the H_2SO_4–AcOH binary solvent under consideration, the activity of the more acidic species $AcOH_2^+$ and $H_3SO_4^+$ in reaction (4) is suppressed because of the presence

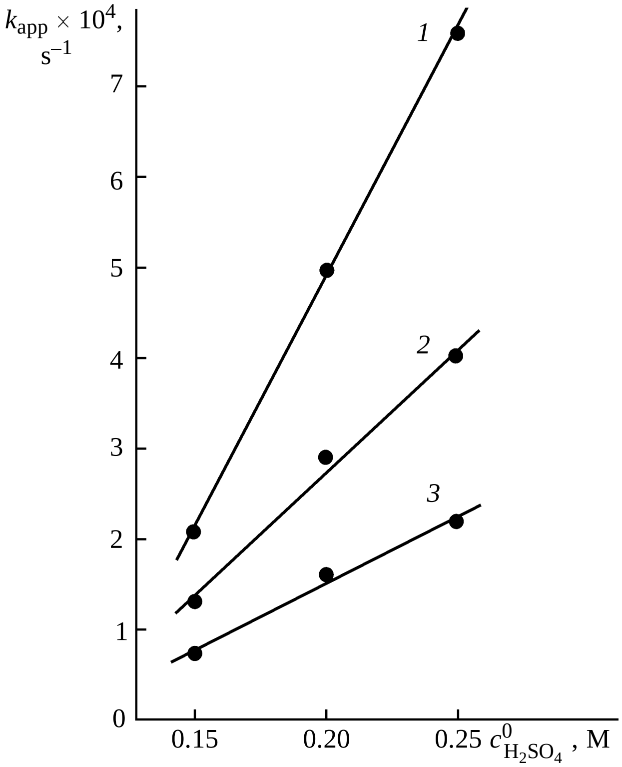

Fig. 3. Plot of apparent CuOEP dissociation rate constants (k_{app}) vs. initial concentration of H_2SO_4 in AcOH. Temperature, K: (*1*) 343, (*2*) 333, and (*3*) 323.

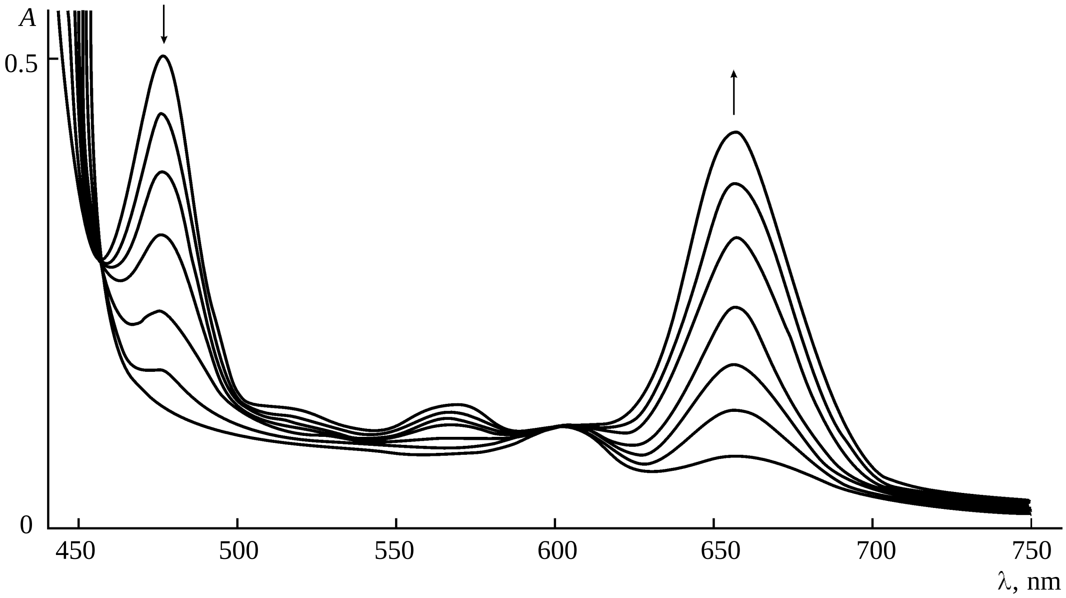

Fig. 4. Changes in the electronic absorption spectrum of (Cl)MnTPP in the course of thermostating in the H_2SO_4–AcOH binary solvent ($c^0_{H_2SO_4}$ 6.61 M, 298 K).

Table 2. Apparent kinetic parameters of (Cl)MnTPP dissociation in the AcOH–H_2SO_4 binary solvent

$c^0_{H_2SO_4}$, M	$k_{app} \times 10^4$, s^{-1}				E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
	298 K[a]	333 K	343 K	353 K		
3.00	0.0050±0.0003	0.153±0.008	0.36±0.01	0.79±0.01	80±2	–105±4
4.00	0.0047±0.0003	0.4030±0.0005	1.23±0.02	3.47±0.03	105.4±0.8	–22±2
5.00	0.031±0.006	1.910±0.002	5.67±0.08		100±4	–30±10
	288 K	298 K	308 K	318 K		
6.00			1.3±0.1	3.5±0.2		
6.61	0.24±0.02	0.87±0.05	3.3±0.2		97±5	–3±16
7.13	0.50±0.04	1.4±0.1	5.8±0.4		100±7	11±24
7.85	1.8±0.2	3.6±0.2	9.1±0.9		67±4	–93±13

[a] Found by extrapolation of the k_{app}–$1/T$ plot. [b] k_{app} at 290 K.

of higher concentrations of molecular H_2SO_4 which is less active in this reaction.

$$-dc_{(\mathrm{Cl})\mathrm{MnTPP}}/d\tau = kc_{(\mathrm{Cl})\mathrm{MnTPP}}h_0^2. \qquad (5)$$

Here $c_{(\mathrm{Cl})\mathrm{MnTPP}}$ is the concentration of manganese porphyrin and h_0 is the acidity of the medium.

Comparison of Eqs. (2) and (5) shows that the stoichiometric mechanisms of CuOEP and (Cl)MnTPP dissociation are common.

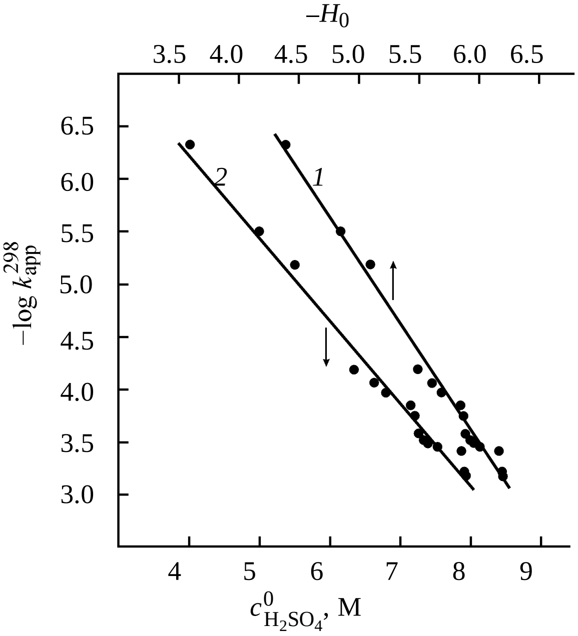

Fig. 5. Semilogarithmic plots of apparent (Cl)MnTPP dissociation rate constants (k^{298}_{app}) vs. (*1*) acidity function of the solvent and (*2*) initial concentration of H_2SO_4 in AcOH (298 K).

The participation of molecular H_2SO_4 along with solvated protons in reaction (4) increases E and $\Delta S^{\neq}$ (Tables 1 and 2) compared with the reaction in media with a low H_2SO_4 concentration [reaction (1)]. When H_2SO_4 molecules participate in the limiting stage (dissociation of two metal–nitrogen bonds), the energy consumed for activation of the reacting system is not compensated for by metal cation solvation on the way to transition state. Such a compensation takes place during attack of a metal porphyrin by solvated protons [Eq. (3)] whose electron-donor solvent molecule has a higher affinity to the metal cation than H_2SO_4.

At H_2SO_4 concentration in AcOH of 3 and 4 M, the (Cl)MnTPP dissociation rate at 298 K is the same, while the H_0 values are different. As $c^0_{H_2SO_4}$ increases from 3 to 4 M, the activation energy increases by 25.4 kJ/mol, and the activation entropy, by 83 J mol^{-1} K^{-1}. The sharp change in E and $\Delta S^{\neq}$ points to decreased role of solvation of the transition state of reaction (4), which, in its turn, provides evidence for the conclusion that the solvated protons $AcOH_2^+$ are involved in the reaction at low H_2SO_4 concentrations.

A fair linear correlation between $\log k^{298}_{app}$ and H_0 was found for (AcO)CrTPP, $(Cl)_2$ZrTPP, and $(Cl)_2$HfTPP and for the indium complex of tetraphenylchlorine (Cl)InTPC (Table 3). Their dissociation rates were determined previously [2, 5, 6, 16]. The complexes dissociate at a measurable rate in AcOH–H_2SO_4 mixtures at $c^0_{H_2SO_4}$ 1.5–4.0 M. The order of these dissociations with respect to the total acidity $h0_0$ is close to unity (Table 3).

Another group of complexes characterized by a similar linear correlation and by a second dissociation order with respect to h_0 comprises, along with the (Cl)MnTPP complex discussed above, (Cl)RhTPP

[17], (AcO)MnTPP [14], (AcO)MnTPP(X)$_4$ (X = *n*-Br, *n*-F, *n*-OMe) [18] and CuTPP [4]. As a rule, these complexes dissociate at higher concentrations of H_2SO_4 compared to the complexes whose dissociation order with respect to h_0 is close to unity (Table 3). An exception is CuTPP whose dissociation order with respect to h_0 (2.33) relates to low-acidity media ($c^0_{H_2SO_4}$ 0.5–2.0 M). At the same time, the linear k^{298}_{app}–$f(c^0_{H_2SO_4})$ correlation typical of other complexes in such media [11, 12], is not observed with CuTPP. The increased dissociation order in the latter case is probably explained by the fact that in CuTPP there is free access of reagents from both sides of the macroring plane. All the other complexes under consideration have an axial acido ligand in the coordination sphere, which creates steric hindrance for attacking M–N bonds.

The above regularities allow us to recognize the ranges of H_2SO_4 concentrations in the AcOH–H_2SO_4 binary solvent, where different metal porphyrins have common rate equations including the concentration of solvated protons or the total acidity in the degrees of 1 or 2. These ranges are: 0.15–2 M, proton donor species $AcOH_2^+$, reaction order in $AcOH_2^+$ concentration ~2; 2–4 M, all the proton species, order in h_0 ~1; and 4–8 M, all proton species, order in h_0 ~2.

As seen, as the H_2SO_4 concentration increases, the $AcOH_2^+$ cation which is the most active in the solvoprotolytic dissociation and is the only reagent at low $c^0_{H_2SO_4}$ concentrations is replaced by other species, H_2SO_4 molecules inclusive. In media with sufficiently high H_2SO_4 concentrations, two parallel dissociation reactions seem to occur, involving $AcOH_2^+$ and H_2SO_4. Then the experimental order in total acidity h_0 depends on the relative rates of these reactions. When the rates of the two reactions become commensurate, the order in h_0 becomes close to two. The first order in proton donor in each of these reactions is accounted for by screening of the coordination center of the metal porphyrins in question (except for CuTPP) by the acido ligand on one side of the macroring plane.

In conclusion we note that partial kinetic equations for the limiting stage of dissociation of metal porphyrins at various compositions of the AcOH–H_2SO_4 solvent can be obtained only when the equilibrium compositions of species over a wide range of solvent compositions will become available, as is the case with concentrated aqueous H_2SO_4.

Table 3. Concentration range of H_2SO_4 in the AcOH–H_2SO_4 binary solvent for dissociation of metal porphyrins and numerical values of coefficients in the equation $\log k^{298}_{app} = nH_0 - \log k^{298}$

Complex	$c^0_{H_2SO_4}$, M	Coefficients	
		n	$-\log k^{298}$
(AcO)CrTPP	1.43–2.86	0.89	7.7
(Cl)$_2$ZrTPP	2.0–4.0	1.10	8.7
(Cl)$_2$HfTPP	2.0–4.0	1.29	10.3
(Cl)InTPC	2.0–3.0	0.69	6.2
(Cl)RhTPP	3.0–5.0	1.66	11.1
(AcO)MnTPP	3.0–5.0	1.76	13.8
(AcO)MnTPP(OMe-*p*)$_4$	4.3–5.4	1.94	13.7
(AcO)MnTPP(F-*p*)$_4$	4.3–6.3	1.97	14.9
(AcO)MnTPP(Br-*p*)$_4$	5.4–7.0	2.11	16.5
CuTPP	0.5–2.0	2.33	11.5

EXPERIMENTAL

Octaethylporphyrin H_2OEP (provided by A.S. Semeikin) and tetraphenylporphyrin H_2TPP were synthesized by the procedures [19, 20]. The complexes were obtained by reacting $Cu(AcOH)_2 \cdot H_2O$ (analytical grade) with H_2OEP and $MnCl_2 \cdot 4H_2O$ (analytical grade) with H_2TPP in boiling DMF for 10–15 min. CuOEP was isolated by precipitation on dilution of the reaction mixture with water. (Cl)MnTPP was extracted with chloroform from the reaction mixture diluted with equal volume of H_2O and repeatedly washed with water to remove excess salt and the solvent. Spectrally pure complexes were obtained by double chromatography on a column of Al_2O_3 (eluent chloroform). Electronic absorption spectrum ($CHCl_3$), λ_{max}, nm (log ε): CuOEP: 563 (4.54), 528 (4.26), 400 (5.88); and (Cl)MnTPP: 616 (3.03), 582 (4.00), 478 (4.98).

Acetic acid solutions of H_2SO_4 of specified concentration were prepared by the gravimetric procedure from 100% AcOH and sulfuric acid monohydrate. 100% AcOH was obtained from glacial acetic acid (chemically pure grade) by stepwise defrosting, sulfuric acid monohydrate was obtained from 60% oleum and H_2SO_4 (chemically pure grade) by the conductometric procedure.

The dissociation rates were determined spectrophotometrically [3]. The electronic absorption spectra were recorded on Hitachi-2000 and SF-26 spectrophotometers. The apparent rate constants (k_{app}) were refined by the least-squares method. The k^{298}_{app} values for CuOEP were determined by extrapolation of the $\log k$–$1/T$ plot to the standard temperature. The activation energies E_a were determined by least-squares fit of the $\log k$–$1/T$ plot. The activaton entropies $\Delta S^{\neq}$ were calculated by the basic equation of the transition state theory, transformed to form (6).

$$\Delta S^{\neq} = 19.1\log k^T + E_a/T - 19.1\log T - 205. \quad (6)$$

Here k^T is the true dissociation rate constant at temperature T.

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