STABILITY OF TETRA(TETRAMETHYLENE)TETRAAZAPORPHINE IN SULFURIC ACID SOLUTIONS

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In sulfuric acid solutions tetra(tetramethylene)tetraazaporphine undergoes hydrolytic destruction. The reaction is first order in the porphyrin concentration and second order in the hydronium ion concentration.

Porphyrins and their metal complexes are highly effective catalysts for many chemical reactions. These reactions are often carried out in acidic media, and a study of the behavior of porphyrins under these conditions and the elucidation of the factors that stabilize them are therefore of great practical value.

The behavior of unsubstituted tetraazaporphine in sulfuric acid solutions has been previously investigated [1-3]. The aim of the present research was to study the effect of tetramethylene substituents in the pyrrole rings of tetraazaporphine on the state and stability of the macroring (C_8N_8) of porphyrazine in acidic media.

Substitution changes the acid-base properties of tetraazaporphine substantially. Unsubstituted tetraazaporphine in CH_3COOH–H_2SO_4 has five forms, and four of them are spectrally distinguishable [1]. Tetra(tetramethylene)tetraazaporphine (H_2TTMTAP) has six acid-solvated forms (Table 1), of which the neutral (I) and acidic (II) symmetrical solvates are spectrally indistinguishable (Fig. 1). According to the assumption in [1], form III is an associate of the $H_2TTMTAP(HX)_{n-1}...H^+...X^-$ form ($HX = H_2SO_4$). Its electronic spectrum is similar to the spectra of forms I and II but is shifted to the long-wave region. An increase in the basicity and polarizability of the C_8N_8 chromophore as a consequence of substitution is reflected in the large bathochromic shift of the first absorption band of form

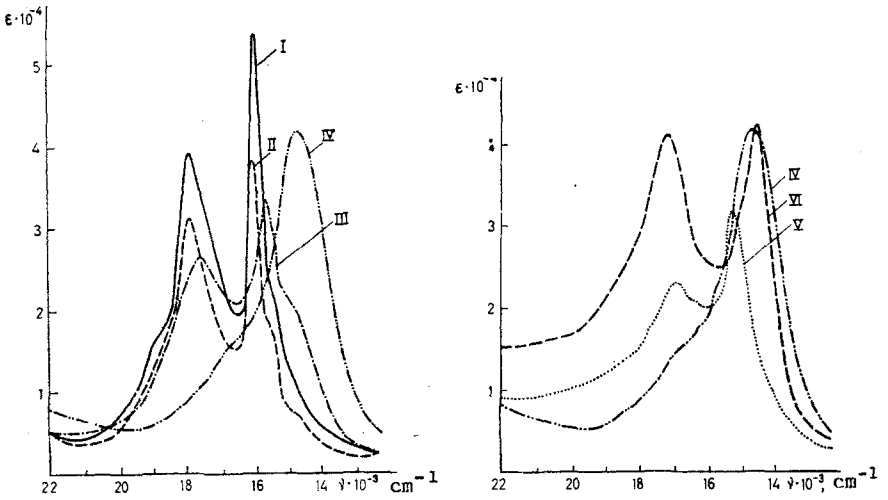

Fig. 1. UV spectra of the acid-solvated forms of tetra(tetramethylene)tetraazaporphine: I) in pyridine; II) in 100% CH_3COOH; III), IV), and V) in a solution of CH_3COOH in H_2SO_4 ($H_0 = 0.90$ for III, $H_0 = -1.07$ for IV, and $H_0 = -8.10$ for V); VI) in 100% H_2SO_4.

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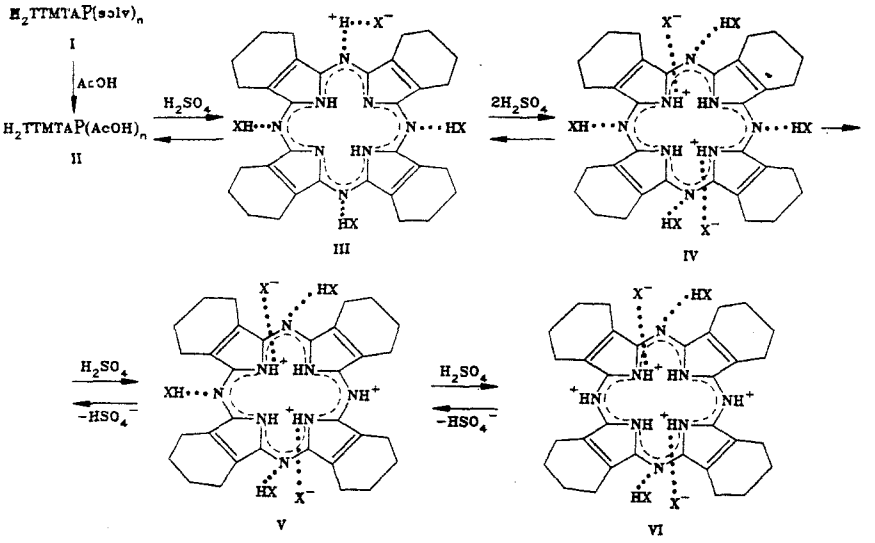
TABLE 1. Characteristics of the Acid-Solvated Forms of Tetraazaporphyrins

Compound	Forms*					
	I	II	III	IV	V	VI
Tetraazaporphine [1]	613	613	625 (0,15±0,03)	571 (−4÷−5)	643 (−7)	
Tetra(tetramethylene)tetraazaporphine	625	624	642 (1,81±0,05)	685 (0,80±0,02)	667 (−7,21± ±0,02)	691 (−9.32± ±0,04)

*The conditions of the existence of the forms are given in the caption to Fig. 1. The position of the first absorption band λ_{max} in nanometers is presented (the pK_a value is given in parentheses).



III: 18 nm for H_2TTMTAP as against 12 nm in the case of tetraazaporphine. The increase in pK_{III} also attests to greated basicity.

Form IV, which exists over a very wide range of acidities from 0.01% to 60% H_2SO_4 in CH_3COOH (up to $H_0 = -7$), develops with a further slight increase in the acidity ($H_0 \leq 1$). In the spectrum the lone broad band in the long-wave region corresponds to it. Just as in the case of tetraazaporphine, form IV is a symmetrical product that develops on reaction of the acid with the central tertiary nitrogen atoms:

A similar form was detected in a solution of H_2TTMTAP in dimethyl phthalate acidified with HCl [4]. The high symmetry (D_{4h}) of this form was demonstrated by polarization measurements, and it was assumed that acid-base interaction occurs at the endocyclic nitrogen atoms [4]. In contrast to the analogous form in the case of tetraazaporphine, the bathochromic shift of the absorption maximum for form IV is probably a manifestation of the specific effect of the electron-donor tetramethylene substituents, the favorable geometrical orientation of which makes possible their hyperconjugation with the pyrrole rings of the macrocycle. This can also explain the high stability of form IV as compared with the analogous form of tetraazaporphine.

A further increase in the H_2SO_4 concentration to 85% shifts the equilibrium to favor form V. Its spectrum is similar to the spectrum of form III but is shifted to the long-wave region. Form V has lower symmetry than form IV and is probably a double H-associate (at the endocyclic nitrogen atoms) of the singly protonated molecule. Protonation of an exocyclic nitrogen atom again occurs at this stage; in contrast to the conditions for the existence of form III, the medium in this case already has sufficient ionizing strength, and interaction with an exocyclic nitrogen atom does not stop with a step involving the formation of an H-associate or an ion-ion associate but probably proceeds up to complete ioniza-

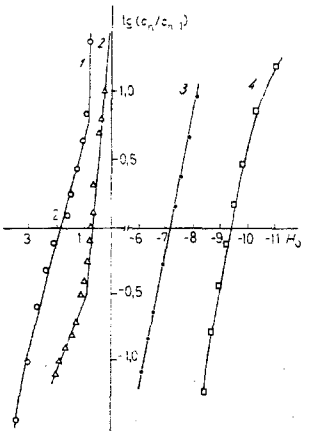


Fig. 2

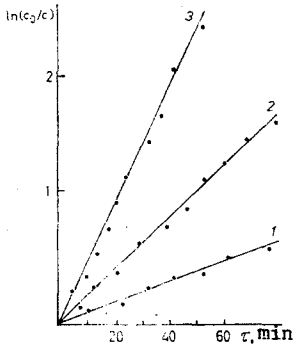


Fig. 3

Fig. 2. Dependence of log (c_n/c_{n-1}) on H_0 for the equilibria between the various forms of tetra-(tetramethylene)tetraazaporphine in H_2SO_4–CH_3COOH: 1) II ⇄ III; 2) III ⇄ IV; 3) IV ⇄ V; 4) V ⇄ VI.

Fig. 3. Dependence of ln (c_0/c) on the time for the hydrolytic cleavage of the H_2TTMTAP macrocycle in 99.13% H_2SO_4: 1) 298 K); 2) 308 K; 3) 318 K.

tion with the formation of a strong $\overset{+}{N}$–H bond. This interaction also leads to a bathochromic shift, but the λ_{max} value of the long-wave band is 18 nm smaller than in the case of form IV.

New acidic form VI with maximum polarization of the chromophore develops in a strongly proton-donor and ionizing medium (90-100% H_2SO_4 in CH_3COOH, chlorosulfonic acid). Its spectrum contains two bands (λ_{max} 691 and 583 nm) of identical intensity. The character of the spectrum makes it possible to ascribe this form to a doubly protonated particle. Double protonation at exocyclic nitrogen atoms weakens somewhat the interaction of H_2SO_4 with two central nitrogen atoms. The possibility of the existence of this particle requires, however, futher theoretical substantiation.

Titration curves (Fig. 2) were constructed for each of the indicated spectrally distinguishable forms, the pK_n values were determined, and the number of acidic particles that participate in each of the equilibria was also determined from the slope of the titration curve. The schemes presented above were written in conformity with this.

In 98-100% sulfuric acid H_2TTMTAP, which exists in form VI, undergoes cleavage with time. The reaction rate increases with a decrease in the sulfuric acid concentration, i.e., with an increase in the H_3O^+ ion concentration. Thus the cleavage of H_2TTMTAP is hydrolytic, just as in the case of phthalocyanine [5] and unsubstituted tetraazaporphine [2]. This reaction is first order in the porphyrin concentration, as evidenced by the rectilinear dependence of ln (c_0/c) on the time (Fig. 3). The effect rate constant (k_{eff}) of the reaction was calculated from the change in the optical density of the starting solution when λ = 688 nm from the equation

$$k_{eff}=\frac{1}{\tau}\ln\frac{c_0}{c}=\frac{1}{\tau}\ln\frac{A_0-A_\infty}{A_\tau-A_\infty},$$

where c_0 and c are the initial and instantaneous concentrations of form VI, and A_0, A_τ, and A_∞ are the initial, instantaneous, and final optical densities.

The reaction order in the H_3O^+ ion, which was determined as the slope of the dependence of log (k_{eff}) on log $(c_{H_3O^+})$, was two. The H_3O^+ concentrations were taken from [6]. Second order in hydronium ion concentration was also previously found for tetraazaporphine [2].

The energy of activation (E_a) of the reaction was calculated from the Arrhenius equation, which, in integral form, is

TABLE 2. Kinetic Parameters of the Hydrolytic Cleavage of Tetra(tetramethylene)tetraazaporphine in Sulfuric Acid

$c_{H_2SO_4}$, mass %	$c_{H_3O^+}$, moles/liter	T, K	$k_{eff} \cdot 10^5$, sec^{-1}	$k_V \cdot 10^{-5}$, $sec^{-1} \cdot mole^{-2} \cdot liter^2$	E_a, kJ/mole	$\Delta S^{\neq}$, J/(mole·deg)
99,66	0,346	298	1,59±0,07	13,28±0,65	81±1	−72±2
		308	4,67±0,10	39,01±0,80		
		318	12,53±0,23	104,66±2,00		
99,50	0,508	298	4,62±0,11	17,90±0,43	79±2	−70±2
		308	13,33±0,14	51,65±0,50		
		318	34,43±0,32	133,40±1.20		
99,35	0,661	298	7,32±0.13	16,78±0,30	72±5	−90±8
		308	20,22±0,21	46,28±0,50		
		318	45,78±0,30	104,70±0,70		
99,13	0,884	298	12.97±0,24	16,58±0,30	64±3	−96±4
		308	33,16±0,31	42,32±0,40		
		318	74,75±0,45	96,52±0,60		
98,76	1,220	298	21,00±0,27	14,11±0.18	66±2	−100±3
		308	49,16±0,36	33,16±0,30		
		318	113,37±0,68	77,90±0,46		

$$E_a = 8.314 \frac{T_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1},$$

where k_1 and k_2 are the reaction rate constants at temperatures T_1 and T_2.

The entropies of activation were calculated from the equation

$$\Delta S^{\neq} = 8.314 \ln k_{298} + E_a/298 - 253.22.$$

The kinetic parameters of the cleavage fo the H_2TTMTAP macrocycle in form VI are presented in Table 2. The kinetic equation of the hydrolytic cleavage ot form VI in sulfuric acid has the form

$$-\frac{dc_{VI}}{d\tau} = k_v \cdot c_{VI} c^2_{H_3O^+},$$

where k_V is the virtual rate constant of the reaction.

The average value of k_V at 298 K is $1.57 \cdot 10^{-4}$ $sec^{-1} \cdot mole^{-2} \cdot liter^2$, i.e., tetra(tetramethylene)tetraazaporphine in H_2SO_4 solutions is 17 times more stable than tetraazaporphine ($k_V^{298} = 2.69 \cdot 10^{-3}$ $sec^{-1} \cdot mole^{-2} \cdot liter^2$). Attack by the H_3O^+ cation on the reaction center of particle VI is probably hindered as a consequence of the presence on it of a higher positive charge (as compared with the monoprotonated form of tetraazaporphine). The energy parameters of the cleavage of the H_2TTMTAP macrocycle are very close to the parameters of the cleavage of tetraazaporphine. A decrease in the energy and entropy of activation is observed with a decrease in the sulfuric acid concentration; this is probably due to an increase in the solvation of the transition state as the H_2SO_4 is diluted with water.

The kinetic stabilities of tetraazaporphine, phthalocyanine, and tetrapyridineporphyrazine were previously studied, and mechanisms of their hydrolytic cleavage were proposed [7]. The reaction order in the H_3O^+ concentration is four for phthalocyanine, as compared with three for tetrapyridineporphyrazine. The lower reaction order in the H_3O^+ concentration for tetraazaporphyrins is in agreement with their lower stability and the greater ease of opening of the macrocycle. The following scheme of the hydrolytic cleavage of H_2TTMTAP in the VI form in aqueous sulfuric acid can be proposed:

$$VI + H_3O^+ \rightleftharpoons VI \cdot H_3O^+$$
$$VI \cdot H_3O^+ + H_3O^+ \rightarrow [VI(H_3O^+)_2]^{\neq} \rightarrow \text{Cleavage of the macrocycle}$$

The first step proceeds as reversible solvation of the macrocycle by means of H_3O^+.

EXPERIMENTAL

The electronic absorption spectra were recorded with a Specord UV-vis spectrophotometer.

Tetra(tetramethylene)tetraazaporphine was synthesized by the method in [8]. It was identified and its degree of purity was determined from the electronic absorption spectra and the results of elementary analysis. UV spectrum (in chlorobenzene), λ_{max} (log ε): 343 (4.84), 560 (4.64), 598 (3.95), 628 nm (4.80) (according to the data in [8]: 342.5 (4.84), 560 (4.63), 600 (3.99), 628 nm (4.79)). Found: C 72.4; H 6.7; N 21.0%. $C_{32}H_{34}N_8$. Calculated: C 73.4; H 6.5; N 21.1%.

The 100% sulfuric acid was prepared from chemically pure-grade 60% oleum and chemically pure-grade concentrated H_2SO_4 with conductometric monitoring of the concentration. Aqueous sulfuric acid was prepared from 100% sulfuric acid gravimetrically. Monitoring was accomplished by titration.

The glacial acetic acid was frozen repeatedly and refluxed with the calculated amount of acetic anhydride, after which it was fractionated.

The values of the H_0 function for the solutions with various compositions were taken from [9, 10]. The investigations over the range of H_0 values from +4 to −13.8 were carried out at 298 K. The constants of the acid-base interaction were calculated from the Hammett equation:

$$pK_n = H_0 + \lg(c_n/c_{n-1}).$$

The stability of tetra(tetramethylene)tetraazaporphine was investigated in 98.76-99.66% sulfuric acid at 298-318 K. The initial porphyrin concentration in all of the experiments was $1 \cdot 10^{-5}$ M. The solution was placed in the thermostatted cuvette of the spectrophotometer at the experimental temperature, and the optical density of the solution at λ = 688 nm was measured at definite time intervals.

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