4. G. V. Ponomarev, Khim. Geterotsikl. Soedin., No. 7, 943 (1980).
5. G. V. Ponomarev, V. P. Suboch, and A. N. Lyashko, Khim. Geterotsikl. Soedin., No. 6, 773 (1978).

KINETIC STABILITY OF TETRAZAPORPHIN IN BINARY H_2SO_4–AcOH AND H_2SO_4–DMSO SOLUTIONS

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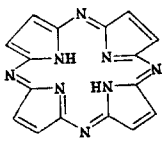
The state and kinetic stability of tetrazaporphin (I) in acetic acid and in dimethyl sulfoxide (DMSO) in the presence of H_2SO_4 were investigated. Partial protonation of I to give I-$AcOH_2^+$ associates occurs in acetic acid. The kinetic parameters of the reaction involving the destruction of tetrazaporphin in the presence of H_2SO_4 in acetic acid and DMSO solutions were determined. The mechanism of the destruction is discussed.

Tetrazaporphin (I) is a structural analog of both porphin itself and phthalocyanine. The aim of the present research was to establish the effect of tetrasubstitution in porphyrins on their stability in proton-donor media.

I



In a preceding communication [1] the state and kinetic stability of tetrazaporphin in sulfuric acid were investigated. In the present research, the kinetics of the destruction of tetrazaporphin under the influence of H_2SO_4 in acetic acid and DMSO solutions, i.e., in solvents that are widely used in the chemistry of porphyrins, were investigated.

In contrast to many porphyrins, in glacial acetic acid tetrazaporphin is not protonated and does not undergo destruction, as does phthalocyanine [2]. The electronic absorption spectrum of I in AcOH does not differ from its absorption spectrum in other organic solvents.

As in the case of phthalocyanine [2], a shift of the spectrum to the long-wave region with a simultaneous decrease in the intensity of the absorption bands of I and II is observed when anhydrous acid is added to a solution of I in glacial acetic acid (in the spectra of porphyrins we have adopted numbering of the absorption bands commencing with the long-wave band). An increase in the bathochromic shift (Table 1); the absorption bands of I and II have a maximum shift at ~15 nm in this case. The shift may be a consequence of partial protonation without complete ionization to give an associate of the I•••H_2SO_4 or I•••$AcOH_2^+$ type, since in a medium with a low dielectric constant the interaction of porphyrin with a strong acid may stop at the stage involving the formation of a hydrogen bond [2].

The shift of the first band in the electronic absorption spectrum is bathochromic, and therefore one should expect protonation at the meso nitrogen atoms of tetrazaporphin.

At H_2SO_4 concentrations on the order of 4 M, virtually no further bathochromic shift of the spectrum is observed. At this concentration of H_2SO_4, tetrazaporphin begins to undergo appreciable destruction. The destruction is accompanied by a change in the color from blue violet to light yellow; in the process one observes a disappearance of the absorption bands of I and II (Fig. 1).

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TABLE 1. Positions of the First Absorption Band of a Solution of Tetrazaporphin in AcOH as a Function of the H_2SO_4 Concentration

$C_{H_2SO_4}$, M	0	0.0013	0,49	0,97	2,9	3,9	4,9
λ_{max}^I, nm	614	617	625	627	628	628	629

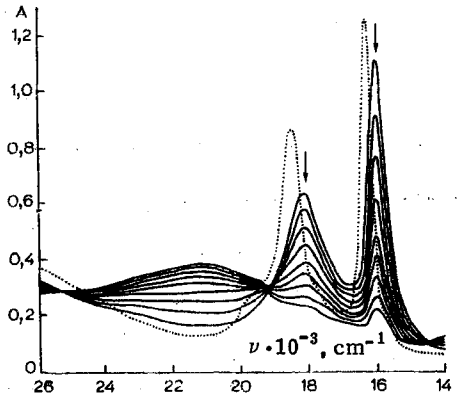

Fig. 1

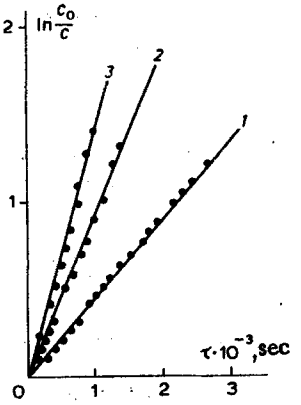

Fig. 2

Fig. 1. Change in the electronic absorption spectrum of tetrazaporphin in AcOH solution in the presence of 0.97 M H_2SO_4 at 25°C: the dots indicate tetrazaporphin in 100% acetic acid.

Fig. 2. Dependence of $\ln C_0/C$ on τ during the destruction of tetrazaporphin in AcOH in the presence of 0.97 M H_2SO_4: 1) 15°; 2) 25°; 3) 35°.

TABLE 2. Kinetic Parameters of the Destruction of the Tetrazaporphin Macroring in AcOH in the Presence of H_2SO_4

$C_{H_2SO_4}$, moles/liter	T, K	$K_{eff} \cdot 10^4$, sec^{-1}	K_V, sec^{-1} · liter · mole^{-1}	E_a, kJ/mole	$\Delta S^{\neq}$, J/(mole · deg)
0,487	288	2,67±0,05	0,00237	29±1	−219±10
	298	4,03±0,19			
	308	5,94±0,15			
0,975	288	4,51±0,07	0,00225	43±2	−167±7
	298	8,21±0,23			
	308	14,56±0,66			
1,46	288	6,69±0,13	0,00207	38±1	−180±4
	298	12,29±0,26			
	308	18,89±0,18			
1,95	288	11,73±0,30	0,00169	33±1	−192±7
	298	18,33±0,29			
	308	29,29±1,11			
2,92	288	27,13±0,24	0,00156	30±2	−195±10
	298	41,87±2,27			
	308	62,51±1,57			

The kinetic stability of tetrazaporphin in glacial acetic acid at various concentrations of 100% sulfuric acid was studied over the temperature range 15-35°C (Table 2).

The experimental data in coordinates of $\ln C_0/C$ vs. τ have a rectilinear dependence (Fig. 2), which indicates first order in the reaction with respect to I:

$$\frac{dC_1}{d\tau} = K_{eff} \cdot C_1 \qquad (1)$$

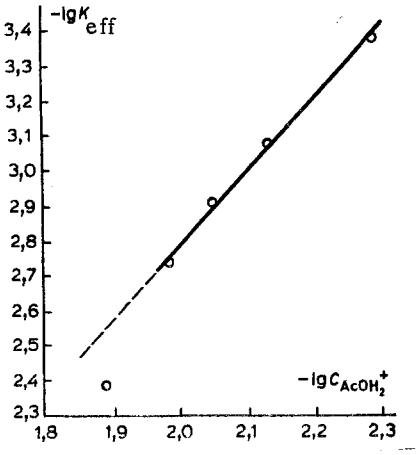

Fig. 3

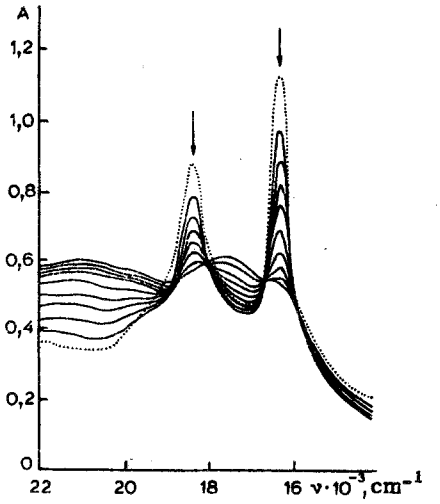

Fig. 4

Fig. 3. Dependence of log K_{eff} of the destruction of tetrazaporphin in H_2SO_4–AcOH solution on log $C_{AcOH_2^+}$.

Fig. 4. Change in the electronic absorption spectrum of tetrazaporphin in DMSO solution in the presence of 2 M H_2SO_4 at 50°C: the dots pertain to the spectrum of tetrazaporphin in DMSO.

TABLE 3. Kinetic Parameters of the Destruction of the Macroring of Tetrazaporphin in DMSO in the Presence of H_2SO_4

$C_{H_2SO_4}$, moles/liter	T, °K	$K_{eff} \cdot 10^4$, sec^{-1}	E_a, kJ/mole	$\Delta S^{\neq}$, J/(mole·deg)
1,96	298*	0,14	88±1	−48±4
	313	0,79±0,03		
	323	2,23±0,03		
	333	6,17±0,29		
2,45	298*	0,22	89±2	−42±4
	313	1,16±0,05		
	323	3,26±0,16		
	333	9,12±0,74		
2,95	298*	0,52	75±3	−83±4
	313	2,22±0,12		
	323	5,82±0,27		
	333	12,59±0,98		
3,44	298*	2,41	59±5	−121±10
	313	7,67±0,26		
	323	14,05±0,73		
	333	30,45±2,23		

*Calculated from the Arrhenius equation.

Destruction of phthalocyanine and tetrabenzoporphin proceeds similarly [2, 3].

The destruction of the ligands of phthalocyanine and porphyrins in aqueous sulfuric acid occurs under the influence of H_3O^+ [2-4]. Acetic acid molecules act as a base in an H_2SO_4–AcOH medium:

$$H_2SO_4 + AcOH \rightleftarrows AcOH_2^+ + HSO_4^- \quad (2)$$

Thus the protonation and rate-determining step in the cleavage of the macroring proceeds in this case under the influence of $AcOH_2^+$.

The $AcOH_2^+$ concentration in experiments in the case of all types of additions of H_2SO_4 are evaluated from the equation:

$$K = \frac{[AcOH_2^+][HSO_4^-]}{[H_2SO_4][AcOH]} \quad (3)$$

The pK value is 4.25 [5].

In order to determine the reaction order with respect to the $AcOH_2^+$ concentration, we constructed the dependence of $\log K_{eff}^{25}$ on $\log [AcOH_2^+]$ (Fig. 3). The dependence has rectilinear character with a certain deviation in the region of the 2.9 M concentration, which is associated with an increase in the ionic association in acetic acid, i.e., with a substantial change in the activity coefficients of the ions, which were not taken into account in the calculation of the $AcOH_2^+$ concentrations.

The reaction order with respect to the $AcOH_2^+$ concentration, determined as the slope of the rectilinear part of the curve is two, i.e., the same value that is observed in the destruction of tetrazaporphin in sulfuric acid [1]. Thus, the mechanism of the cleavage of the macroring of tetrazaporphin differs from that proposed for phthalocyanine and azaphthalocyanine in the rate-determining and subsequent steps, since in the case of the latter the reaction orders with respect to the solvated proton are four and three, respectively [2, 4].

The process involving the destruction of I in glacial acetic acid containing added H_2SO_4 proceeds with low energy and entropy of activation; this is probably explained by the strong solvation of the transition state and the kinetic compensation effect, which is often observed in reactions in which porphyrins participate [2].

We also investigated the state and stability of tetrazaporphin in dimethyl sulfoxide (DMSO) in the presence of sulfuric acid. The electronic absorption spectrum of tetrazaporphin in a solution of H_2SO_4 in DMSO does not differ from its spectrum in DMSO either with respect to form or the position of the bands. One only observes a decrease in the intensities of the absorption bands of I and II as the amount of H_2SO_4 is increased.

In DMSO solution H_2SO_4 dissociates virtually irreversibly:

$$(CH_3)_2SO + H_2SO_4 \rightarrow (CH_3)_2SOH^+ + HSO_4^- \qquad (4)$$

and the proton carrier is primarily $(CH_3)_2SOH^+$. The insufficiently pronounced proton-donor properties of protonated DMSO result in the fact that I is not protonated, and, we assume, $I \times n[(CH_3)_2SOH^+]_n$ associates with symmetrical specific solvation of the shell are formed.

The change in the absorption spectrum of I in 2 M H_2SO_4 in DMSO with time at 50°C due to destruction of the chromophore of the macroring is shown in Fig. 4.

We also determined the kinetic parameters of the destruction of I in 1.96-3.44 M H_2SO_4 in DMSO at 40-60°C (Table 3).

As in the preceding case, the destruction reaction is first order in the I concentration. The dependence of K_{eff} on the H_2SO_4 concentration has complex character. As the amount of H_2SO_4 introduced is increased, the reaction rate increases sharply, and the energy and entropy of activation decrease simultaneously. In all cases the destruction of I with cleavage of the macroring proceeds very readily (at rather high rates) with a low energy of activation and a very low $\Delta S^{\neq}$ value. The low energy of activation is due to the active participation of the solvent in the formation of the transition state. The very low $\Delta S^{\neq}$ values are also associated with this.

It follows from the kinetic data obtained that the stability of the tetrazaporphin macroring in H_2SO_4 is significantly lower than the stability of the phthalocyanine macroring as a consequence of the greater aromatic character of the latter.

EXPERIMENTAL

Tetrazaporphin was obtained and purified by the method in [6]. The identification and determination of its purity were carried out from the electronic absorption spectra [6]. The chemically pure glacial acetic acid (AcOH) was subjected to repeated freezing and refluxing with the calculated amount of acetic anhydride, after which it was subjected to fractional distillation. The chemically pure-grade dimethyl sulfoxide (DMSO) was purified by distillation *in vacuo* in a stream of pure dry nitrogen [7]. The 100% sulfuric acid was prepared from 60% chemically pure-grade oleum and chemically pure-grade sulfuric acid with conductometric monitoring of the amount of water. The absence of water in the solvents was monitored by titration by the Fischer method [8]. In order to carry out the kinetic measurements, a solution of tetrazaporphin was placed in a thermostatted cuvette of an SF-5 spectrophotometer. The variation in the temperature was no more than ±0.1°C. At definite time intervals we measured

the optical densities at λ 613 nm in H_2SO_4—DMSO solutions and at λ 629 nm in H_2SO_4—AcOH solutions. The initial concentration of I was $1 \cdot 10^{-5}$ M.

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

LITERATURE CITED

1. O. G. Khelevins, P. A. Stuzhin, S. V. Svinova, and B. D. Berezin, Zh. Fiz. Khim., 58 (1984).
2. B. D. Berezin, Coordination Compounds of Porphyrins and Phthalocyanine [in Russian], Nauka, Moscow (1978).
3. B. D. Berezin, T. I. Potapova, E. B. Karavaeva, Z. A. Yakovleva, and T. V. Marinina, 29, 865 (1978).
4. A. S. Akopov, V. V. Bykova, and B. D. Berezin, Zh. Org. Khim., 17, 1027 (1981).
5. Yu. Ya. Fialkov and Yu. Ya. Borovikov, Ukr. Khim. Zh., 30, 119 (1964).
6. R. P. Linstead and M. J. Whalley, J. Chem. Soc., 4839 (1952).
7. Organicum (translated from German) Vol. 2, Mir, Moscow (1979), p. 360.
8. G. Charlot, Methods in Analytical Chemistry [Russian translation], Part 2, Khimiya, Moscow (1969), p. 829.

SYNTHESIS AND PROPERTIES OF 1,2,2,6,6-PENTAMETHYL-3,5-DIMETHYLENE-4-PIPERIDONE

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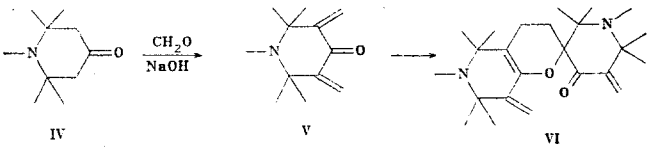
1,2,2,6,6-Pentamethyl-3,5-dimethylene-4-piperidone was synthesized, whereas analogous compounds in the 4-piperidone series could not be isolated. An unusual reaction of the compound obtained with primary aliphatic amines, consisting of successive addition of the amine at the C=C bonds, with a possible formation of an intermediate bicyclic adduct and further elimination of methylamine, was detected.

The reaction of 4-piperidones with formaldehyde has been described in cases of 1,2,5-trimethyl-4-piperidone (I) (the 3-hydroxymethyl derivative was produced) [1], 2,2,6,6-tetramethyl-4-piperidone and its N-oxide (a product of diene synthesis is immediately formed from the unstable bis-adduct by crotonic condensation) [2, 3].

We studied the interaction of 4-piperidones with formaldehyde under conditions of strongly alkaline catalysis (1 N NaOH solution) on the examples of 1-methyl-4-piperidone (II), tropinone (III), and 1,2,2,6,6-pentamethyl-4-piperidone (IV). It was found that only the piperidone IV gives a stable crotonic condensation product V. The corresponding product of diene synthesis VI is formed at an appreciable rate from the unsaturated ketone V only at temperatures above 110-120°C.



IV V VI

The piperidones I-III form polymer reaction products; the condensation of the ketones I and II is accompanied by reduction of the carbonyl group to a hydroxyl by excess formaldehyde (the absence of the carbonyl absorption bands in the region of 1660-1740 cm^{-1} in the IR spectra of the reaction products; the absorption bands of C=C bonds in the region of 1620-

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