KINETICS OF THE BROMINATION OF TETRAAZAPORPHIN

O. G. Khelevina, N. V. Chizhova, and B. D. Berezin

The kinetics of the bromination of tetraazaporphin by bromine in glacial acetic acid were studied. It is suggested that bromination takes place through the formation of a molecular complex between porphyrin and bromine. Possible reaction schemes are proposed.

The kinetics and mechanism of bromination of a large number of aromatic compounds have been studied quite widely. There are no published data on the kinetics of the bromination of macrocyclic systems. We have investigated for the first time the effect of multicontour conjugation in aromatic polyamines on the kinetics of their bromination in the case of tetraazaporphin (I).

The bromination of compound (I) was realized with molecular bromine in glacial acetic acid. The reaction was monitored by electronic spectroscopy.

At room temperature with the bromine and porphyrin in a molar ratio of 1:1 the position and intensity of the absorption bands of compound (I) in acetic acid do not change (λ_{max} 613, 542 nm), but additional absorption bands appear at λ_{max} 771 and 692 nm. The obtained compound (II) was isolated from the reaction mixture. Its electronic spectrum in chloroform is shown in Fig. 1. After treatment of compound (II) with pyridine its ESR spectrum in chloroform corresponds to the spectrum of tetraazaporphin. We suppose that a molecular complex $I \cdot Br_2$ is formed when the bromine and porphyrin are in a ratio of 1:1 in acetic acid. Such complexes are well known for phthalocyanine with bromine and iodine [1,2]. When the complex (II) dissolves in pyridine it decomposes, since pyridine is a stronger n-donor than tetraazaporphin.

An acetic acid solution of porphyrin and bromine in a ratio of 1:1 was sealed into an ampul and left at room temperature for 14 days. The electronic spectrum of the solution became a two-band spectrum with λ_{max} 620, 559 nm. It is known [3] that the introduction of one bromine atom into the pyrrole ring of tetraphenylporphin leads to a bathochromic shift of the first absorption band by 6 nm. In our case, therefore, it can be supposed that the monobromo derivative of tetraazaporphin is formed.

In the electronic spectrum of the acetic acid solution of bromine and porphyrin in a ratio of 2:1 the charge-transfer bands typical of the molecular complex increase for 40 min. The acetic acid solution with the above-mentioned composition was kept at room temperature for 14 days. The electronic spectrum of the solution contained two bands at λ_{max} 626 and 564 nm. The even more bathochromic shift of the spectrum indicates substitution of more than one hydrogen atom in compound (I) by bromine.

Thus, the disappearance of the charge-transfer bands in the electronic spectrum of the acetic acid solutions of porphyrin and bromine (in ratios of 1:1 and 1:2), obtained after prolonged holding, may indicate that the bromination of tetraazaporphin under these conditions takes place through the formation of a molecular complex with subsequent migration of the bromine into the pyrrole ring.

In order to accelerate the bromination and to introduce the maximum possible number of bromine atoms into the molecule of compound (I) we increased the ratio of bromine to porphyrin to 10:1. In the electronic spectrum of the acetic acid solution at room temperature there was a decrease in the intensity of the absorption bands corresponding to the initial compound (I) and an increase in the absorption bands (λ_{max} 639 and 572 nm) that did not disappear after the addition of pyridine. The

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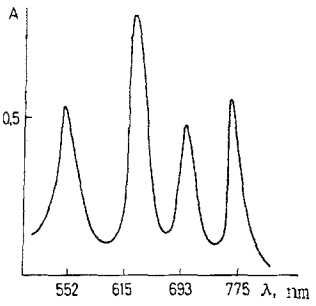


Fig. 1. The electronic spectrum of the molecular complex of (I) with bromine in chloroform.

TABLE 1. The Kinetic Parameters of the Bromination of Tetraazaporphin by Bromine in Glacial Acetic Acid ($C_{(I)}^0$ = $2.67 \cdot 10^{-5}$ M, E_{av} = 41 ± 5 kJ/mole, $\Delta S^{\neq}$ = −204 ± 17 J/mole·deg)

$C^0_{Br_2} \cdot 10^3$, M	T, K	$k_{eff} \cdot 10^5$, sec^{-1}	$k_v \cdot 10^3$, $sec^{-1} \cdot mole^{-1} \cdot liter^{-1}$
3,16	288	1,21 ± 0,07	3,83 ± 0,22
3,63	288	1,60 ± 0,09	4,41 ± 0,25
4,67	288	2,02 ± 0,11	4,32 ± 0,24
7,21	288	2,62 ± 0,12	3,63 ± 0,17
2,81	298	2,08 ± 0,11	7,40 ± 0,39
3,14	298	2,40 ± 0,14	7,64 ± 0,45
4,83	298	3,74 ± 0,18	7,74 ± 0,37
5,74	298	4,32 ± 0,18	7,54 ± 0,31
2,69	308	3,40 ± 0,15	12,60 ± 0,56
3,23	308	3,89 ± 0,25	12,04 ± 0,77
4,80	308	4,78 ± 0,21	9,96 ± 0,44

spectrum also contained charge-transfer bands typical of a molecular complex. The final reaction product [compound (III)] contains eight bromine atoms to one molecule of tetraazaporphin. After treatment of the obtained substance with pyridine the tetrabromotetraazaporphin (IV) separated. It is possible to assume that the molecular complex (IV)·$2Br_2$ is formed if a large excess of bromine is used.

The kinetics of the bromination of the compound (I) were studied with bromine and porphyrin in molar ratios of between 100:1 and 1000:1, i.e., under the conditions of a pseudofirst-order reaction.

The kinetic parameters of the bromination of tetraazaporphin to the monobromo derivative are given in Tables 1 and 2.

The bromination of compound (I) has first order in the porphyrin (Fig. 2). The kinetic equation of the reaction has the following form:

$$-\frac{dC\,(I)}{d\tau} = k_{eff} \cdot C_{(I)}. \tag{1}$$

$$k_{eff} = k_v \cdot C^n_{Br_2}. \tag{2}$$

where $k_{eff} = k_v \cdot C_{Br_2}^n$.

The order of the reaction with respect to bromine was determined graphically as the tangent of the slope for the log $k_{eff} = f(\log C_{Br_2})$ relationship (Fig. 3). It was found that it depends on the molar ratio of the reagents. With the bromine and

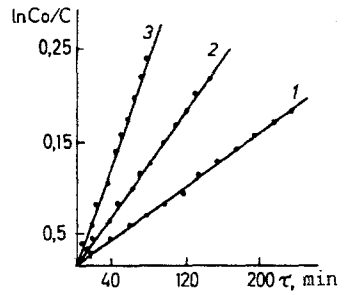
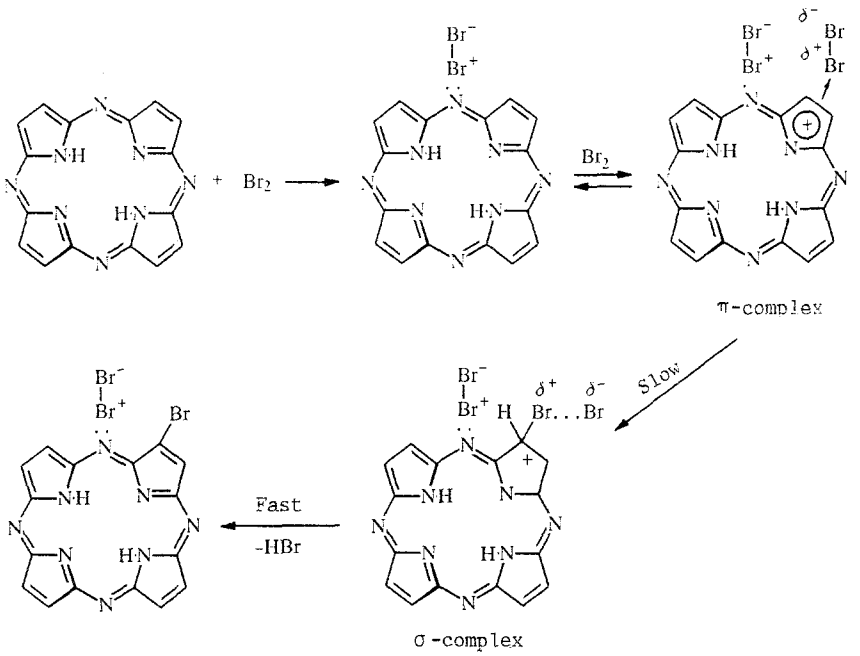


Fig. 2. The dependence of ln C_0/C on the duration of the bromination of compound (I) with bromine in acetic acid (C_{Br_2} = $0.32 \cdot 10^{-2}$ M). 1) 288 K; 2) 298 K; 3) 308 K.

porphyrin in ratios between 100:1 and 300:1 the order with respect to bromine is first, and the kinetic equation has the following form:

$$- \frac{dC\,(I)}{d\tau} = k_V \cdot C_{(I)} \cdot C_{Br_2}, \tag{3}$$

We propose the following reaction scheme:



With the bromine and porphyrin in ratios between ~350:1 and 1000:1 (Table 2) the order of the reaction in the bromine is 1.7, i.e., approximates to second. The reaction takes place according to the following equation:

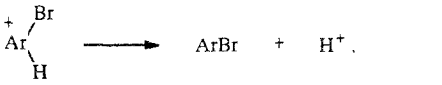
$$- \frac{dC\,(I)}{d\tau} = k_V \cdot C_{(I)} \cdot C^2_{Br_2}, \tag{4}$$

TABLE 2. The Kinetic Parameters for the Bromination of Tetraazaporphin with Bromine in Glacial Acetic Acid ($C_{(I)}^0$ = $1.78 \cdot 10^{-5}$ M, E_{av} = 49 ± kJ/mole, $\Delta S^{\neq}$ = −164 ± 17 J/mole·deg)

$C^0_{Br_2} \cdot 10^2$, M	T, K	$k_{eff} \cdot 10^4$, sec^{-1}	$k_\nu \cdot 10$, $sec^{-1} \cdot mole^{-2} \cdot liter^2$
1,41	288	0,63 ± 0,04	3,16 ± 0,20
1,87	288	0,89 ± 0,08	2,55 ± 0,23
2,12	288	1,20 ± 0,05	2,67 ± 0,11
2,45	288	1,66 ± 0,03	2,77 ± 0,05
1,34	298	1,19 ± 0,09	6,62 ± 0,50
1,41	298	1,22 ± 0,06	6,14 ± 0,30
1,85	298	2,02 ± 0,05	5,91 ± 0,15
3,27	298	4,82 ± 0,10	4,51 ± 0,10
0,62	308	0,50 ± 0,02	13,02 ± 0,52
1,41	308	2,40 ± 0,01	12,07 ± 0,05
1,56	308	2,95 ± 0,06	12,12 ± 0,25
2,01	308	3,97 ± 0,10	9,83 ± 0,24

which is also typical of the bromination of simple aromatic compounds in acetic acid [4]. In [4] the equation was interpreted by the following reaction mechanism:

(5)



(6)

The participation of a second molecule of bromine is due to the greatly increasing capacity of the higher halogens for self-combination with expansion of the electronic valence shell, particularly in the presence of a negative charge [4].

Investigations of the kinetics of the production of tetrabromotetraazaporphin showed that the formation rate of compound (IV) is approximately a quarter of the formation rate of the monobromo derivative of compound (I). (The k_ν^{298} values are 0.15 and 0.59 $sec^{-1} \cdot mole^{-2} \cdot liter^2$ respectively.) The formation of di- and tribromotetraazaporphin was not observed spectrally in the kinetic experiments.

The absence of published data on the kinetics of the bromination of porphyrins does not make it possible to establish the effect of aza substitution (—CH═ → —N═) on the kinetic parameters of bromination. There are published data on the kinetics of the bromination of pyrrole in an aqueous medium [5]. The rate constant of the bimolecular reaction was extremely high (10^8 liter·$mole^{-1} \cdot sec^{-1}$ at 298 K).

Thus, the reactivity of the pyrrole ring entering a multicontour multinitrogen conjugated π system is reduced by 8-10 orders of magnitude as a result of its deactivation by tetraaza substitution and loss of the autonomy of the π system of the pyrrole ring [6].

EXPERIMENTAL

The electronic absorption spectra were obtained on a Specord M-40 instrument. The IR spectra were obtained in potassium bromide on an IR-20 spectrophotometer. The PMR spectrum was obtained on a Bruker instrument at 25 MHz in a 2:1 mixture of deuterochloroform and trifluoroacetic acid with TMS as internal standard.

The elemental analyses of compounds (II, III, IV) for C, H, Br, and N corresponded to the calculated data. The bromine (analytical) was washed with water, kept with a saturated aqueous solution of potassium bromide for 3 days, distilled, separated from water, and mixed with concentrated sulfuric acid which had been previously heated with potassium bichromate

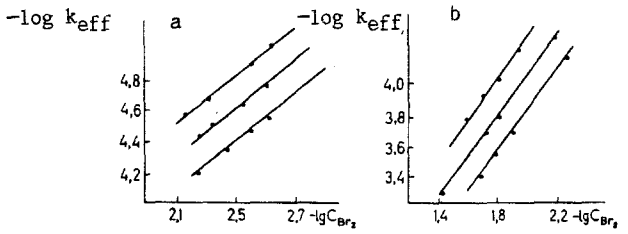


Fig. 3. The log k_{eff} = f(log C_{Br_2}) relationship for the bromination of compound (I) by bromine in acetic acid. a) C_{Br_2} = 0.002-0.006 M; b) C_{Br_2} = 0.01-0.04 M. 1) 288 K; 2) 298 K; 3) 308 K.

and potassium permanganate at 100°C for 2 h. It was then distilled, and the fraction boiling at 58°C was collected. The glacial acetic acid (of chemical purity) was submitted to repeated freezing out and boiling with the calculated amount of acetic anhydride. It was then submitted to fractional distillation, and the fraction boiling at 118°C was collected.

The tetraazaporphin (I) was obtained by the method in [7].

The Molecular Complex of (II) and I·Br_2. To a solution of 0.1 g of compound (I) in 20 ml of acetic acid we added 0.015 ml of bromine in 5 ml of acetic acid (molar ratio 1:1). The mixture was kept at 20-25°C for 40 min. It was then poured into a tenfold excess of water, and the precipitate was washed with water and ethanol and dried under vacuum. We obtained 0.083 g (55%) of compound (II). After the compound had been dissolved in pyridine, precipitated with water, and dried compound (I) was obtained.

2,7,12,17-Tetrabromotetraazaporphin (IV). To a solution of 0.1 g of magnesiotetraazaporphin in 20 ml of acetic acid, while stirring, we added a solution of 0.15 ml of bromine in 10 ml of acetic acid (molar ratio 1:10). The mixture was stirred at 20-25°C for 6 h. It was then poured into water, and the precipitate [compound (III)] was filtered off and washed with water and ethanol. Compound (III) was dissolved in pyridine and precipitated with water. The precipitate was filtered off, washed with water and ethanol, and dried under vacuum. The product was purified by column chromatography on silica gel with a 4:1 mixture of benzene and 2-propanol as eluant. The yield of compound (IV) was 75 mg (40%).

The IR spectrum of compound (IV) showed a change in the position or a redistribution in the intensities of the individual bands in comparison with unsubstituted porphyrin. The intensity of the deformation vibrations of the C—H and N—H bonds in the regions of 1280, 1235-1170, and 1004 cm^{-1} increased. The PMR spectrum of compound (IV) contained the following signals: 10.16 (β-pyrrole fragments) and 1.43 ppm (N—H protons).

Kinetics of the Bromination of Tetraazaporphin. The reaction was studied on an SF-26 spectrophotometer. Equal volumes of solutions of porphyrin and bromine in acetic acid were poured into an optical cuvette at the experimental temperature and placed in the thermostated chamber of the spectrophotometer. The temperature fluctuations were not greater than 0.1°C. During study of the kinetics of the formation of monobromotetraazaporphin the optical density of the solution at λ = 613 nm, corresponding to the first absorption band of compound (I), was measured at intervals of 1-20 min. The kinetics of the formation of tetrabromotetraazaporphin were studied at λ = 639 nm, corresponding to the first absorption band of compound (IV). The initial concentration of compound (I) was 10^{-5} M, and the concentration of bromine varied between 10^{-3} and 10^{-2} M. The kinetic measurements were made in the range of 15-35°C. Two parallel experiments were conducted for each temperature and concentration. The solutions of bromine in acetic acid were prepared just before each kinetic measurement. The bromine concentration was calculated from the difference between the weights of the bromine in acetic acid and of the pure acid. The bromine content of the acetic acid was monitored by titration of an aliquot portion of the solution with a standard solution of sodium thiosulfate. Control tests showed that the concentration of bromine in the solution did not change under the reaction conditions (in the absence of porphyrin).

The kinetic parameters were calculated on a B3-28 microcomputer. The error in the determination of the kinetic parameters was determined by Student's method. The kinetic parameters of the investigated reactions are given in Tables 1 and 2 in the form of the interval value a ± tSa, where Sa is the standard deviation, and t is the Student test for 95% confidence probability. The error of the SF-26 instrument was not greater than 1%.

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LUMINESCENCE-SPECTRAL CHARACTERISTICS AND CONFORMATIONAL TRANSFORMATIONS IN THE ELECTRONICALLY EXCITED STATE OF THE DIMETHYLAMINOPHENYL DERIVATIVES OF PYRIDINE AND PYRIDINIUM AND PYRYLIUM CATIONS

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The electronic absorption spectra and luminescence-spectral characteristics of the 4-dimethylaminophenyl derivatives of pyridine and pyridinium and pyrylium cations in solutions and polymeric films were studied. The obtained data make it possible to suppose that conformations with the orthogonal arrangement of the donating and accepting fragments (TICT structure) both in the cations and in the neutral molecules are formed as a result of structural relaxation in the excited S_1 state.

Study of the conformational behavior in solutions of excited organic molecules containing conjugated fragments capable of rotating about the formal single bonds is of substantial interest for modern photochemistry [1]. During photoexcitation to the nonequilibrium (Frank—Condon) state the balance of the electronic and steric factors determining the equilibrium conformation of the molecule in the S_0 state is destroyed. Structural relaxation is therefore possible both toward greater (TICT structure [2,3]) and toward smaller acoplanarity in the conjugated fragments compared with the ground state (e.g., biphenyl [4], 2,4,6-aryl-substituted pyridinium and pyrylium cations and the isoelectronic pyridines, in which the acoplanarity of the α-aryl rings to the plane of the heterocycle in the S_1 state is reduced [5,6]).

The aim of the present work was to investigate, on the basis of data from the electronic absorption spectra and luminescence-spectral characteristics, the nature of the structural relaxation in compounds for which the two above-mentioned types of relaxation changes in the structure are possible in the excited S_1 state. In this connection we chose the compounds presented below, in which the π-accepting fragments are heterocycles with different accepting ability.

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