10. A. M. Zhidkova, V. G. Granik, R. G. Glushkov, T. F. Vlasova, O. S. Anisimova, T. A. Gus'kova, and G. N. Pershin, Khim. Geterotsikl. Soedin., No. 5, 670 (1974).
11. I. B. Marchenko, V. G. Granik, R. G. Glushkov, E. M. Peresleni, A. I. Polezhaeva, and M. D. Mashkovskii, Khim.-Farm. Zh., No. 11, 49 (1976).
12. V. G. Granik, A. M. Zhidkova, S. S. Kiselev, R. G. Glushkov, A. I. Polezhaeva, and M. D. Mashkovskii, Khim.-Farm. Zh., No. 7, 66 (1978).

KINETICS OF THE N OXIDATION OF SOME COMPOUNDS OF THE PYRIDINE SERIES WITH PERBENZOIC ACID IN CHLOROFORM AND AQUEOUS DIOXANE

R. E. Lokhov

UDC 547.824:541.127:542.943

A comparative study of the kinetics of the N oxidation of 19 derivatives of the pyridine series with perbenzoic acid in chloroform and aqueous dioxane at 20, 25, 30, and 35°C was made. The rate constants, the parameters of the Arrhenius equation, and the activation energies of the N oxidation of the indicated monoazines were determined. The scale of the reactivities of the derivatives of the pyridine series was calculated within the framework of the Pearson hard-soft acid—base concept.

It is known [1-3] that the methods for the preparation of N-oxides of aromatic nitrogen-containing heterocycles by oxidation of the latter with peracids have important practical value. Despite this, the mechanism of N oxidation has not been adequately studied. The timeliness of research of this sort is due among other things to the possibility of investigation of the interaction of the ring nitrogen atom of the monoazine with the electron-deficient δ^+(OH) group of the peracid. The importance of data on such interactions becomes evident if one takes into account the fact that most electrophilic and nucleophilic reactions in series of nitrogen-containing heterocycles proceed with initial coordination at the hetero nitrogen atom both as a kinetically independent electropositive particle and as an electropositive part of an ion pair [4].

Extensive use has recently been made of hydroperoxide oxidation in the azine series [5]; however, this method is less acceptable for the study of the indicated problems by virtue of the fact that the ease of hydroperoxide oxidation is not determined by the affinity of the nucleophile for the hydroperoxide but rather by the affinity for the metal (the catalyst). It is not surprising that the reaction is also complicated by the possibility of the formation of a complex between the catalyst and the functional group.

The formal kinetics of the N oxidation with perbenzoic acid was studied for the first time [6, 7] only in the case of alkyl- and chloropyridines at a single temperature in aqueous dioxane.

Somewhat later [8] the activation energy (E) of the N oxidation of pyridine was determined (the rate constants were determined at 0, 13, and 25°C). On the basis of a limited amount of kinetic data Dondoni and co-workers [7] concluded that there is a correlation between the rate of N oxidation and the basicity of the heterocycle. However, this assumption seems insufficiently substantiated even from the point of view of the experimental data presented. For example, although the basicity of 4-methylpyridine (pK_a 6.02) is considerably higher than that of 3-methylpyridine (pK_a 5.68), the rate constants for their oxidation virtually coincide ($7.25 \cdot 10^3$ and $7.20 \cdot 10^3$ liters/mole-sec, respectively), whereas the rate constant for 2-methylpyridine (pK_a 5.94) is higher by a factor of 1.2 ($8.40 \cdot 10^3$ liters/mole-sec). The highly basic isomeric aminopyridines do not undergo N oxidation at all [1]. Other examples of the anomalous behavior of some monoazines in preparative N oxidation are

---

K. L. Khetagurov North Ossetian State University, Ordzhonikidze 362021. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 354-362, March, 1980. Original article submitted September 18, 1979.

0009-3122/80/1603-0264$07.50

TABLE 1. Rate Constants, Parameters of the Arrhenius Equation, and Activation Entropies for the N Oxidation of Derivatives of the Pyridine Series in 50% Aqueous Dioxane

No.	Substituent in the pyridine ring	pK_a from the data in [18]	$K \cdot 10^3$, liters/mole-sec				E, kcal/mole	lg pZ	$-\Delta S^{\neq}$, cal/deg
			20°	25°	30°	35°			
1	4-NH_2	9.17	Not oxidized						
2	2-CH_3—5-C_2H_5	6.40	8,81	9,52	10,32	11,20	3,085	0,242	31,95
3	2,5-CH_3	6.45	7,97	9,00	9,51	10,42	2,75	−0,03	33,20
4	2-CH_3	5.94	8,15	8,78	—	—	2,607*	−0,04	42,50
5	4-CH_3	6.02	—	7,80	—	—	—	—	—
6	3-CH_3	5.68	7,37	7,78	8,31	**8,83**	2,18	1,14	27,88
7	2-NH_2	6.86	Not oxidized						
8	3-NH_2	5.98	Not oxidized						
9	4-C_6H_5	5.55	4,16	4,83	5,20	6,05	4,491	0,98	28,60
10	H	5.25	4,13	4,74	5,40	6,08	4,65	1,1	28,07
11	2-CH_3—3-OH	6.71 [19]	0,413	0,424	0,44	—	11,04	4,73	2,28
12	3-COOEt	3.13	4,20	4,38	—	—	1,684	−1,33	38,20
13	2-C_6H_5	4.48	0,943	1,02	1,09	—	3,834	−0,18	33,88
14	3-OH	4.86	3,23	3,27	3,32	3,39	0,572	−2,07	47,2
15	6-CH_3—3-OH	6,34 [19]	0,456	0,476	0,495	—	4,05	−0,39	25,53
16	2-OH	0.70	0,140	0,186	0,237	0,262	8,94	2,83	10,97
17	3-$CONH_2$		0,330	0,36	0,413	0,451	2,38	−1,70	31,69
18	4-$COOCH_3$	3.26	0,357	0,36	0,390	—	2,264	−1,782	32,06

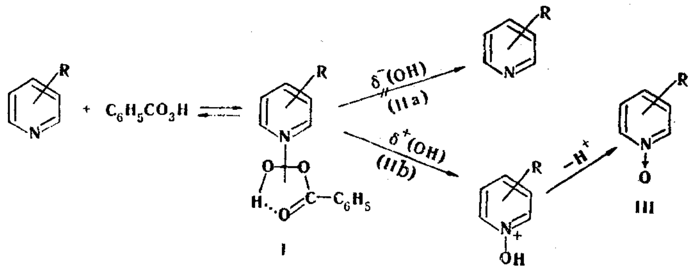
* †

TABLE 2. Rate Constants, Parameters of the Arrhenius Equation, and Activation Energies for the N Oxidation of Derivatives of the Pyridine Series in Chloroform

No.	Substituent in the pyridine ring	pK_a from the data in [18]	$K \cdot 10^3$, liters/mole-sec				E, kcal/mole	lg pZ	$-\Delta S$, cal/deg
			20°	25°	30°	35°			
1	4-NH_2	9,17	Not oxidized						
2	2,6-CH_3—3-OH	7,67	—	3,40	4,75	5,93	10,52	5,25	9,05
3	2,5-CH_3	6,45	3,24	3,57	3,86	4,29	3,26	−0,056	33,31
4	4-C_6H_5	5,55	4,165	4,90	5,22	6,754	5,85	1.982	24,0
5	2-CH_3—5-C_2H_5	6,40	3,23	3,39	3,49	3,60	1,234	−1,565	40,21
6	2-CH_3	5,94	2,51	3,13	3,85	4,71	7,61	3,078	18,98
7	4-$C(CH_3)_3$	5,99	—	2,58					
8	2-NH_2	6,86	Not oxidized						
9	4-CH_3	6,02	—	2,162					
10	3-CH_3	5,68	1,92	2,01	2,18		3,18	−0,364	34,72
11	4-C_2H_5	6,02	—	2,09					
12	3-NH_2	5,98	Not oxidized						
13	2-C_6H_5	4,48	2,091	2,20	2,34	2,44	2,611	−0,742	36,45
14	H	5,25	1,23	1,32	1,37	1,464	2,90	−0,752	36,50
15	3-OH	4,86 [18]; 5,75 [19]	1,071	1,14	1,213	1,315	1,99	−1,487	46,52
16	3-CN	1,45	5,16	5,40	5,82	6,144	2,14	−0.717	36,34
17	3-COOEt	3,13	1,925	2,00	2,128	2,291	2,471	−0,8863	37,11
18	2-OH	0,70	0,188	0,26	0,28	0,363	8,237	2,458	12,667

also known [1, 8]. At the same time that the basicity of dimethylaniline (pK_a 5.18) is somewhat lower than that of pyridine (pK_a 5.25), the rate of N oxidation of the former under similar conditions is higher by a factor of 1000 than the rate for the latter [8].

For a better understanding of the peculiarities of N oxidation we proposed that this reaction is carried out via the following probable scheme.



---

†Footnote to Table 1 omitted as in Russian Original — Publisher.

It is assumed that the oxidation proceeds through a step involving a dynamic complex formed by transfer of the unshared pair of electrons from the nitrogen atom of the heterocycle to the vacant orbitals of the acceptor peracid (I) with subsequent heterolysis of the O–O bond to the δ^-(OH) hydroxide anion or δ^+(OH) hydroxyl cation. Heterolysis of the O–O bond via IIb shifts the equilibrium to favor final product III, whereas heterolysis via scheme IIa shifts the equilibrium to favor the starting compounds.

In the case of validity of the assumption of N oxidation via an ionic mechanism through I one might have expected close activation energies of the indicated reaction and epoxidation under similar conditions, for which the ionic character of the mechanism and its occurrence through a complex between the olefin and the peracid have been clearly proved [5].

In order to ascertain the legitimacy of the proposed mechanism and the mutual effect of coordinately bonded molecules in a dynamic complex within the framework of the perturbation theory presented and the Pearson hard-soft acid–base concept we studied the kinetics of N oxidation of a large number of pyridine derivatives and the epoxidation of four alkenes in 50% aqueous dioxane and in chloroform at four temperatures.

The oxidation rate constants (K) were described by a second-order equation for unequal concentrations:

$$K=\frac{1}{t(a-b)}\ln\frac{b(a-x)}{a(b-x)}. \tag{1}$$

The activation energy (E) was determined graphically from the slope of the line constructed in coordinates of log K and 1/T from the formula

$$E=2.303\cdot R\,|\mathrm{tg}\,\alpha|\,\xi, \tag{2}$$

where α is the slope of the line relative to the abscissa; ξ, ratio of the scales with respect to the abscissa and the ordinate; and R, gas constant (1.986 cal/deg-mole).

The log pZ value of the Arrhenius equation was calculated from formula (3) for T = 298°K:

$$\lg pZ=\lg K+\frac{E}{2.303\cdot R\mathrm{T}}. \tag{3}$$

The activation entropies were calculated from formula (4) for T = 298°K:

$$-\Delta S^{\neq}=2.303R\,\lg\frac{k\cdot\mathrm{T}}{h}-2.303\lg K-\frac{E}{\mathrm{T}}+R. \tag{4}$$

The scale of the reactivities of the compounds of the pyridine series for N oxidation at 25°C was composed from the basic equation of general perturbation theory for the centers with variable electrophilicity [9]:

$$\Delta E_p=-q_rq_s\frac{\Gamma_{rs}}{\Xi}+\Delta_{\mathrm{solv}}+\sum\sum\left[\frac{2C_{rj}^2\cdot C_{sk}^2\beta_{rs}^2}{E_m-E_n}\right], \tag{5}$$

where Γ_{rs} is the coulombic interaction between the r and s centers with formal charges q_r and q_s within the central field approximation; Ξ, dielectric constant of the solvent; E_m, energy of the m-occupied MO of the nucleophile, which is under the influence of the electrophile; and E_n, orbital energy of the unoccupied n-th MO of the electrophile; the coefficients of the AO are normalized $C_{rj}^2 = C_{sk}^2 = 1$ (when r = j, and s = k), and β is the resonance integral, which is equivalent to the energy of cleavage of the chemical bond. The Δ_{solv} term expresses the energy of partial desolvation in the case of coulombic interaction of the r and s centers.

The limiting situations of solution (5) were analyzed by Klopman [9, 10] and virtually represent a theoretical substantiation of the hard-soft acid–base concept.

In connection with the fact that the determination of the energy parameter E_m in Eq. (5) presents great difficulties [9], we used the two-parameter Edwards Equation (6) [11,12]:

$$\lg K_R/K_0=xE_m+yH, \tag{6}$$

where E_m is the redox potential (or a certain similar property that characterizes the nucleophile), H is a measure of the relative basicity of the nucleophile and is equal to

TABLE 3. Consolidated Table of the Rate Constants for Epoxidation and Activation Energies of Olefins in Systems of Various Solvents for $R^1{-}CH{=}CH{-}R^2$

No.	R^1	R^2	Olefin : perbenzoic acid ratio	Solvent	$K \cdot 10^3$, liters/mole-sec				E, kcal/mole
					20°	25°	30°	33°	
1	C_6H_5	C_6H_5	0,2 : 0,1	Chloroform	2,52	5,25	10,8	22,94	6527,9
	C_6H_5	C_6H_5	0,23 : 0,13	50% aqueous dioxane	1,26	3,59	—	—	9370,6*
	C_6H_5	C_6H_5	0,17 : 0,062	90% formic acid	—	0,364	0,75	1,55	6527,9
2	p-Cl—C_6H_4	C_6H_5	0,3 : 0,047	Chloroform	0,93	1,00	1,01	1,054	1508,1
	p-Cl—C_6H_4	C_6H_5	0,25 : 0,047	50% aqueous dioxane	2,59	2,7	2,78	2,91	1332,0
3	p-Br—C_6H_4	C_6H_5	0,16 : 0,03	50% aqueous dioxane	4,81	4,88	4,96	5,25	517,0
4	$C_5H_5N^+$ ClO_4^-	C_6H_5	0,186 : 0,06	50% aqueous dioxane	4,23	—	5,38	—	3642,5*

*The activation energies were calculated theoretically.

pK_a + 1.74, and the x and y constants characterize the electrophile. From the condition for pyridine that log K_R/K_0 = 0, x = 1, and E_m = 1.20 [12], for aqueous dioxane (6a) and chloroform (6b) media, Eq. (6) will have the form

$$\lg K_R/K_0 = E_m - 0.172H \quad (6a); \qquad \lg K_R/K_0 = E_m - 0.162H. \tag{6b}$$

They satisfactorily describe the relative reactivities of the pyridine derivatives (see Table 4 and Figs. 1 and 3). Substituting the E_m values calculated for each monoazine from (6a) and (6b) into Eq. (5) we obtain the following computational Eqs. (7) and (8) when $E_m > E_n$ and Eqs. (8) and (9) when $E_m < E_n$:

$$\Delta E_p = -\frac{4{,}803^2}{1{,}37}\Big/\Xi + 0{,}2850 + \sum \frac{2\beta^2}{E_m - E_n}, \tag{5}$$

$$\Delta E_p = 0{,}0745 + \frac{2\beta^2}{E_m - E_n}\ (7), \qquad \Delta E_p = 0{,}0745 + \frac{2\beta}{E_m - E_n}, \tag{9}$$

$$\text{when} \quad \Xi = 80,$$

$$\Delta E_p = -3{,}2793 + \frac{2\beta^2}{E_m - E_n}\ (8), \qquad \Delta E_p = -3{,}2793 + \frac{2\beta}{E_m - E_n}. \tag{10}$$

$$\text{when} \quad \Xi = 4{,}724$$

The overall energy of the donor-acceptor bond (ΔE_p) from Eqs. (7) and (8) is determined primarily by the forces of electrostatic interaction, since a very small amount of charge transfer will occur. This type of reaction is designated as a charge-controlled reaction. For cases (9) and (10) ΔE_p will be determined primarily by the covalent (last) term, since the interacting orbitals are degenerate. In this case electron density is transferred from the donor to the acceptor, and this type of interaction is called a boundary orbital-controlled reaction.

The β values in Eqs. (7), (8), (9), and (10) are determined from [13, 14] for the following parameters [15]: the length of the $\rangle\overset{+}{N}{-}OH$ = 1.37 Å, $q_r = q_s = 1$, the ionization potential (IP) of pyridine is 9.30 ± 0.01 eV, the IP of the OH^+ group is 13.2 eV, the electron affinity (EA) of pyridine is 0.675 eV, the EA of the OH^+ group is 2.8 or 2.11 eV [10, 13, 14], the energy of cleavage of the N-oxide bond is 3 eV, and the resonance integral (β) of the $\rangle\overset{+}{N}{-}OH$ bond in pyridine N-oxide for these parameters is

$$2\beta = 3.369 \text{ eV} \tag{11}$$

It is apparent that the β value varies as a function of the character of the substituent in the ring of the heterocycle. Since the activation energies for N oxidation lie in the ranges characteristic for hydrogen bonds (see Tables 1 and 2), to take this change into account one can use Eq. (12) [16]

$$\Delta pK_a = -2.86\Delta H + 27.6, \quad (12)$$

where $\Delta pK_a = pK_a$ (acid) − pK_a (base).

If one takes into account the fact that equality of the dissociation energies and the heats of reaction (ΔH) is observed for some equilibrium reactions [17], one can on the basis of the $2\beta_{NO} = 3.369$ value [Eq. (11)] make an additional estimate for pyridine derivatives as a function of their nucleophilicities.

Consequently, by substituting the β and E_m values obtained into Eqs. (7), (8), (9), and (10) and by assigning arbitrary but regular changes in E_n one can calculate a number of series of perturbation energies for the N oxidation of pyridine derivatives.

Consolidated data on the rate constants, parameters of the Arrhenius equation, and activation entropies of the N oxidation of pyridine derivatives in 50% aqueous dioxane and chloroform are presented in Tables 1 and 2, and data on the epoxidation of a number of alkenes are presented in Table 3. The E_m values calculated from (6a) and (6b) and the order of the nucleophilicities according to (5) are presented in Table 4. The $\log K_R/K_o = E_m - yH$ dependences from (6a) and (6b) and the dependence of log K on 1/T are shown in Figs. 1-4.

The following conclusions can be drawn from the data presented in Tables 1-4.

1. The reliability of the kinetic data obtained is confirmed by the satisfactory agreement between the K values presented in Table 1 and the data in [7], which pertain to analogous conditions for pyridine ($4.80 \cdot 10^3$ liter/mole-sec), 2-methylpyridine ($8.40 \cdot 10^3$ liter/mole-sec), 3-methylpyridine ($7.20 \cdot 10^3$ liter/mole-sec), and 4-methylpyridine ($7.25 \cdot 10^3$ liter/mole-sec).

A direct relationship between the consumption of perbenzoic acid and the formation of the corresponding oxides is observed in general in [5-8] both with respect to the N oxidation of some tertiary amines and with respect to the epoxidation of olefins.

2. The N oxidation of pyridine derivatives, as in [7, 8], follows second-order kinetics, first-order in each of the components, viz., the heterocycle and perbenzoic acid. The activation energies (E) range from 1 to 10 kcal/mole, and the activation entropies $\Delta S^{\neq}$ belong to the first series and range from 9 to 47 cal/deg. The $\Delta S^{\neq}$ values overlap the opposing E effect, and this indicates that the reaction has a bimolecular character.

3. The molar ratio of the reacting heterocycle and perbenzoic acid of 1:0.5 was selected for a twofold purpose. First, this ratio was selected to exclude or reduce to a minimum the occurrence of side processes. Second, in the case of the existence of an OH^+ particle of the peracid in a kinetically independent form [1] the rate of N oxidation should have been determined by the rate of dissociation of the peracid and should have been independent of the concentration of the heterocycle or olefin.

However, this assumption contradicts our data and the literature data [20]. The rates of N oxidation of monoazines and epoxidation of olefins are described satisfactorily by a second-order equation for unequal concentrations and lie within the range of one order of magnitude (Tables 1-3). All of this constitutes evidence in favor of the assumption, in contrast to the well-known concepts [1, 7], of the possibility of N oxidation through a step involving a dynamic molecular complex (1) of the donor-acceptor type between the heteroring and the peracid.

It is apparent that cleavage of the O—O bond in the molecule (1) theoretically may lead to the formation of three particles, viz., OH^+, OH^-, and $^{\cdot}OH$. The generation of a hydroxyl radical under the conditions of N oxidation of monoazines is unlikely [21]. The effect of the heteroring on the heterolysis of the O—O bond may be manifested in polarization of the peracid in the complex with the development of $\delta^+(OH)$ or $\delta^-(OH)$, depending on the energy possibility of one or the other direction of polarization.

4. The data obtained on the reactivity of pyridine calculated for the centers with variable electrophilicity (Table 4) show relatively greater agreement with the order of nucleophilicity corresponding to the "hard" center $E_n = +3$ (an orbitally controlled interaction).

TABLE 4. Scale of Reactivities of Some Pyridine Derivatives Relative to N Oxidation Calculated from the Equation for Centers with Variable Electrophilicity (E_n) at 25°C

E_n	Order of nucleophilicity												
+3 (calc.)	2-CH_3—5-C_2H_5	2,5-CH_3	2-CH_3	4-CH_3	3-CH_3	4-C_6H_5	H	3-OH	3-COOEt	2-C_6H_5	2-CH_3—3-OH	6-CH_3—3-OH	2-OH
$K \cdot 10^3$, exptl., aqueous dioxane	9,50	9,0	8,78	7,80	7,78	4,83	4,74	3,27	4,38	2,03	0,413	0,456	0,19
E_m [calc. from (6a)]	1,70	1,69	1,59	1,55	1,49	1,26	1,20	0,98	0,80	0,70	0,39	0,37	−0,99
pK_a	6,40	6,45	5,94	6,02	5,68	5,55	5,25	4,86	3,13	4,48	6,71	6,34	0,70
+3 (calc.)	2,5-CH_3	2-CH_3—5-C_2H_5	2-CH_3	4-C$(CH_3)_3$	4-CH_3	3-CH_3	H	3-OH	2-OH				
$K \cdot 10^3$, exptl., chloroform	3,57	3,39	3,13	2,58	2,16	2,01	1,32	1,14	0,26				
E_m [(calc. from (6b)]	1,76	1,73	1,62	1,54	1,47	1,44	1,20	1,15	−0,30				
pK_a	6,45	6,40	5,94	5,99	6,02	5,68	5,25	4,86	0,70				

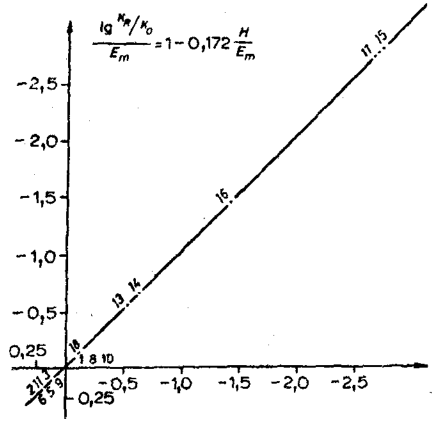


Fig. 1

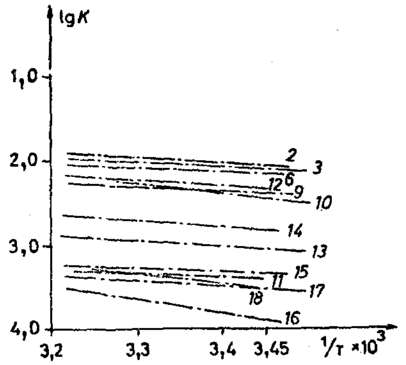


Fig. 2

Fig. 1. Dependence of the relative reactivities of derivatives of the pyridine series for N oxidation in 50% aqueous dioxane on the parameters of the Edwards equation (the numbering of the compounds corresponds to the numbering presented in Table 1).

Fig. 2. Dependence of log K on 1/T in the N oxidation of derivatives of the pyridine series with perbenzoic acid in 50% aqueous dioxane (the numbering corresponds to the numbering in Table 1).

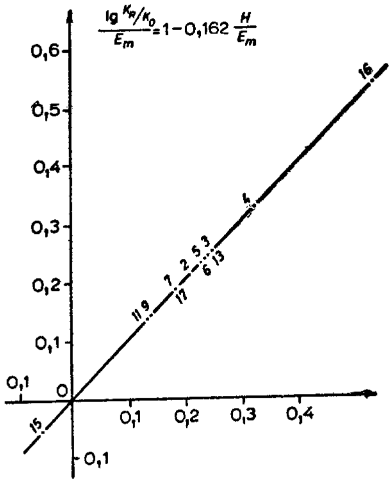


Fig. 3

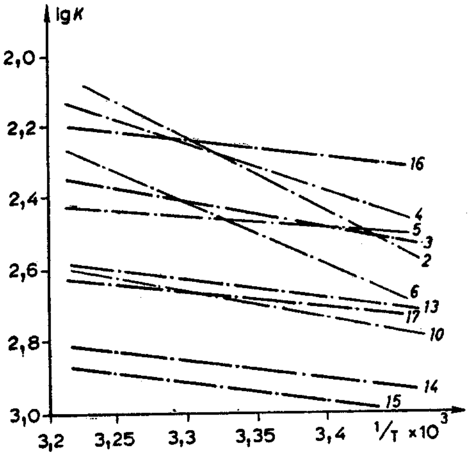


Fig. 4

Fig. 3. Dependence of the relative reactivities of derivatives of the pyridine series in N oxidation in chloroform on the parameters of the Edwards equation (the numbering corresponds to the numbering in Table 2).

Fig. 4. Dependence of log K on 1/T in the N oxidation of derivatives of the pyridine series with perbenzoic acid in chloroform (the numbering corresponds to the numbering in Table 2).

It may be assumed that in the case of compounds for which good agreement between the experimental data and the calculated values is observed, δ^{+}(OH) is generated from complex I. The δ^{-}(OH) group (a charge-controlled interaction) is generated for compounds that deviate from this dependence, such as compounds 1, 7, 8, 11, 12, and 15 (Tables 1 and 4) and 1, 8, 12, 2, 4, 13, 16, and 17 (Tables 2 and 4).

5. The anomalously high reactivities of compounds 4, 13, 16, and 17 (Table 2) and 12 (Table 1) can partially be explained by possible simultaneous (with the ring nitrogen atom) oxidation of ester nitrile, and other groups under the N-oxidation conditions.

EXPERIMENTAL

The compounds with stable liquid fractions were subjected to fractional distillation with a column. The remaining pyridine derivatives were recrystallized twice. The purity of the preparations was monitored by chromatography on plates in a thin layer of aluminum oxide [19] and by gas chromatography [22]. The constants of the investigated compounds were in agreement with the values presented in the literature.

trans-Stilbene and p-chloro- and p-bromostilbenes were obtained by the methods in [23, 24].

Preparation of N-Styrylpyridinium Perchlorate. A mixture of 8.5 g (0.05 mole) of pyridinium-N-acetic acid chloride and 10 g (0.094 mole) of benzaldehyde in 30 ml of pyridine was heated at 70-80°C for 3-4 h, after which the benzaldehyde and pyridine were removed by steam distillation, and the residue was removed by filtration, dried, and heated with 7 ml (0.05 mole) of benzoyl chloride to 190°C and maintained at this temperature for 5-10 min. The crystalline precipitate was removed by filtration and washed thoroughly with ether. The residue was dissolved in 10 ml of 50% perchloric acid, and the precipitated N-styrylpyridinium perchlorate was recrystallized from alcohol to give 6.7 g (49.1%) of a product with mp 170-171°C. No melting-point depression was observed for a mixture of this product with a genuine sample [25].

Determination of the Kinetics of Oxidation. A weighed sample of the investigated compound was dissolved in 50% aqueous dioxane or chloroform, and the resulting solution was mixed with a sufficient amount of a chloroform solution of perbenzoic acid to obtain a ~0.2 N solution and a heterocycle:perbenzoic acid molar ratio of 1:0.5. The oxidation was carried out at 20, 25, 30, and 35°C (±0.1°C).

Samples (2 ml) were selected after 5, 10, 15, and 20 min and were immediately transferred to a beaker containing 4 ml of a 10% solution of KI and 0.5 ml of an acetic acid solution of ferric chloride. The samples were allowed to stand in the dark for no less than 30 min and were titrated with a 0.1 N solution of sodium thiosulfate. A control sample (2 ml) of a chloroform solution of perbenzoic acid was titrated simultaneously. The determination of the perbenzoic acid consumption with time was accomplished by the method in [26].

A graph in the following coordinates was constructed to make allowance for the experimental error associated with the uncertainty in the determination of the initial time:

$$\lg\frac{b(a-x)}{a(b-x)} - t_{\mathrm{exp}}$$

The experimental points lie satisfactorily on a line that does not always pass through the origin. Segment t cut out by this line on the abcissa was used as the correction for the experimental time. As a rule, this error was substantially small as compared with the half-conversion period. The N oxidation was carried out at two initial concentrations for each temperature; the rate constants obtained in this case differed from one another by no more than 10%.

A linear dependence of the N-oxidation rate constants on the temperature (log k vs 1/T) was observed for the investigated compounds. The rate constants were determined with an accuracy of up to 5%, the E values were determined with an accuracy of ±0.5 cal/mole, the log pZ values were calculated with an accuracy of ±0.07, and the $\Delta S^{\neq}$ values were calculated with an accuracy of ±1.0 cal/deg.

LITERATURE CITED

1. E. Ochiai, Aromatic Amino Oxides, Amsterdam (1967), p. 19.
2. A. R. Katritzky and I. M. Lagowsky, Chemistry of the Heterocyclic X-Oxides, Vol. 3, Academic Press, New York (1971), p. 99.
3. R. A. Abramovitch, in: Pyridine and Its Derivatives, Supplement, Part 2, New York (1974).
4. Zh. I. Aksel'rod and V. M. Berezovskii, Usp. Khim., 33, 1337 (1970).
5. G. A. Tolstikov, Hydroperoxide Oxidation Reactions [in Russian], Nauka, Moscow (1976), p. 149.
6. G. Modena and P. E. Todesco, Gaz. Chim. Ital., 90, 703 (1960).
7. A. Dondoni, G. Modena, and P. E. Todesco, Gaz. Chim. Ital., 91, 613 (1961).
8. A. Dondoni and B. Todesco, Boll. Sci. Fac. Chim. Ind. Bologna, 20, 79 (1962).
9. G. Klopman (ed.), Chemical Reactivity and Reaction Paths, Wiley (1974).
10. G. Klopman, J. Am. Chem. Soc., 90, 223 (1968).
11. V. A. Pal'm, Fundamentals of the Quantitative Theory of Organic Reactions [in Russian], Khimiya, Leningrad (1977), p. 289.
12. A. Gordon and R. Ford, Chemist's Companion: A Handbook of Practical Data, Techniques, and References, Wiley (1973).
13. G. Klopman, J. Am. Chem. Soc., 86, 4550 (1964).
14. G. Klopman, J. Am. Chem. Soc., 87, 3300 (1965).
15. V. N. Kondrat'ev (ed.), Energies Required to Cleave Chemical Bonds, Ionization Potentials, and Electron Affinities [in Russian], Nauka, Moscow (1974).
16. A. A. Mashkovskii and S. E. Odinokov, Dokl. Akad. Nauk SSSR, 204, 1165 (1972).
17. C. D. Nenitzescu, Organic Chemistry [Russian translation], IL, Vol. 1 (1962), p. 145.
18. A. Albert, in: Physical Methods in the Chemistry of Heterocyclic Compounds, A. R. Katritsky (ed.), Khimiya, Moscow—Leningrad (1966), p. 15.
19. N. N. Grandbert, G. K. Fanzova, and A. N. Kost, Khim. Geterotsikl. Soedin., No. 4, 561 (1966).
20. V. G. Dryuk, M. S. Malinovskii, S. P. Shamrovskaya, S. A. Vasil'chenko, and S. A. Maslov, Zh. Org. Khim., 9, 1228 (1973).
21. V. L. Antonovskii, Organic Peroxide Initiators, Khimiya, Moscow (1972), p. 352.
22. V. M. Nabivach and L. A. Venger, Zh. Anal. Khim., 30, 604 (1975).
23. R. Schreiner and A. Berger, Organic Syntheses [Russian translation], Coll. Vol. 3, IL, Moscow (1952), p. 395.
24. Weygand, and Hilgetag, Preparative Organic Chemistry, Wiley (1972).
25. L. C. King and W. B. Brownell, J. Am. Chem. Soc., 72, 2507 (1950).
26. N. D. Cheronis and T. S. Ma, Organic Functional Group Analysis by Micro- and Semimicro Methods, Wiley (1964).