KINETICS AND MECHANISM OF HYDROLYSIS
OF 3-ANILINOPHTHALIDES

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Hydrolysis rates of sixteen substituted 3-anilinophthalides have been measured in 20% aqueous–ethanolic media having certain pH or H_0 values. It has been found that the cyclic form of 3--anilinophthalide stands in equilibrium with the open form of 2-carboxybenzylideneaniline. Reactivity of these substrates is identical with that of N-benzylideneanilines except for the pH region 2 to 6, where the hydrolysis rate is lowered due to competitive cyclization. Under the conditions of pseudomonomolecular reaction the concentrations of individual reacting forms depend on acidity, and it is the open form of the substrate which undergoes the reaction with water. In strongly acidic medium linear dependence log k_{exp} *vs* —H_0 has been found with a slope 1·4. The value of log k_{exp} has been correlated with the Hammett constants ($\varrho = 3·92$ at H_0 4·0). The rate-limiting step in this medium consists in reaction of the protonated open form with water. In media having pH 1 to 3 linear dependence on the proton activity has been found, its slope being about unity, and the substituent effects were opposite ($\varrho = -1·12$ at pH 1·97). Splitting of the protonated lactone ring is the slowest step. In the pH range 3 to 6 the value of k_{exp} was independent of the proton activity and electron-attracting substituents slowed down the hydrolysis ($\varrho = -1·06$ at pH 4·76). In the pH region 6 to 10 the open dipolar form of the substrate reacts with water (slope of the dependence log k *vs* pH is about unity), and the dependence log k_{exp} on the substituent constants shows a break caused by a change in the rate-limiting step. In strongly basic media (pH 12 to 14) the hydrolysis rate again increases with increasing hydroxyl ion concentration, and electron-attracting substituents accelerate the hydrolysis ($\varrho = 1·30$ at pH 13·02).

Recently intramolecular catalysis by a neighbouring carboxyl[1], carboxylate[2], hydroxyl[2,3], formyl or ketonic group[4,5] was studied in detail. The reason was its use as a potential model in studies of enzymatic intramolecular reactions, because each of these groups can be present as a substituent in enzymes. So far the knowledge about the carboxyl group participation as an intramolecular catalyst in arylideneamine hydrolysis was obtained but marginally in connection with studies of intramolecular catalytic effects of aldehydic group[5]. We chose the ring opening of 3-anilinophthalide (*I*) into 2-carboxybenzylideneaniline (*II*) in solution as a model for a study of the splitting catalyzed intramolecularly by carboxyl group; in solid state this compound exists only in cyclic form (Eq. (*A*)). Hydrolysis of these compounds has not yet been described in literature. Bender[5] found that the hydrolysis rate of the structurally close 3-morpholinophthalide is pH·independent (spontaneous solvolysis) in neutral medium and proportional to hydroxyl ion concentration at higher pH values. He presumed that the nucleophile attacked the carbonyl carbon atom (Eq. (*B*)). Most probably the spontaneous hydrolysis of 3-morpholinophthalide proceeds by synchronic mechanism according to Eq. (*B*), the transition state stabilized by a resonance of formyl group (Eq. (*C*)) being formed.

The purpose of the present paper is to contribute to elucidation of the hydrolysis of 3-anilinophthalides and influence of carboxyl group on the reaction course. Therefore, the substituent effects from aniline nucleus *I*, influence of acidity of medium, and hydrolysis by labelled water were studied. The reaction was carried out in 20% aqueous ethanol.

EXPERIMENTAL

Reagents. Substituted 3-anilinophthalides: Solution of 0·05 substituted aniline in 50 ml benzene was mixed with a solution of 7·5 g (0·05 mol) 2-formylbenzoic acid in 50 ml benzene. The reaction mixture was heated in an apparatus with a phase separator and reflux condenser until the volume of the water separated reached minimum 0·85 ml. After cooling the product crystallized (in some

(A)

(B)

(C)

(D)
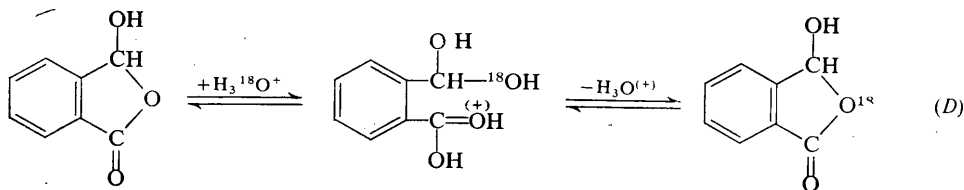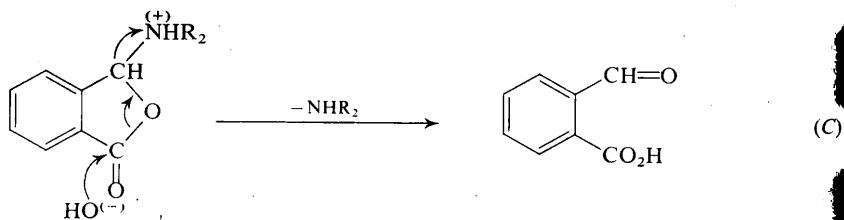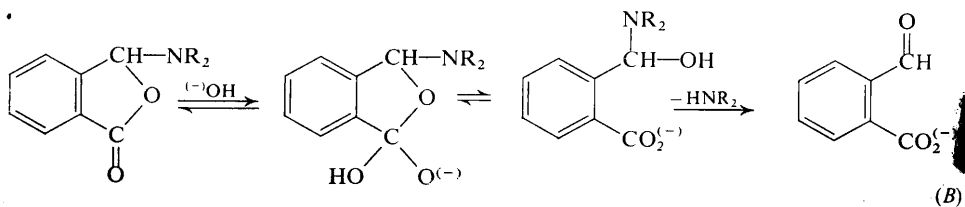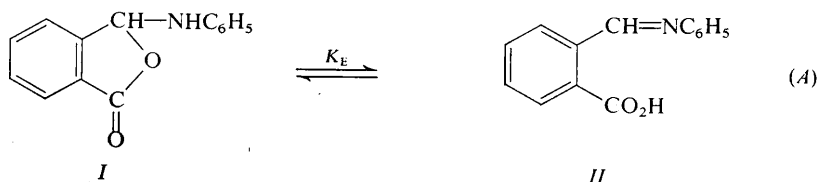
cases it separated during the reaction) and was purified by crystallization from benzene. The physical constants are given in Table I. In the same way benzylideneaniline, N-(4-carboxybenzyl-idene)aniline, 4-carboxy-N-benzylideneaniline and ^{15}N-3-anilinophthalide were prepared.

Kinetic measurements were carried out in aqueous ethanolic media (20% ethanol by vol.) prepared from aqueous solutions of sulphuric and hydrochloric acids, acetate, chloroacetate, phosphate, borax and carbonate buffers and solution of 0·25M-NaOH. Constant ionic strength 0·25 was adjusted by addition of potassium chloride. For measurement about 10 µl ethanolic solution of the substrate was injected in 5 ml 20% aqueous–ethanolic buffer solution or sulphuric acid. The measurements were carried out in thermostatted cells at 25°C, concentrations of 3--anilinophthalides in the reaction mixtures were (1 to 2) . 10^{-5} mol/l. The hydrolysis rate at pH values above 7 or in the H_0 region −7 to 3·5 (where it was sufficiently slow) was followed by means of a spectrophotometer Specord UV VIS (Zeis, Jena) in the range 310 to 350 nm. Concentration of the hydrolytic products was read at the time corresponding to about 6 to 7 half-lives. Absorbance measurements of the starting compounds and kinetic experiments in acetate and chloroacetate buffers and diluted hydrochloric acid were carried out with the use of a Durrum Stopped-Flow SpectrophotometerModelD-110. The solution of substrate in 20% aqueous ethanol having pH adjusted at 10 to 12 was mixed with 20% aqueous–ethanolic buffer solution (double concentration) in the mixing chamber of the apparatus at 25°C. The pH values of the solutions were measured with a pH-meter 4 c (Radiometer, Copenhagen) at 25°C. The sulphuric acid concentration was determined titrimetrically with 0·5M-NaOH and Tashiro indicator. The rate constants of the rapid reactions were calculated by the method of reading the half-lives from the screen of the apparatus, those of slower reactions were obtained by analogous method to that published by Hoffman[3].

Hydrolysis of 3-anilinophthalides by water enriched in $H_2^{18}O$. *A*) Acid hydrolysis. About 0·1 g 3-anilinophthalide was heated to boiling with 0·8 ml 53% $H_2^{18}O$ saturated with gaseous hydrogen chloride (pH ∼ 1) in a test tube equipped with a cooling jacket in its upper part. After 1 to 2 minutes (all the solid material dissolved) the reaction mixture was cooled and the 2-formylbenzoic acid separated was filtered and washed with about 0·5 ml acidified water enriched in $H_2^{18}O$. After drying over phosphorus pentoxide *in vacuo* the product melted at 94·0—95·0°C (ref.[8] m.p. 96°C for non-labelled 2-formylbenzoic acid). For comparison the same procedure was applied also to the reaction of pure 2-formylbenzoic acid with labelled water.

B) Alkaline hydrolysis. 3-Anilinophthalide 0·1 g was mixed with 2 ml 53% $H_2^{18}O$ alkalized before with solid potassium hydroxide (pH about 14). The reaction mixture was heated in a miniature extractor where the evolved aniline distilled with water vapour, condensed and was extracted continuously with chlorobenzene. After two hours the reaction mixture was cooled and acidified with gaseous hydrogen chloride, and the free acid was recrystallized from $H_2^{18}O$; m.p. 93·5 to 95·0°C.

IR *spectra* of the individual compounds were measured with a spectrophotometer UR-20 (Zeiss, Jena) and Spectromom 2000 (MOM, Budapest). The wavenumber scale was calibrated with polystyrene sheet. The measurements in solution were carried out in 1 mm NaCl cells. Measurements in solid state were carried out in nujol, the spectra of the both derivatives with N isotope (^{15}N and ^{14}N) were measured in KBr disc. The solvents — pyridine, tetrahydrofuran, acetonitrile, dimethyl sulphoxide and triethylamine — were purified by standard procedure. Mass spectra were measured with a MS 902 AEI spectrometer.

RESULTS AND DISCUSSION

Structure of 3-anilinophthalide. IR spectra of the compounds investigated (in nujol) show (in accord with the works of Wheeler[7]) the bands of characteristic frequencies $v(C=O)$, $v_{sym}(C-O-C)$ and $v_{as}(C-O-C)$ which indicate the closed structure.

TABLE I

Physical Constants and Analyses of 3-Anilinophthalides

No	Derivative m.p., °C	Formula mol. wt.	Calculated/Found		
			% C	% H	% N
1	H	$C_{14}H_{11}NO_2$	74·65	4·92	6·22
	177—178[a]	225·2	75·17	5·01	6·32
2	4-OCH$_3$	$C_{15}H_{13}NO_3$	70·58	5·13	5·49
	145—146	255·3	70·22	5·23	5·37
3	4-CH$_3$	$C_{15}H_{13}NO_2$	75·30	5·48	5·85
	148—149	239·3	75·01	5·52	5·52
4	3-Cl	$C_{14}H_{10}ClNO_2$	64·75	3·88	5·39
	186—187	259·7	64·65	3·90	5·61
5	3-NO$_2$	$C_{14}H_{10}N_2O_4$	62·22	3·73	10·37
	227—228[b]	270·2	62·16	3·98	10·61
6	4-NO$_2$	$C_{14}H_{10}N_2O_4$	62·22	3·73	10·37
	247—249	270·2	62·41	3·80	10·33

[a] Ref.[6] gives m.p. 178°C; [b] ref.[7] gives m.p. 227—229°C.

TABLE II

Characteristic Vibrations Frequencies (cm^{-1}) in IR Spectra of Studied 3-Anilinophthalides

Compound[a]	$v(N-CH)$	$v(N-C_6H_5)$	$v(C-OC)$ sym	$v(C-OC)$ asym	$\delta(N-H)$	$v(C=O)$	$v(N-H)$
1	1 148 m	1 262 vs	863 s	1 078 vs	1 532 s	1 735 s	3 328 m
2	1 152 m	1 260 m	560 m	1 078 s	1 527 s	1 742 vs	3 312 m
3	1 150 m	1 262 m	858 m	1 078 s	1 529 s	1 740 vs	3 338 m
4	1 152 m	1 264 s	860 mb	1 078 vs	1 530 s	1 727 vs	3 350 m
5	1 149 m	1 258 s	858 s	1 079 s	—	1 733 vs	3 368 m
6	1 140 m	1 258 s	855 s	1 070 s	—	1 748 vs	3 315 m

[a] See Table I (vs very strong band, s strong, m medium, b broad band).

Frequencies of valence vibrations of N—H group (Table II) of a series of six 3-anilinophthalides gave linear correlation with the Hammett σ constants, 4-nitro derivative being strongly deviated. For further verification of the structure we tried to ascribe the absorption bands with the use of spectra of 3-anilinophthalides containing ^{15}N and [14]N. By comparison of the both spectra we found a lowering of frequencies due to the mass effect: $3328(-8)$ $v(N—H)$, $1532(-5)$ $\delta(N—H)$, $1265(-5)$ $1148(-12)$ $v(C—N)$, $838(-5)$ and $823(-3)$ cm^{-1} deformation vibration of N—H or C_6H_5—N bonds. The absorption bands of further functional group of aromatic skeletons were found at usual frequencies.

In order to examine the tautomeric isomerization of the both forms we measured the region $1600-1800$ cm^{-1} of these compounds in a series of solvents of increasing basicity: acetonitrile, dimethyl sulphoxide, tetrahydrofuran, pyridine and triethylamine. In this series the band $v(C=O)$ $1762-1790$ cm^{-1} (I) shifts to higher wavelengths, the spectra of the compounds in pyridine and tetrahydrofuran show a further band at $1718-1730$ cm^{-1} ascribed to the carbonyl group of carboxylic acid group in the open form II (Eq. (A)). From the extinction values of the both carbonyl bands (Table III) it is obvious that pyridine, being a stronger base, shifts the equilibrium in favour of the form II more than tetrahydrofuran does. The spectra measured in triethylamine
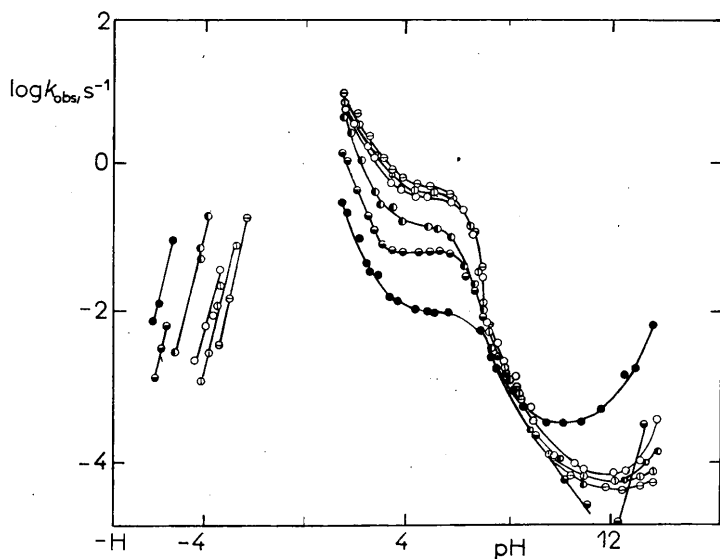

F<small>IG</small>. 1

Dependence of Hydrolysis Rate of 3-Anilinophthalides on pH resp. H_0 Function in 20% Aqueous Ethanol Medium at 25°C

H (○), 4-OCH$_3$ (⊖), 4-CH$_3$ (⊕), 3-Cl (◔), 3-NO$_2$ (◑), 4-NO$_2$ (●).

solutions do not show any carbonyl band in the given region, because the amine, being a strong base, causes ionization and salt formation. The absorption bands ν_{sym} and ν_{as} of the carboxylate anion are out of the spectral region measured.

Hydrolysis of 3-*anilinophthalide in media enriched with* $H_2^{18}O$. The hydrolysis produces 3-formylbenzoic acid which (in solid state and mostly in solutions, too) is present in its cyclic form — 3-hydroxyphthalide[9] (*III*). The following percentage (in brackets) of ^{18}O was found at positions 1 and 3 of the heterocyclic system: pH 1 — substrate *I*, position 1 (0), 2(20), 3(50); substrate *III*, position 1(1), 2(17), 3(52); pH 14 — substrate *I*, position 1(0), 2(17), 3(45). The absence of ^{18}O at position 1 is interpreted by that in 3-anilinophthalide hydrolysis the nucleophilic attack does
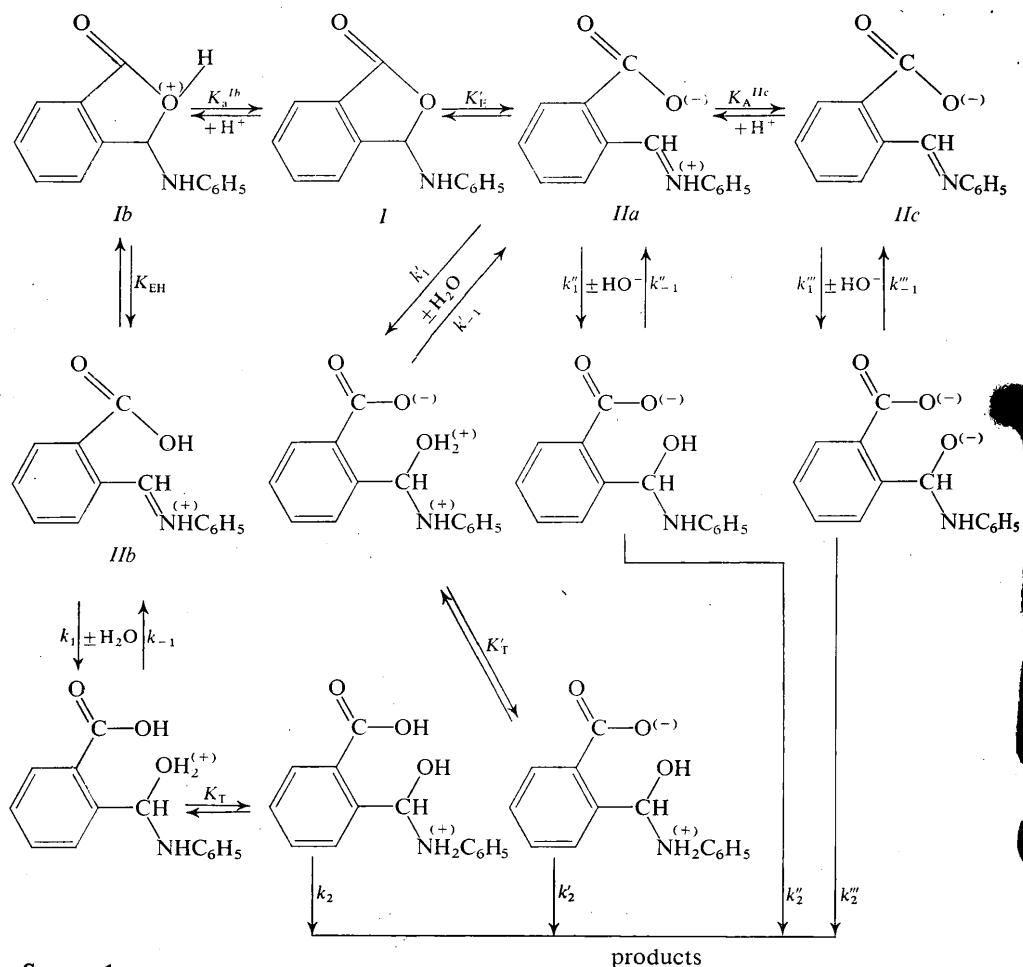
SCHEME 1

not occur at the carbonyl carbon atom at position 1, as Bender presumed[5] in hydrolysis of 3-morpholinophthalide. The presence of ^{18}O at position 2 of the phthalide *III* is interpreted by subsequent hydrolysis of the formed 3-hydroxyphthalide during isolation from acid medium (Eq. (D)). The exchange of oxygen at the position 2 was confirmed independently by reaction of 3-hydroxyphthalide (*III*) in aqueous medium enriched in $H_2{}^{18}O$.

Hydrolysis of 3-anilinophthalides in 20% *aqueous ethanol.* The results of measurements of hydrolysis rate of substituted 3-anilinophthalides are given in Fig. 1. The rate constants found agree with pseudomonomolecular reaction. From the comparison of the results of kinetic measurements of N-benzylideneanilines[3,10-12] with the model chosen it follows that the character of the dependence log k *vs* pH in basic and strongly acidic media are comparable. Therefore we mean that in basic and strongly acidic media the open form of the substrate *II* predominates (Eq. (A)). The discussion of the hydrolysis of 3-anilinophthalides is based on the dependence log k_{exp} *vs* pH values (Fig. 1) and reaction Scheme 1.

In diluted sulphuric acid (H_0 -2 to -7) we presume that the substrate is fully protonated[17] (*cf.* pK of N-(4-chlorobenzylidene)aniline 2·75), and the reaction rate decrease at higher sulphuric acid concentrations (Fig. 1) is due to activity decrease of the water which attacks the substrate in the rate-limiting step. If solvation were important for stabilization of the transition state, it would be possible to consider
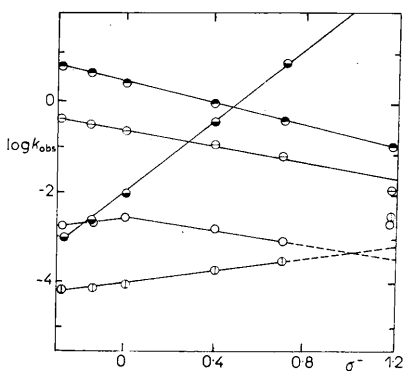

FIG. 2

Dependence of Logarithms of Hydrolysis Rate Constants of 3-Anilinophthalides on σ^- Constants in 20% Aqueous Ethanol at 25°C

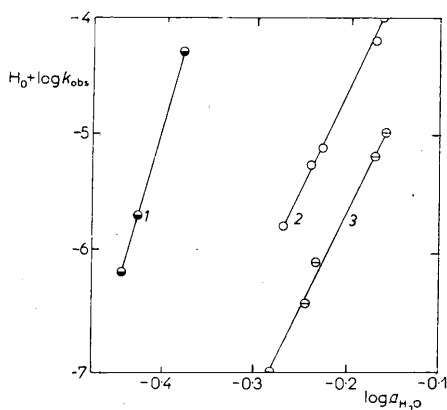H_0 -4 (◓), pH 1·97 (●), 4·76 (⊖), 7·95 (○), 13·02 (⊙).

FIG. 3

Dependence of Hydrolysis Rate Constants of 3-Anilinophthalides on Water Activity for Derivatives 4-NO$_2$ (*1*), H (*2*), 4-CH$_3$ (*3*)

the mechanism S_N1 for the hydrolysis, *i.e.* the protonated substrate would split in the rate-limiting step and the carbonium ion would be quickly hydrated. In this way *e.g.* the hydrolysis of 3-methoxy-3-phenylphthalide takes place[13]. The monomolecular mechanism does not exclude the found order of substituent effects in aniline nucleus either $\left(\varrho = 3.92 \text{ at pH } 4.0 \right)$ (Fig. 2). However, the slope of the dependence $\log k_{obs}/$ $/H_0 \approx 1.4$ is close to the value 1.8 found in the series of N-salicylideneanilines[10] resp. in amide hydrolysis[14-17], where the substrate is fully protonated as in our case. This dependence is characteristic for the reactions which need more water molecules in the transition state, the water molecules acting both as nucleophilic and proton--transfer agents. From the dependence $H_0 + \log k_{obs} = w . \log a_{H_2O}$ it is possible to estimate the number of water molecules in the transition state of the rate-limiting step[18-20]. The value $w \approx 10$ found (Fig. 3) is typical for the reactions proceeding by bimolecular mechanism, which is in accord also with the high ratio $k_{H_2O}/k_{D_2O} \approx 8$ (Fig. 4). As the hydrolysis rate of the substituted 3-anilinophthalides is comparable with that of N-benzylideneanilines[3], we presume that the protonated substrate in its open form *IIb* (Scheme 1) reacts with water. (The existence of the protonated open form in acid medium was found with 3-hydroxyphthalide[9].) In the acidity range H_0 -2 to pH 1 the hydrolysis of all the 3-anilinophthalides proceeds so quickly that it was impossible to determine the hydrolysis rate even by the method of stopped flow.
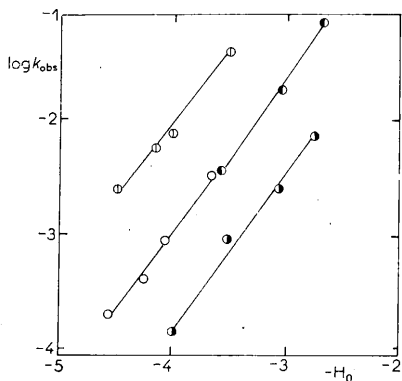

FIG. 4

Dependence of Logarithms of Hydrolysis Rate Constants on H_0 for Compound *1* in System H_2SO_4–H_2O–20% Ethanol (◐) and System D_2SO_4–D_2O–20% Ethanol (◑) and Compound 2 in System H_2SO_4–H_2O–20% Ethanol (○) and System D_2SO_4–D_2O–20% Ethanol (◑)
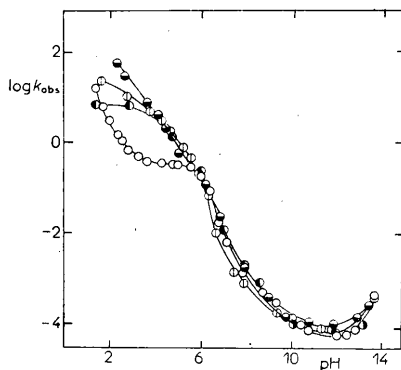

FIG. 5

pH Dependences of Hydrolysis Rates of 3-Anilinophthalide (○), N-(4-Carboxy-benzylidene)aniline (◐), 4-Carboxybenzylideneaniline (◓) and N-Benzylideneaniline (◑) in 20% Aqueous Ethanol at 25°C

As it can be seen from Fig. 1, log k_{obs} depends linearly on pH with the slope about unity in the pH range 1 to 3. The reaction rate is directly proportional to the concentration of the protonated form of the substrate Ia. The rate constants of N-benzylideneanilines and the derivatives substituted in position 4 resp. 4′ with a carboxyl group are substantially greater in this region (0·5 to 1 order of magnitude) (Fig. 5) than those for hydrolysis of 3-anilinophthalide. The influence of substituents in the aniline nucleus has an opposite direction to that in strongly acid medium, electron-attracting substituents slow down the hydrolysis rate; at pH 1·97 the reaction constant ϱ was found to be −1·12 (Fig. 5). Monomolecular decomposition of the protonated form Ia proceeding by splitting of the bond C—N in the rate-limiting step would be in accord with the found negative reaction constant, but the found value $\Delta S^{\ddagger} = 24\cdot5$ e.u. is much too high for a monomolecular reaction. The monomolecular mechanism is inconsistent with the found value $k_{H_2O}/k_{D_2O} = 1\cdot62$, too. Therefore, we presume that the reaction rate is determined by ring splitting of the protonated substrate $Ib \rightleftarrows$ $\rightleftarrows IIb$. Then the imonium ion IIb reacts quickly with water to give the products. An alternative mechanism involving the attack of the carbon 1 of the protonated substrate Ia (resp. Ib) by water is little likely as it follows from our experiments with hydrolysis in $H_2{}^{18}O$-enriched water.

TABLE III

Solvent Effects in Tautomeric Equilibria of 3-Anilinophthalides

No	$\nu(C{=}O)$, cm^{-1}		E		No	$\nu(C{=}O)$ cm^{-1} $(I)^a$	$E(I)$
	I	II	I	II			
	Pyridine					Acetonitrile	
1	1 672	1 715	0·818	1·199	1	1 770	0·924
2	1 765	1 727	0·787	1·265	2	1 766	0·725
3	1 765	1 724	0·685	0·884	3	1 768	0·730
4	1 765	1 719	0·778	0·681	4	1 772	0·788
5	1 770	1 719	0·680	0·097	5	1 770	0·684
6	1 774	1 721	0·835	0·670	6	1 775	0·855
	THF^b					DMSO^c	
1	1 780	1 730	0·334	0·021	1	1 765	0·352
2	1 778	1 730	0·438	0·089	2	1 765	0·260
3	1 778	1 730	0·447	0·243	3	1 766	0·358
4	1 781	1 725	0·376	0·031	4	1 770	0·146
5	1 781	1 725	0·521	0·093	5	1 771	0·418
6	1 790	1 725	0·238	0·164	6	1 772	0·465

^{a} II not found; ^{b} tetrahydrofuran; ^{c} dimethyl sulphoxide.

Spontaneous hydrolysis at pH 3 *to* 6. In this pH range the hydrolysis of 3-anilino-phthalides is practically independent of the proton activity (Fig. 1). The substituents effects are manifested in similar way as those in mildly acidic medium, the value $\varrho = -1 \cdot 06$ was found at pH 4·76. As the extinction coefficient of the studied compounds changes considerably in pH range about 6 at 310 nm, we presume that it is due to increased concentration of the dipolar ion *IIa* produced by splitting of the phthalide ring. This presumption was supported by the finding that N-benzylidene-anilines with a carboxyl group at position 4 (resp. 4′) do not behave in this way. (The absorbance change is connected with concentration increase of the open form *IIa* which represents a more conjugated system. In the case of 4-carboxyderivative the extinction coefficient does not change with pH, which confirms that the extinction changes are connected not only with ionization but also with various magnitudes of K_{EH} and K_E'.) From the pH dependence of absorbance of the starting compounds it was estimated that the concentration of the both forms (*i.e. IIb* and *IIa*) is equal at pH 6·2. Electron-attracting substituents shift the equilibrium $I \rightleftarrows IIa$ in favour of the cyclic form and thus diminish the concentration of the reacting substrate, on the other hand, however, they facilitate the addition of water molecule. From the resulting negative reaction constant $\varrho = -1 \cdot 06$ (Fig. 2) then it follows that the overall reaction is more sensitive to the C^3—O bond splitting in 3-anilinophthalide (form *I*) than to addition of water to the dipolar ion (*IIa*).

Neutral and alkaline hydrolysis. In pH range 6 to 8·5 the hydrolysis rate decreases with increasing pH (the slope being about unity). This reaction rate decrease can be interpreted by concentration decrease of the form *IIa* due to its rapid dissociation into slightly reactive anion *IIc*. From these facts it follows that water molecules are the attacking nucleophile. The substituent effects show a break in this range (Fig. 2). At pH about 8 is $\varrho = -0 \cdot 48$ and $+0 \cdot 60$ for electron-attracting and -repulsing substituents, respectively. Similar break can be observed in the dependence log k_{obs} *vs.* substituents constants (*cf.* hydrolysis of benzylideneanilines[10,21]) and is caused by a change in the rate-limiting step. It can be stated that, in this region, the studied substrates behave in similar way as the Schiff's bases inclusive of the deviation in the case of 4-nitroderivative which was explained[22] by a greater significance of $-M$ effect in decomposition of the protonated carbinolamine than that in the antecedent equilibrium.

The reaction rate decreases in the pH range 8·5 to 12 (in some cases it becomes pH-independent) (Fig. 1). Again the reaction rate decrease can be explained by decreasing concentration of the dipolar ion *IIa*, provided that water molecules act as nucleophile. In the cases where pH-independence was observed it is necessary to consider hydroxyl ion as the nucleophile reacting with the form *IIa*. Fig. 2 represents the influence of substituents on the reaction rate ($\varrho = 1 \cdot 10$ at pH 13·02). Both the hydrolysis rate increase with increasing pH and the substituent effects suggest that the rate-limiting step consists in addition of hydroxyl ions to the anion *IIc*.

In conclusion it can be stated that the presence of carboxylic group in the position 2 of benzylideneanilines decreases their reactivity with water in pH range 2−6. In this pH region the competing cyclization to 3-anilinophthalides (which decreases concentration of the reactive open form) is most significant.

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