EFFECT OF OH^- CONCENTRATION ON ALKALINE HYDROLYSIS OF DIPHENYL (4-NITROPHENYL) PHOSPHATE CATALYZED BY 2-IODOSOBENZOIC AND 3-IODOSO-2-NAPHTHOIC ACIDS

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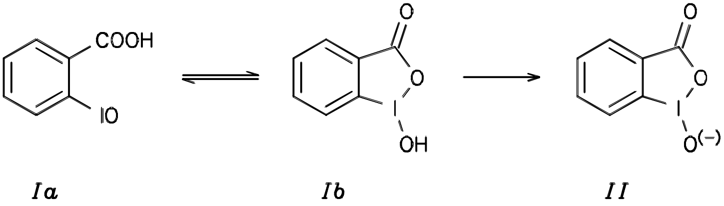
Received February 24, 1993
Accepted April 15, 1993

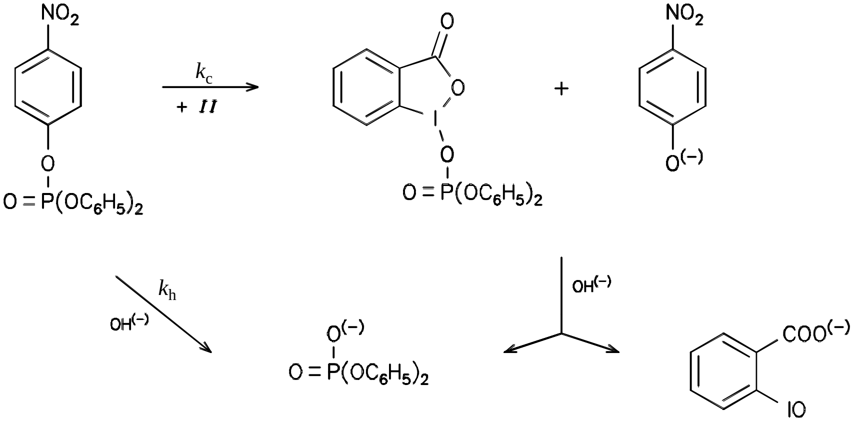
The hydrolysis of diphenyl (4-nitrophenyl) phosphate catalyzed by 2-iodosobenzoic and 3-iodoso-2-naphthoic acids has been studied at different pH values in the presence of hexadecyltrimethylammonium bromide as a micellar agent. It was found that 3-iodoso-2-naphthoic acid is better catalyst than 2-iodosobenzoic acid. At amounts of the acids higher than stoichiometric, the reaction is independent of pH in the 8.00 to 10.00 region while on using substoichiometric amounts, the reaction rate depends on OH^- ion concentration only when the acid to diphenyl (4-nitrophenyl) phosphate molar ratio amounts to 12.5 : 1 for 2-iodosobenzoic acid and 6.25 : 1 for 3-iodoso-2-naphthoic acid.

Polyvalent iodine derivatives having the iodoso (IO) or iodyl (IO_2) group in *ortho*-position to the carboxyl group (*Ia*) exist as valence tautomers[1,2] (*Ib*). In the alkaline region, the dissociation of 1-oxido-1,2-benziodoxol-3(1*H*)-one (*Ib*, $pK_a = 7.25$) produces the strong nucleophile *II* which is the efficient hydrolytic catalyst[3,4] (Scheme 1). Mechanism of the hydrolysis for diphenyl (4-nitrophenyl) phosphate as an example is depicted[5] in Scheme 2. The first step involves the attack of the anion *II* on the phosphate, giving phenoxide ion and the compound of *II* with the ester residue. In the second step the latter compound suffers decomposition by the action of OH^- ion.



SCHEME 1

The aim of the present work was to test catalytic efficiency of the so far not synthesized 3-iodoso-2-naphthoic acid and to extend thus data on the action of the catalysts of this type. Special attention has been paid to the examination of the still not fully studied reaction factors such as the pH effect at different concentration conditions. For this purpose the alkaline hydrolysis of diphenyl (4-nitrophenyl) phosphate catalyzed by the above acid and by 2-iodosobenzoic acid (taken for comparison) has been chosen as a model reaction.



SCHEME 2

EXPERIMENTAL

Chemicals

2-Iodosobenzoic acid (*Ia*) was prepared as reported[6,7] and obtained in 82% yield (m.p. 231 °C, reported[2] 230 °C), the activity of the iodoso group determined iodometrically was 99 %.

3-Iodoso-2-naphthoic acid (*IIIa*) was prepared by a two-step procedure. In the first step, 3-amino-2-naphthoic acid was converted into 3-iodo-2-naphthoic acid, using procedure reported by Wachter[6] (the route worked out by Goldstein and Cornamusaz[8] did not yield satisfactory results). The acid was obtained in 30% yield (m.p. 211 – 213 °C, reported[8] 214 °C). In the subsequent step involving the chlorination and hydrolysis[7] of 3-iodoso-2-naphthoic acid in glacial acetic acid as the solvent, 3-iodoso-2-naphthoic acid was obtained in 36% yield, melting at 222 – 224 °C. For $C_{11}H_7IO_3$ (318.1) calculated: 42.05% C, 2.23% H, 40.42% I; found: 41.97% C, 2.27% H, 40.52% I. Because of the insolubility of the acid in acidic medium, the activity of the iodoso group could not been determined iodometrically.

Diphenyl (4-nitrophenyl) phosphate, prepared as reported[9,10], was recrystallized three times from heptane, giving 45% yield of the product melting at 49 °C (reported[10] 49 – 51 °C).

Kinetic Measurements

The rate of the hydrolysis of diphenyl (4-nitrophenyl) phosphate was measured at 20 °C spectrophotometrically at a constant wavelength of 402 nm (i.e. at the maximum of the absorbance of the formed 4-nitrophenoxide ion). The Spekol 210 (Zeiss Jena, Germany) spectrophotometer used was modified for the direct input via A/D convertor to IBM XT computer. Measurements were carried out at pH values 10.00, 9.00, and 8.00, using a borate buffer prepared in deionized redistilled water (H_3BO_3 concentration 0.015 mol dm^{-3}, after adjusting the appropriate pH value by addition of calculated amount of 0.1 M NaOH, the ionic strength was made to $\mu = 0.1$ mol dm^{-3} by adding NaBr). The hexadecyltrimethylammonium bromide (HDTAB) used was recrystallized twice from methanol. The pH value of the buffer was checked by a digital pH meter OP-208 (Radelkis, Hungary) with the use of a combined glass electrode OP 0808 P (of the same producer). The calibration buffers were a phosphate buffer of pH 7.00 and a borate buffer of pH 9.00. Hydrolysis was carried out in a 1 cm glass cell into which 2 cm^3 of the buffer solution of the catalyst (2-iodosobenzoic or 3-iodoso-2-naphthoic acid) and HDTAB of required pH value were introduced. The reaction was started by injection of 0.02 cm^3 of dioxane solution of diphenyl (4-nitrophenyl) phosphate ($c = 2.00 \cdot 10^{-3}$ mol dm^{-3}). The first-order rate constants k (in s^{-1}) were calculated from the relation $A_{ti} = A_\infty - (A_\infty - A_0) \exp^{-kt_i}$, where A_0 is the absorbance in time t_0, A_{ti} is the absorbance in time t_i and A_∞ is the absorbance in infinite time. The experimental error was 5% at maximum for the whole examined region.

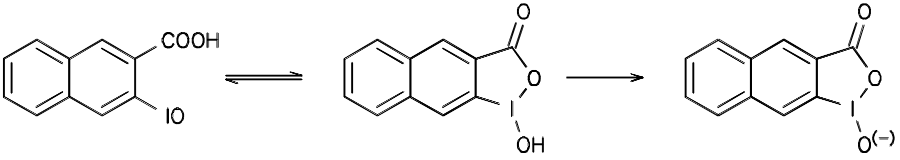
Dissociation Constants

Dissociation constants of l-oxido-1,2-benziodoxol-3(1*H*)-one (*Ib*) and 3-iodoso-2-naphthoic acid at 20 °C were measured with the use of an automated burette OP-930 (Radelkis, Hungary) in the following way: a total of $5 \cdot 10^{-4}$ mol of the substance was dissolved in 100 cm^3 of redistilled water containing $1 \cdot 10^{-3}$ mol dm^{-3} HDTAB concentration and then the solution was titrated by constant 0.1 cm^3-additions of 0.1 M NaOH while following pH (under conditions identical with those used in kinetic measurements). Then p*K*a value was determined by graphical derivation of the pH vs NaOH volume dependence.

RESULTS AND DISCUSSION

For purposes of comparison of both acids prepared, we have first measured their dissociation constants. The pK_a value found for the benzoic acid *Ia* (7.05 ± 0.05) agrees well with reported values which vary from 6.22 (ref.[2], measured in a nonmicellar medium) up to 7.25 (ref.[3]), although our data were obtained by the different method (cf. ref.[3]). The pK_a value of 3-iodoso-2-naphthoic acid was found to be 6.80 ± 0.05. With regard to the common structural features of both acids *Ia* and *IIIa* which at the same time ensure conditions for tautomeric substance formation[11] as well as due to similar dissociation constants, one can suppose that also the acid *IIIa* exists in its valence tautomeric form *IIIb* in alkaline medium (Scheme 3).

The evaluation of the hydrolytic activity of both acids was made by comparison with the noncatalyzed hydrolysis of diphenyl (4-nitrophenyl) phosphate carried out in the presence of HDTAB as the micellar agent. The comparison was based on the maximum rate constants k_{max} (s^{-1}) which were determined from the rate dependence on HDTAB concentration, having the values $2.46 \cdot 10^{-3}$ s^{-1} at pH 10.00, $6.20 \cdot 10^{-4}$ at pH 9.00, and $1.50 \cdot 10^{-4}$ s^{-1} at pH 8.00. A typical dependence of k (s^{-1}) of the hydrolysis of diphenyl (4-nitrophenyl) phosphate on HDTAB concentration in the presence of the higher than stoichiometric amount of *IIIa* at pH 8.00, 9.00, and 10.00 is shown in Fig. 1, the one obtained in the presence of the substoichiometric amount of the catalysts at the same pH values is presented in Fig. 2. Similar dependences were found also for 2-iodosobenzoic acid *Ia*. As evident from Figs 1 and 2, there exists here a sharp maximum on the *k* vs HDTAB concentration plot which lies in the 0.80 – 1.00 . 10^{-3} mol dm^{-3} region. This region is identical with the values at which k_{max} were determined in the case of the



IIIa *IIIb* *IV*

SCHEME 3

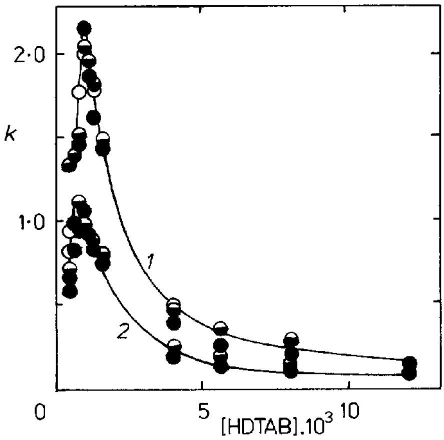


FIG. 1

Rate constant *k* (s^{-1}) of hydrolysis of diphenyl (4-nitrophenyl) phosphate (2 . 10^{-3} mol dm^{-3}) in dependence on concentration of hexadecyltrimethylammonium bromide (HDTAB, mol dm^{-3}) in the presence of 3-iodoso-2-naphthoic acid of concentrations *1* 2.5 . 10^{-2} mol dm^{-3}, *2* 1.25 . 10^{-2} mol dm^{-3} at pH 10.00 (❍), 9.00 (❍), and 8.00 (●) (0.015 M borate buffer, μ = 0.1 mol dm^{-3}, *t* = 20 °C)

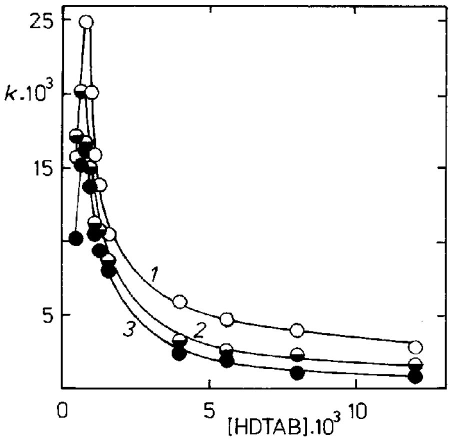


FIG. 2

Rate constant *k* (s^{-1}) of the hydrolysis (see Fig. 1) in the presence of 3-iodoso-2-naphthoic acid of the concentration 1.63 . 10^{-4} mol dm^{-3} at pH 10.00 (*1*) , 9.00 (*2*), and 8.00 (*3*) (other conditions see Fig. 1) noncatalyzed hydrolysis. From Fig. 1 it becomes further clear that the rate of diphenyl (4-nitrophenyl) phosphate hydrolysis in the presence of the catalysts in stoichiometric excess is independent of OH^- ions concentration and depends only on the concentration of the acids *Ia* and *IIIa*. This provides support for the proposed mechanism of the hydrolysis[5] which involves substances *II* or *IV* as the attacking agent. The highest rate constants observed for the acids *Ia* and *IIIa* as catalysts, designated as $k(Ia)$ and $k(IIIa)$, respectively, are presented in Table I. The k/k_{max} ratio, designated as k_a has been taken as the measure of the catalytic activity of the corresponding acid, and the k_r values ($k_r = k(IIIa)/k(Ia)$) were used for estimation of the relative activity of the acid *IIIa* in relation to the acid *Ia*. The k_r values document that *IIIa* is the better catalyst than *Ia*, and that roughly 4.8 times at the catalyst to substrate ratio 12.5 : 1 and about 5.1 times at the ratio amounting to 6.25 to 1. The high activity of 3-iodoso-2-naphthoic acid is

TABLE I

Dependence of rate constants, k (s^{-1}), of the alkaline hydrolysis of diphenyl (4-nitrophenyl) phosphate at pH 8 – 10 on the relative amount of 2-iodosobenzoic (*Ia*) and 3-iodoso-2-naphthoic (*IIIa*) acids in the presence of HDTAB as a micellar agent at 20 °C (for other conditions see Experimental)

Ia (*IIIa*) $c \cdot 10^4$ mol dm^{-3}	*Ia* (*IIIa*) : phosphate molar ratio	pH	*Ia*[a]		*IIIa*[b]		k_r[c]
			$k(Ia) \cdot 10^3$	$k_a(Ia)$	$k(IIIa) \cdot 10^3$	$k_a(IIIa)$	
250	12.50 : 1	10.00	422	172	2 010	817	4.75
		9.00	445	718	2 060	3 323	4.63
		8.00	423	2 820	2 170	14 466	5.13
125	6.25 : 1	10.00	216	88	1 130	459	5.22
		9.00	226	365	1 130	1 823	5.00
		8.00	210	1 400	1 080	7 200	5.14
20	1 : 1	10.00	437	18	242	98	5.53
		9.00	424	68	234	377	5.44
		8.00	373	249	235	1 567	6.29
3.25	1 : 6.25	10.00	107	4	42.1	17	3.93
		9.00	88	14	38.3	62	4.33
		8.00	75	50	33.8	225	4.50
1.63	1 : 12.5	10.00	85	3.5	24.9	10	3.30
		9.00	58	9	20.2	33	3.49
		8.00	41	27	16.2	108	3.93

[a] $k(Ia)$ denotes the maximum rate constant found in the presence of acid *Ia*, $k_a(Ia)$ denotes the relative rate constant related to the maximum constant of the noncatalyzed hydrolysis expressed by the ratio $k(Ia) : k_{max}$. [b] $k(IIIa)$ and $k_a(IIIa)$ are defined similarly to the constants for *Ia* in note *a*. [c] Relative reactivity of acid *IIIa* with respect to acid *Ia*, k_r, is expressed by the ratio of the maximum rate constants ($k(IIIa) : k(Ia)$).

surprising. The reason can be likely looked for by comparison with the catalysts in which the benzene ring of the acid *Ia* was substituted via the oxygen in position 5 by a long nonbranched alkyl or by a quaternary ammonium group (cf. refs[11,12]), which ensured their easy comicellization with HDTAB micelles. In the case of the acid *IIIa*, such an effect could be made possible by the higher hydrophobicity of the naphthalene ring compared to benzene one. The difference in interactions between *Ia* or *IIIa* molecules and HDTAB micelles is apparent also from the course of the k vs HDTAB concentration dependences. Thus, while with *Ia* the ratio of the maximum rate constant to constant k at HDTAB concentration $12 \cdot 10^{-3}$ mol dm^{-3} equals to 3.7, the same ratio for *IIIa* is 13.3 (for the same catalyst concentration in both cases $2.5 \cdot 10^{-2}$ mol dm^{-3}). The rate constant of the hydrolysis catalyzed by *IIIa* is more (about 3.6 times) dependent on HDTAB concentration, when compared to that catalyzed by *Ia*. The same conclusions can be deduced also from data obtained at the catalysts concentration $1.25 \cdot 10^{-2}$ mol dm^{-3}, regardless of the pH value. When studying the substances with tenside properties, it has been found that at the higher then stoichiometric amounts of the catalyst, the components react frequently as “burst kinetic”. However, with *IIIa* such a phenomenon has not been observed, and the absorbance versus time dependence always obeys the first-order kinetics.

Similarly to the above discussed cases, also on using stoichiometric or substoichiometric amounts, the acid *IIIa* is more active than *Ia*. This is documented by k_r values (Table I) where the relative rate acceleration (k_r) compared to *Ia* was 5.8 at the catalyst to substrate ratio 1 : 1, 4.25 at the ratio 1 : 6.25, and 3.6 in average at the ratio 1 : 12.5.

With both catalysts we have further found a linear dependence of k_a on the catalyst to substrate ratio (designated as X).

For *Ia*:

$$k_a = 224.00\,X + 13.47 \qquad (\text{pH } 8.00)$$
$$k_a = 56.98\,X + 7.00 \qquad (\text{pH } 9.00)$$
$$k_a = 13.56\,X + 2.93 \qquad (\text{pH } 10.00)$$

For *IIIa*:

$$k_a = 1\,144.00\,X + 138.45 \qquad (\text{pH } 8.00)$$
$$k_a = 265.73\,X + 63.87 \qquad (\text{pH } 9.00)$$
$$k_a = 65.34\,X + 19.85 \qquad (\text{pH } 10.00)$$

For all the measurements, the correlation coefficient was higher than 0.998. From the above relations it becomes evident that the catalytic activity of both acids is the most efficiently utilized at pH 8.00, since it is this pH at which k_a attains the highest value.

A more detailed evaluation of the effect of the catalysts stems from the fact that diphenyl (4-nitrophenyl) phosphate reacts both with *II* or *IV* and with OH^- ions. The overall reaction is depicted in Scheme 2 by two parallel steps with the rate constants k_c

and k_h (for the hydrolysis by OH^-). The observed rate constant is then given as $k = k_c + k_h$, where k_c is the rate constant of the hydrolysis induced solely by the catalyst *Ia* or *IIIa*, and k_h is the rate constant of the simple alkaline hydrolysis. The measurements carried out at pH 8.00 should be also corrected with respect to the not fully ionized form of the catalyst *II*. The dissociation constant of *Ib*, obtained as an average of several measurements, was 7.05 ± 0.05, which at pH 8.00 corresponds to about 90% ionization of the catalyst *Ib*. On recalculating this value to 100% ionization, k_c has to be corrected by a factor of 1.1, and the correction equation has the form $k_c' = 1.1\,k_c$. The dissociation constant for *IIIb* 6.80 ± 0.05 corresponds at pH 8.00 to ca 95% ionization, and the correction factor is here 1.05 (the correction equation $k_c' = 1.05\,k_c$). The corrected values of the rate constant k_c (i.e. k_c') in dependence on pH are given in Fig. 3. As it is seen, the effect of pH on the rate of hydrolysis catalyzed by *Ia* begins to play a role only at the substoichiometric amount of the catalyst 1 : 12.5. On the other hand, in the case of *IIIa*, the pH effect is observed already at the ratio 1 : 6.25, and the dependence is by far more distinct compared to *Ia*.

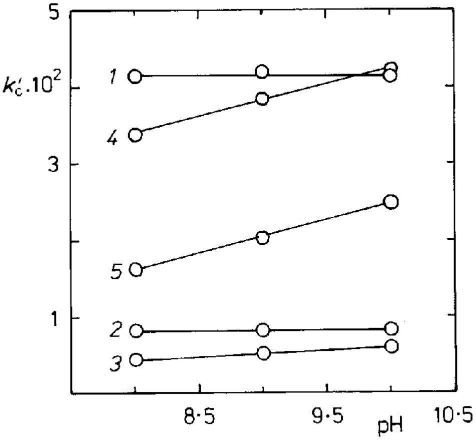


FIG. 3

Corrected rate constant of the hydrolysis of diphenyl (4-nitrophenyl) phosphate k_c' (s^{-1}) in dependence on pH in the presence of 2-iodosobenzoic acid of concentrations *1* 2 . 10^{-3}, *2* 3.25 . 10^{-4}, and *3* 1.63 . 10^{-4} mol dm^{-3}, and of 3-iodoso-2-naphthoic acid of concentrations *4* 3.25 . 10^{-4} and *5* 1.63 . 10^{-4} mol dm^{-3}

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Translated by J. Hetflejs.