ALKALINE HYDROLYSIS OF 4-NITROPHENYL ACETATE AND DIPHENYL (4-NITROPHENYL) PHOSPHATE CATALYZED BY IODOSOARENESULFONIC ACIDS

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Alkaline hydrolysis of 4-nitrophenyl acetate and of diphenyl (4-nitrophenyl) phosphate catalyzed by 2-iodosobenzenesulfonic and 2-iodoso-1-naphthalenesulfonic acids was studied in the presence of hexadecyltrimethylammonium bromide as the micellar agent. It was found that 2-iodosobenzene-sulfonic acid is the better catalyst for the hydrolysis of phenyl acetate while 2-iodoso-1-naphthalene-sulfonic acid is more efficient for the hydrolysis of the phosphate.

It has been known for long time that 2-iodosobenzoic acid and derivatives thereof are efficient hydrolytic catalysts in a micellar medium[1]. Its catalytic activity is ascribed to the tautomeric anion formed in the alkaline medium from 1-oxido-1,2-benziodoxol-3(1*H*)-one (Scheme 1). However, the substitution of the important carboxy group forming the heterocyclic ring for another group capable of similar ring formation has not so far been studied. We have expected that sulfonic acid group could behave analogously.
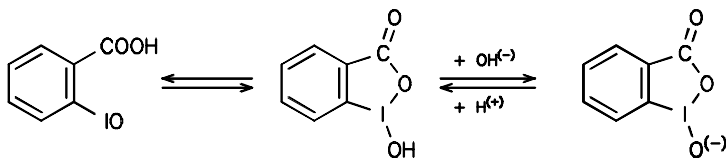
SCHEME 1

Therefore, in the present work we report on verification of this assumption, using 2-iodosobenzenesulfonic and 2-iodoso-1-naphthalenesulfonic acids as catalysts for the hydrolyses of 4-nitrophenyl acetate and diphenyl (4-nitrophenyl) phosphate as model reactions.

EXPERIMENTAL

Chemicals

4-Nitrophenyl acetate (*I*) was prepared as reported[2] in 57% yield, m.p. 82 °C (reported[2] m.p. 82 – 83 °C). Diphenyl (4-nitrophenyl) phosphate (*II*) was obtained by a two-step procedure[3,4] in overall 64% yield, m.p. 49 °C (reported[4] m.p. 49 – 51 °C).

2-Iodosobenzenesulfonic acid (III) *and 2-iodoso-1-naphthalenesulfonic acid* (IV). Both acids were prepared by the same procedure, starting from the corresponding amino acid which was subjected to diazotization[5]. The diazonium salts were then reacted with potassium iodide, yielding 2-iodo-benzenesulfonic acid (70%; for $C_6H_5IO_3S$ (284.1) calculated: 25.36% C, 1.76% H, 11.27% S; found: 25.32% C, 1.75% H, 11.22% S) and 2-iodo-1-naphthalenesulfonic acid (78% yield, for $C_{10}H_7IO_3S$ (334.1) calculated: 35.94% C, 2.09% H, 9.58% S; found: 35.89% C, 2.00% H, 9.59% S), respectively.

The final iodosoarenesulfonic acids were then obtained by chlorination[6] of 0.05 mol of the corresponding iodo acid described above by gaseous chlorine, using acetic acid as the solvent. The di-chloroiodo derivative formed was immediately subjected to base hydrolysis for 2 h. After acidification with diluted hydrochloric acid followed by washing with water, the product was dried in a dessicator at 40 °C for 24 h, yielding 2-iodosobenzenesulfonic acid (6.0 g, 40%) with the content of the iodoso group 97.6% (determined iodometrically); for $C_6H_5IO_4S$ (300.1) calculated: 24.00% C, 1.67% H, 10.67% S; found: 23.95% C, 1.66% H, 10.62% S and 2-iodoso-1-naphthalenesulfonic acid (13.6 g, 78%) with the content of the iodoso group 98.4% (determined iodometrically); for $C_{10}H_7IO_4S$ (350.1) calculated: 34.29% C, 2.00% H, 9.14% S; found: 34.25% C, 1.97% H, 9.17% S.

Kinetic Measurements

Rate of the reactions was measured in a termostatted cell of Specord M-40 (Zeiss, Jena) spectro-photometer at 20 ± 0.2 °C and at a constant wavelength of 402 nm corresponding to the maximum of the absorbance of the formed 4-nitrophenoxide ion. The measurements were carried out in a borate buffer (0.015 mol dm^{-3}) of pH 10.00 and the ionic strength μ = 0.047 mol dm^{-3}, which was prepared with the use of deionized and redistilled water. 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 (the same producer). The calibration buffers were a phosphate buffer of pH 7.00 and a borate buffer of pH 9.00. The reaction was started by injection of 0.05 cm^3 of methanolic 4-nitrophenyl acetate (or of diphenyl (4-nitrophenyl) phosphate dissolved in dioxane) to 5 cm^3 of the solution of the acid *III* or *IV* and hexadecyltrimethylammonium bromide (HDTAB) placed in a 2 cm cell. The time from the injection and mixing of the substrate up to the first measured value of absorbance in the programme "cycle" of the spectrophotometer was measured with a stop watch and was added to the time values of the cycles. The first order rate constants of the hydrolysis k (s^{-1}) were calculated from the relation $A_{ti} = A_\infty - (A_\infty - A_0) \exp^{-kti}$ (A_0 is the absorbance in time t_0, A_{ti} is the absorbance in time t_i, and A_∞ is the absorbance in the infinite time). The experimental error was 5% at maximum for the whole range of the measurements.

Dissociation Constants

Dissociation constants of both acids were measured with the use of an automated burette OP-930 (Radelkis, Hungary) at 20 °C. A total of 5 . 10^{-4} mol of the acid *III* or *IV* was dissolved in 100 cm^3 of redistilled water containing 1 . 10^{-3} mol dm^{-3} HDTAB and the solution was titrated with constant

0.1 cm^3 additions of 0.1 mol dm^{-3} NaOH solution while following pH changes. The titration curve was differentiated to obtain the point of inflexion, which was taken as pK_a.

RESULTS AND DISCUSSION

To compare the properties of both acids *III* and *IV*, we have determined first their dissociation constants pK_a (see Experimental) which were found to be 6.6 ± 0.1 for the iodosobenzenesulfonic acid *III* and 7.9 ± 0.1 for the iodosonaphthalenesulfonic acid *IV*. The micellar agent concentration (1 . 10^{-3} mol dm^{-3}) was chosen close to that used in the kinetic study.
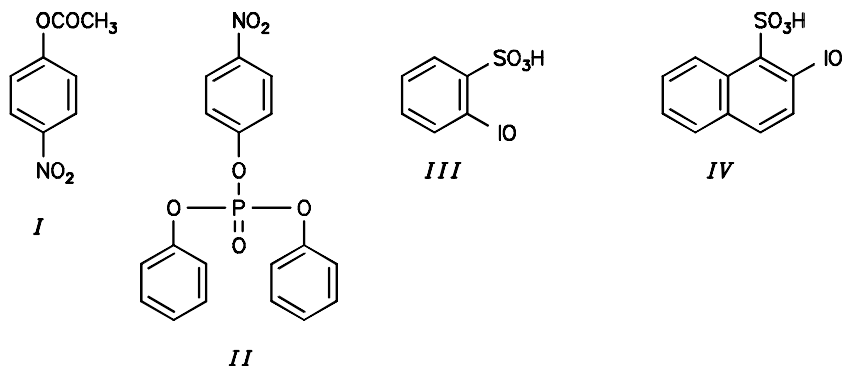
As already mentioned, the catalytic activity of both acids has been tested in the alkaline hydrolysis of 4-nitrophenyl acetate (*I*) and of diphenyl (4-nitrophenyl) phosphate (*II*). It was assumed that the acids behave analogously to 2-iodosobenzoic acid[7] in forming tautomers, the structure of which is demonstrated on example of the iodosobenzenesulfonic acid in Scheme 2 (see formula *IIIa*) with its subsequent dissociation. The course of the hydrolysis of 4-nitrophenyl acetate catalyzed by the acid *III* is depicted in Scheme 3. A similar scheme could be formulated also for the acid *IV*.
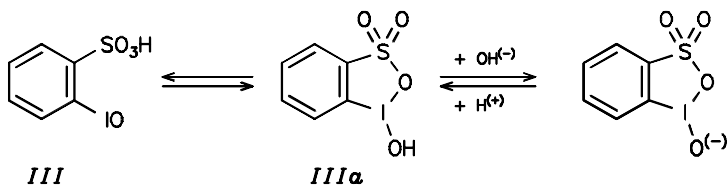
Scheme 2

As shown in Fig. 1, for both acids the first-order rate constants k of the hydrolysis of the nitrophenyl acetate I increase with the acid concentrations over the whole concentration region chosen ($0.16 - 1.12 \cdot 10^{-2}$ mol dm^{-3}). At the same time, the constant k increases also with HDTAB concentration, then attains a maximum, after which it slowly decreases. The optimal concentration of HDTAB lays around $8.0 \cdot 10^{-3}$ mol dm^{-3}.

In this connection it should be mentioned that the experimental rate constants k include the effect of both the acid and the tenzide (HDTAB). In order to determine the catalytic effect of the acid, the effect of the tenzide proper has to be ascertained. For comparative purposes, the k vs [HDTAB] dependences for the hydrolysis of both esters I and II carried out in the presence of only the tenzide (i.e. in the absence of III or IV) are represented graphically in Figs 1 and 2 (see curves 1 in both figures). From these curves the maximum rate constants of hydrolysis, k_a, were read , being $5.32 \cdot 10^{-3}$ s^{-1} for the acetate I and $2.45 \cdot 10^{-3}$ s^{-1} for the phosphate II.

With the aim to evaluate the hydrolytic activity of the arenesulfonic acids III and IV, we have also determined under chosen standard conditions (i.e. in a buffer of pH 10.00 and at the ionic strength 0.047 mol dm^{-3}) the rate constant of the alkaline hydrolysis

FIG. 1
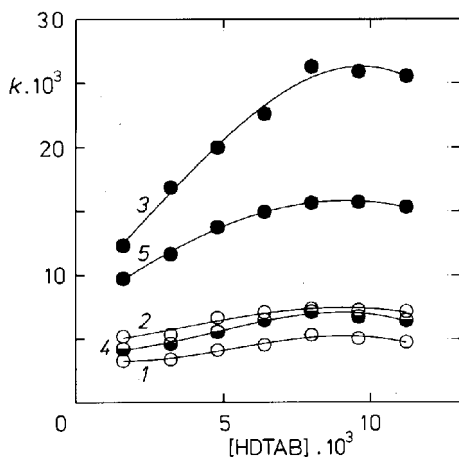
Rate constant, k (s^{-1}), of hydrolysis of 4-nitrophenyl acetate (I) ($c = 8.76 \cdot 10^{-4}$ mol dm^{-3}) in dependence on HDTAB concentration (mol dm^{-3}) at pH 10.00 and $\mu = 0.043$ mol dm^{-3} (1) and in the presence of 2-iodosobenzenesulfonic acid (III) of the concentration $1 \cdot 10^{-4}$ (2) and $1.2 \cdot 10^{-3}$ mol dm^{-3} (3), and in the presence of 2-iodoso-1-naphthalenesulfonic acid of the concentration $1 \cdot 10^{-4}$ (4) and $1.2 \cdot 10^{-3}$ mol dm^{-3} (5)
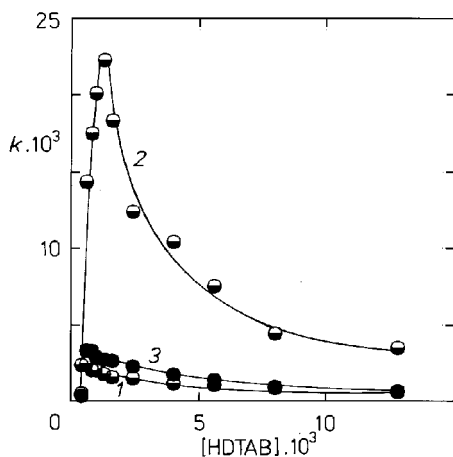
FIG. 2

Rate constant, k (s^{-1}), of hydrolysis of diphenyl (4-nitrophenyl) phosphate (II) ($c = 2 \cdot 10^{-3}$ mol dm^{-3}) in dependence on HDTAB concentration (mol dm^{-3}) at pH 10.00 and $\mu = 0.043$ mol dm^{-3} (1) and in the presence of 0.0125 mol dm^{-3} 2-iodoso-1-naphthalenesulfonic acid (2) and of $1.6 \cdot 10^{-4}$ mol dm^{-3} 2-iodosobenzenesulfonic acid (3)

proceeding without addition of the tenzide, k_h, which equaled to $1.17 \cdot 10^{-3} \text{ s}^{-1}$ for the acetate *I* and $1.26 \cdot 10^{-4} \text{ s}^{-1}$ for the phosphate *II*.

Based on these data, with the acid *III*, the greatest rate acceleration of the hydrolysis of the phenyl acetate *I* is achieved at the acid concentration $1.2 \cdot 10^{-3} \text{ mol dm}^{-3}$, where the k/k_h ratio is 24.5. When compared with the rate obtained for the tenzide proper (k/k_a), the rate of the hydrolysis in the presence of the acid *III* increases roughly five times. It is worth mentioning that the increase of the acid concentration above the mentioned value, i.e. above $1.2 \cdot 10^{-3} \text{ mol dm}^{-3}$, does not affect the rate of the hydrolysis of the nitrophenyl acetate *I*.

A similar comparison for the acid *IV* is shown in Fig. 1 (curves *4* and *5*) and documents similar properties of both acids (optimum HDTAB concentration is again $8.0 - 9.6 \cdot 10^{-3} \text{ mol dm}^{-3}$). Also here the maximum k/k_h ratio was obtained at the acid *IV* concentration of $1.2 \cdot 10^{-3} \text{ mol dm}^{-3}$, amounting to 13.4. When compared to the micellar medium as such, the rate increased here ca three times (compare with the factor of 5 obtained for the acid *III*).

The maximum rate constants k of the hydrolysis of the acetate *I* obtained with the other acid *III* and *IV* concentrations are listed in Table I, along with the k/k_a and k/k_h values.

From comparison of the hydrolytic activities of both acids one can conclude that in the case of the hydrolysis of 4-nitrophenyl acetate (*I*), 2-iodosobenzenesulfonic acid
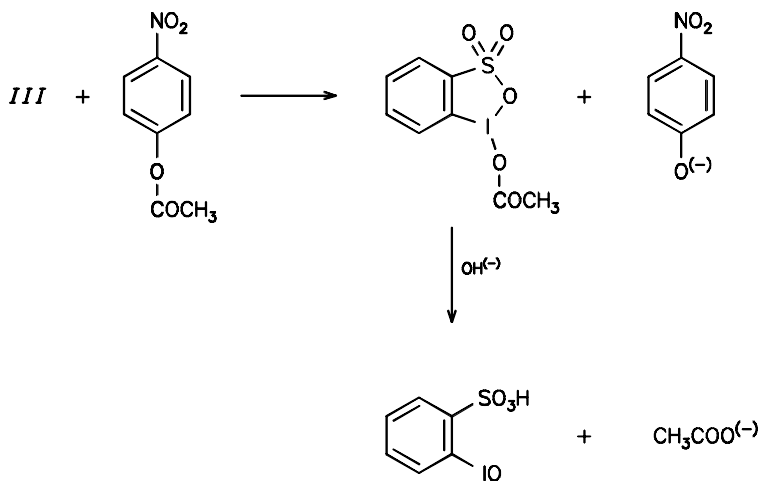
SCHEME 3

TABLE I

Maximum rate constants, k (s^{-1}), of alkaline hydrolysis of 4-nitrophenyl acetate (*I*) at pH 10.00 in dependence on relative amounts of 2-iodosobenzenesulfonic acid (*III*) and 2-iodoso-1-naphthalenesulfonic acid (*IV*) in the presence of HDTAB as the micellar agent at 20 °C (for other conditions see Experimental)

Acid	[Acid] . 10^3 mol dm^{-3}	*III(IV)* : *I* molar ratio	k . 10^{-3} s^{-1}	$k/k_h{}^a$	$k/k_a{}^b$
III	1	11.5 : 1	7.37	6.30	1.39
IV	–	–	7.13	6.10	1.34
III	4	46 : 1	13.33	11.39	2.50
IV	–	–	10.04	8.58	1.89
III	8	92 : 1	22.80	19.49	4.28
IV	–	–	14.40	12.31	2.71
III	12	138 : 1	26.26	24.44	4.94
IV	–	–	15.64	13.37	2.97

[a] k/k_a denotes the ratio of the maximum experimental rate constant of the hydrolysis catalyzed by *III* or *IV* to the rate constant of the hydrolysis carried out without the tenzide and *III* or *IV*. [b] k/k_h denotes the ratio of the maximum experimental rate constant of the reaction catalyzed by *III* or *IV* to the rate constant of the alkaline hydrolysis in the presence of HDTAB but without acids *III* and *IV*.

TABLE II

Maximum rate constants of alkaline hydrolysis of diphenyl (4-nitrophenyl) phosphate at pH 10.00 in dependence on relative amounts of acids *III* and *IV* in the presence of HDTAB as the micellar agent at 20 °C (for other conditions see Experimental)

Acid	[Acid] . 10^3 mol dm^{-3}	*III(IV)* : *I* molar ratio	k . 10^{-3} s^{-1}	$k/k_h{}^a$	$k/k_a{}^a$
IV	100	50: 1	22.29	176.0	9.1
IV	50	25 : 1	17.60	140.0	7.2
III	25	12.5: 1	1.42	11.3	0.6
IV	–	–	16.10	128.0	6.6
III	12.5	6.25: 1	1.68	13.3	0.7
IV	–	–	13.20	105.0	5.4
III	0.32	1 : 6.25	2.69	21.4	1.1
III	0.16	1 : 12.5	3.34	26.5	1.4

[a] For designation see footnotes *a* and *b* in Table I.

(*III*) is the better catalyst than the analogous naphthalene derivative *IV*. This conclusion comports with the pK_a values, according to which the compound *III* is the stronger nucleophile.

Let us turn now to the second of the hydrolytic reactions studied. In harmony with the earlier works it has been found that maxima of the *k* vs [HDTAB] dependences are much more sharper for the hydrolysis of the phosphate *II* compared to the acetate *I* (cf. Figs 1 and 2). The effect of the catalysts *III* and *IV* on this hydrolysis is seen in Fig. 2. The maximum rate constants for the different concentrations of catalysts *III* and *IV* are then listed in Table II (in most cases they were found at HDTAB concentration $0.8 - 1 . 10^{-3}$ mol dm^{-3}). The results further show that on increasing acid *III* concentration, the rate of the phosphate hydrolysis is affected predominantly by the catalytic effect of HDTAB. The rate data obtained seem to indicate that the acid *III* incorporates better into the micelle when present at lower concentrations while the use of the higher concentrations results in inhibition of the reaction. This would be similar to the phenomenon known from the heterogeneous catalysis where for a limited catalyst amount and a high concentration of a reactant, the reaction order decreases owing to the surface coverage to zero order, and further increase of the reactant concentration does not exert any effect on the reaction rate. It seems likely that starting from a certain concentration, the acid *III* would occupy the whole micelle surface, and prevent thus the phosphate *II* from participating in the surface reaction. In contradistinction to the just mentioned compound *III*, the catalyst *IV* behaves as expected, i.e. the rate of the hydrolysis increases linearly with the catalyst concentration.

TABLE III
Comparison of catalytic activity of 2-iodosobenzenesulfonic acid (*III*), 2-iodoso-1-naphthalene-sulfonic acid (*IV*), and 2-iodosobenzoic acid (*V*) in the alkaline (pH 10.00) hydrolysis of diphenyl (4-nitrophenyl) phosphate at 20 °C (other conditions see Experimental)

Acid	[Acid] . 10^3 mol dm^{-3}	*III(IV,V) : II* molar ratio	$k . 10^{3\ a}$ s^{-1}
III	25	12.5 : 1	1.42
IV	–	–	16.10
V	–	–	422.00[b]
III	12.5	6.25 : 1	1.68
IV	–	–	13.20
V	–	–	216.00[b]

[a] See Table II. [b] Taken from ref.[8].

Comparison of the hydrolytic activity of both sulfonic acid derivatives *III* and *IV* with that of 2-iodosobenzoic acid (cf. Table III) documents the higher catalytic efficiency of the carboxylic acid.

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