# CATALYZED ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL ACETATES

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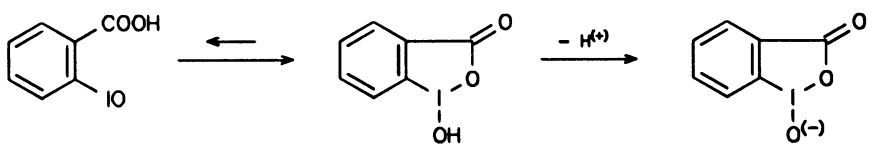
2-Iodosobenzoic acid forming strong nucleophile in alkaline medium – 1-oxido-1,2-benziodoxol-3(1*H*)-one, was used as a catalyst of alkaline hydrolysis of substituted phenyl acetates (4-$NO_2$, 3-$NO_2$, 3-Cl, 4-Br, H, 4-$CH_3$, 3-$CH_3$, 4-$OCH_3$, 3-$OCH_3$) in the presence of hexadecyltrimethylammonium bromide as a micellar agent. It was found that the observed first-order rate constants $k_{obs}$ can be correlated by the Hammett equation: $\log k_{obs} = (-3.29 \pm 0.03) + (1.77 \pm 0.01)\,\sigma$.

In connection with the study of micellar catalysis, attention is also paid to compounds which can accelerate markedly the rate of some reactions. One of these compounds is 2-iodosobenzoic acid and its derivatives which proved to be efficient catalysts of hydrolysis of esters[1]. It was found (Scheme 1) that in this case the catalyst proper is the anion *II* which is formed by hydrogen abstraction from 1-oxido-1,2-benziodoxol-3(1*H*)-one (*Ib*) in alkaline medium[1,2]. Catalytic properties of the anion *II* have most frequently been tested with diphenyl(4-nitrophenyl)phosphate and less with 4-nitrophenyl acetate and 4-nitrophenyl hexanoate. These substrates were chosen due to the easy detection of the 4-nitrophenoxide ion formed by their hydrolysis (for recent review on hydrolysis of esters catalyzed by 2-iodosobenzoic acid and derivatives see ref.[3]).




*Ia* *Ib* *II*

SCHEME 1

However, the effect of the substituent of the ester group on the rate of hydrolysis catalyzed by the above acid has not yet been investigated. For that reason, in the present work the study was performed with the aim to deepen the knowledge about catalytic effectiveness of 2-iodosobenzoic acid and to verify its ability to act as a hydrolytic catalyst for the series of substituted phenyl acetates.

## EXPERIMENTAL

### Chemicals

2-Iodosobenzoic acid was prepared as reported[4] in 82% yield (m.p. 231 °C, literature[5] gives m.p. 230 °C; IO activity 99%). Substituted phenyl acetates of the type 3-$R^1$,4-$R^2$-$C_6H_3COOCCH_3$ were prepared by reported procedures. Their physical properties are presented in Table I.

### Rate Measurements

Rate of the reaction was measured in a thermostatted cell (20 °C) of Specord M-40 (Zeiss, Jena) spectrophotometer, using borate buffer of pH 10.00 and of the ionic strength $\mu$ = 0.047, prepared in deionized redistilled water (0.015 mol $dm^{-3}$ $H_3BO_3$). The pH value of the buffer was checked by digital pH-meter OP-208 (Radelkis, Hungary) with the use of a combined glass electrode OP 0808 (Radelkis, Hungary). The calibration buffers were phosphate buffer of pH 7.00 and borate buffer of pH 9.00 obtained from the Institute of Sera and Vaccinas, Prague. Hydrolysis was carried out in a 2 cm-quartz cell which was filled with 5 ml of the catalyst and hexadecyltrimethylammonium bromide (HDTAB) under the following conditions: $8.75 \cdot 10^{-5}$ mol $dm^{-3}$ 2-iodosobenzoic acid, $5.83 \cdot 10^{-5}$ mol $dm^{-3}$ phenyl acetates (the catalyst to substrate molar ratio 1.5 : 1). The substituted phenyl acetates were dissolved in methanol. The reaction was started by injection of 0.05 $cm^3$ of methanolic ester to

TABLE I
Physical properties of the phenyl acetates 3-$R^1$,4-$R^2$-$C_6H_3OCOCH_3$

| $R^1$ | $R^2$ | M.p. (b.p.)[a], °C found | M.p. (b.p.), °C reported | Ref. |
|---|---|---|---|---|
| H | $NO_2$ | 82 | 82 – 83 | 6 |
| $NO_2$ | H | 55 | 55 – 56 | 7 |
| Cl | H | (237.5) | (238) | 8 |
| H | Br | 21 (237) | 21.5 (235 – 237) | 8 |
| H | H | (196) | (195.7) | 9 |
| $CH_3$ | H | (199) | (198 – 199) | 10 |
| H | $CH_3$ | (212) | (212) | 9 |
| H | $OCH_3$ | 32 (242) | 31 – 32 (243) | 11 |
| $OCH_3$ | H | (254) | (254 – 256) | 12, 13 |

[a] M.p. determined on Boëtius hot plate, b.p. measured in a capillary tube using known procedure.

the solution placed in the 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 added to the time values of the cycles. The measurements were made at the wavelength corresponding to the absorbance of the formed substituted phenolate ion. From the measured absorbance–time dependences we calculated rate constants by a three parameter correlation, using the relation $A_{t_i} = A_\infty - (A_\infty - A_0) \exp^{-k t_i}$ ($A_0$ is the absorbance in time $t_0$, $A_{t_i}$ is the absorbance in time $t_i$ and $A$ is the absorbance in infinite time). The error of the measurement was max. 5% in the whole region of measurements. The so obtained observed first-order rate constants $k_{obs}$ are presented in Figs 1 – 3. The Hammett σ constants were taken from ref.[14].

## RESULTS AND DISCUSSION

Hydrolysis of the substituted phenyl acetates given in Table I in the presence of HDTAB was carried out at the catalyst to substrate molar ratio equaling to 1.5 : 1, as in the region of the wavelengths of the formed phenoxide ions one observes also absorption due to 2-iodosobenzoic acid (except for both nitro derivatives, the maximum absorbance of which is shifted to the higher wavelengths). In order to ensure sufficient accuracy of the given apparatus, the total absorbance was chosen 0.9 at maximum. This corresponds to the initial concentration of 2-iodosobenzoic acid of ca 8.8 . $10^{-5}$ mol dm$^{-3}$ and concentrations of the acetates of ca 5.8 . $10^{-5}$ mol dm$^{-3}$. The procedure is correct only when the concentration (absorbance) of one of both above mentioned compounds remains constant, which is fulfilled here for the iodosobenzoic acid. It is worthy of mentioning that Moss and coworkers[1] prepared the intermediate 1-acetyl-1,2-benziodoxol-3-one (max. absorbance at 276 nm) and measured the rate of its hydrolysis. It was found that the rate of the deacetylation was about 20 times higher compared to $k_{obs}$ obtained by us for the hydrolysis of 4-nitrophenyl acetate in the presence of the acid under comparable reaction conditions. This excludes the possible accumulation of the acetyl derivative during hydrolysis reaction which would interfere with the results. In-

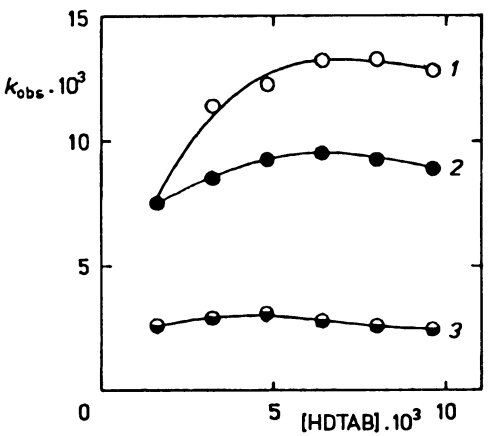



FIG. 1
Rate constant $k_{obs}$ (s$^{-1}$) of hydrolysis of 4-nitrophenyl (*1*), 3-nitrophenyl (*2*), 3-chlorophenyl (*3*) acetates at pH 10.00, μ = 0.047 (8.75 . $10^{-5}$ mol dm$^{-3}$ 2-iodosobenzoic acid, 5.85 . $10^{-5}$ mol dm$^{-3}$ acetate) in dependence on HDTAB concentration (mol dm$^{-3}$)

deed, no increase of the absorbance at 276 nm has been observed in our case. The course of the alkaline hydrolysis of the phenyl acetates in dependence on HDTAB concentration is evident from Figs 1 – 3. It is noteworthy that the maximum of the rate constant–HDTAB concentration dependence lies at 4.8 . $10^{-3}$ mol $dm^{-3}$ HDTAB for most of the esters. It was further found that $k_{obs}$'s can be well correlated with σ substituent constants by Hammett equation (at 4.8 . $10^{-3}$ mol $dm^{-3}$ HDTAB):

$$\log k_{obs} = (-3.29 \pm 0.03) + (1.77 \pm 0.01)\,\sigma, \qquad r = 0.994 .$$

The validity of the Hammett equation demonstrates that the kind of substituent does not influence the nature of the rate determining step of the reaction mechanism. The Hammett correlation in the form:

$$\log k_{obs} = -3.30 + 1.51\,\sigma$$

was obtained[15] in the same buffer also for a different HDTAB concentration (8 . $10^{-3}$ mol $dm^{-3}$ vs 4.8 . $10^{-3}$ in the present work). In spite of this difference, the ρ values (which would theoretically reflect nucleophility of the reagent) can be compared one to another and, as expected, are also well comparable. With respect to the reactions catalyzed by $OH^-$ ions, the higher value of the ρ constant found in this work for the reaction catalyzed by 2-iodosobenzoic acid speaks for the stronger nucleophility of the latter compound.

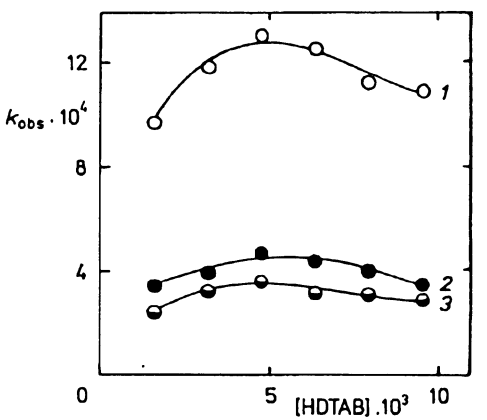



FIG. 2
Rate constant $k_{obs}$ ($s^{-1}$) of hydrolysis of 4-bromophenyl (*1*), phenyl (*2*), and 3-methylphenyl (*3*) acetates in dependence on HDTAB concentration (mol $dm^{-3}$). For conditions see Fig. 1

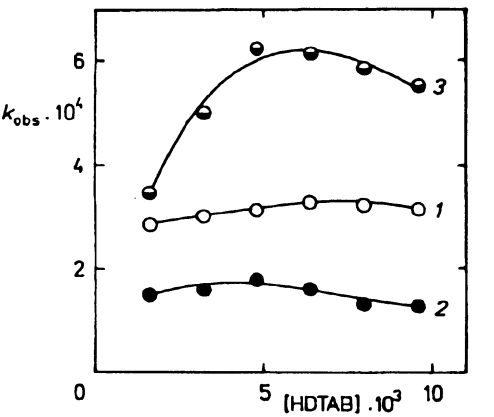



FIG. 3
Rate constant $k_{obs}$ ($s^{-1}$) of hydrolysis of 4-methylphenyl (*1*), 4-methoxyphenyl (*2*), and 3-methoxyphenyl (*3*) acetate in dependence on HDTAB concentration (mol $dm^{-3}$). For conditions see Fig. 1

From the results obtained one can further conclude that the iodosobenzoic acid in micellar medium accelerates the alkaline hydrolysis of all the phenyl acetates studied, and that to such an extent that the same rate of the hydrolysis can be obtained with the half amount of the tenside (HDTAB) compared to the hydrolysis performed under conditions of micellar catalysis (i.e. in the presence of HDTAB only).

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