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ALKALINE HYDROLYSIS OF SUBSTITUTED BENZYL SUBSTITUTED BENZOATES

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The kinetics and mechanism of the alkaline hydrolysis of both acyl- and aryl-substituted benzyl benzoates were studied in 80% (v/v) aqueous acetone at 20, 34, and 40 °C. Each of the substituted benzyl alcohols generated an independent σ–ρ plot which was correlated well with the Hammett equation ($R = 0{\cdot}996$–$0{\cdot}999$). The values of ρ for the acyl moiety showed no tendency either to increase or to decrease with the intrinsic reactivity of the parent benzyl alcohol and were all within $\pm 0{\cdot}098$ of the mean of $2{\cdot}236$. However, the Hammett ρ values for the leaving groups decreased from H to p-NO_2 substituents of the acyl part, in which the values were smaller than those of acyl moieties and fairly accurately obeyed the σ^0 values rather than the σ values. The rate data for benzyl-substituted benzoates were correlated by the Yukawa–Tsuno equation, $\log k/k_0 = 1{\cdot}72(\sigma^0 + 0{\cdot}49\Delta\sigma_{R^-}) - 0{\cdot}020$, $R = 0{\cdot}996$. The results suggested that the alkaline hydrolysis of benzyl benzoates showed a greater sensitivity to acyl than aryl activation, and the rates and activation parameters were largely determined by the addition step. The results are attributed to the preferential partitioning of an unstable tetrahedral intermediate to the products.

INTRODUCTION

A carboxylic ester is hydrolised to a carboxylic acid and an alcohol or phenol when heated with aqueous acid or base. The cleavage of an ester could occur at two different locations, between the acyl group and the oxygen or between the alkyl group and the oxygen. The former acyl–oxygen fission occurs most commonly, although there are some cases in which alkyl–oxygen fission occurs. The most convincing evidence[1] for acyl–oxygen fission is ester hydrolysis comes from tracer studies with ^{18}O. When ethyl propionate labelled with ^{18}O was hydrolysed by OH^- in water, ^{18}O label was found only in EtOH.

Saponification of carboxylic esters also involves acyl–oxygen fission. In early studies, Day and Ingold[2] suggested that alkaline hydrolysis might proceed by two mechanisms, one involving an addition intermediate and the other by direct bimolecular displacement via a transition state. Many workers[3–6] have reported the alkaline hydrolysis of methyl-substituted benzoates, ethyl benzoates and phenyl acetates. Later, Kirsch and Jencks[4] also reported detailed studies on the alkaline hydrolysis of acyl- and aryl-substituted phenyl benzoates in which the ρ value was found to be $1{\cdot}98$ and $1{\cdot}27$ for the substituents in the acyl and aryl portion, respectively. However, detailed studies of substituted benzyl substituted benzoates are scarce.

In this paper, we report the results of the alkaline hydrolysis of benzyl benzoates substituted in both the acyl and aryl moieties, and also discuss the reaction mechanism using the ρ values of both substrates and leaving moieties, resonance parameters and other activation parameters.

EXPERIMENTAL

Materials and solvents. Most of substituted benzyl substituted benzoates were prepared by esterification of sodium salts of substituted benzoic acids with the corresponding benzyl chlorides and triethylamine as catalyst in benzene–water solvent.

The following compounds were prepared by this method and characterized by ^1H NMR spectroscopy and melting point determinations: benzyl p-methoxybenzoate, m.p. 25–26 °C, ^1H NMR ($CDCl_3$) δ 8·0 (d, 2H, $J = 9$ Hz), 7·4 (m, 5H), 6·8 (d, 2H, $J = 9$ Hz), 5·3 (s, 2H), 3·8 (s, 3H) ppm; benzyl p-methylbenzoate, m.p. 35 °C, NMR [$(CD_3)_2C{=}O$] δ 8·0 (d, 2H,-

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$J = 7·5$ Hz), 7·4 (m, 5H), 6·9 (d, 2H, $J = 7·8$ Hz), 5·35 (s, 2H); benzyl *m*-methylbenzoate, m.p. 35 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·0 (d, 2H, $J = 8$ Hz), 7·4 (m, 7H), 5·3 (s, 2H); benzyl *p*-chlorobenzoate, m.p. 28–29 °C, NMR ($CDCl_3$) δ 8·0 (d, 2H, $J = 9$ Hz), 7·4 (m, 7H), 5·3 (s, 2H); benzyl *m*-chlorobenzoate, oil, NMR $[(CD_3)_2C{=}O]$ δ 8·0 (d, 4H), 7·5 (m, 5H), 5·3 (s, 2H); benzyl *m*-nitrobenzoate, m.p. 70–71 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·8 (s, H), 8·4 (m, 3H), 7·4 (m, 5H), 5·3 (s, 2H); benzyl *p*-nitrobenzoate, m.p. 83 °C (lit. m.p. 83·5–84 °C); *p*-methoxybenzyl benzoate, m.p. 34–35 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·1 (m, 2H), 7·5 (m, 5H), 7·0 (d, 2H, $J = 9$ Hz), 5·3 (s, 2H), 3·8 (s, 3H); *p*-methoxybenzyl *p*-chlorobenzoate, m.p. 44–45 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·0 (d, 2H, $J = 7·5$ Hz), 7·4 (d, 4H, $J = 7·5$ Hz) 6·9 (d, 2H, $J = 8$ Hz), 5·3 (s, 2H), 3·8 (s, 3H); *p*-methoxybenzyl *p*-nitrobenzoate, m.p. 911–93 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·3 (m, 4H), 6·9–7·4 (m, 4H), 5·4 (s, 2H), 3·8 (s, 3H); *p*-methylbenzyl benzoate, m.p. 23–25 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·1 (m, 2H), 7·9–7·1 (m, 4H), 5·3 (s, 2H); *p*-methylbenzyl *p*-chlorobenzoate, m.p. 48·5–49 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·2 (d, 2H, $J = 10$ Hz), 7·4–7·1 (m, 6H), 5·4 (s, 2H); *p*-methylbenzyl *p*-nitrobenzoate, m.p. 129 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·3 (d, 2H, $J = 9$ Hz), 7·3–7·1 (m, 6H), 5·3 (s, 2H); *p*-chlorobenzyl benzoate, m.p. 58–59 °C, (lit.[8] m.p. 59 °C); *p*-chlorobenzyl *p*-chlorobenzoate, m.p. 70·5 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·0 (d, 2H, $J = 7·5$ Hz), 7·5–7·3 (m, 6H), 5·3 (s, 2H); *p*-chlorobenzyl *p*-nitrobenzoate, m.p. 106–108 °C, NMR $[(CD_3)_2C{=}O]$ δ 8·3 (s, 4H), 7·4 (d, 4H, $J = 8$ Hz), 5·4 (s, 2H); *m*-nitrobenzyl *p*-nitrobenzoate, m.p. 90 °C, NMR $[(CD_3)_2C{=}O]$ 8·9–8·3 (m, 8H), 5·4 (s, 2H); *p*-nitrobenzyl benzoate, m.p. 87–88 °C (lit.[8] m.p. 88·5 °C); *p*-nitrobenzyl *p*-chlorobenzoate, m.p. 126–128 °C (lit.[9] m.p. 129·5 °C); *p*-nitrobenzyl *p*-nitrobenzoate, m.p. 171 °C (lit.[10] m.p. 171–172 °C).

Benzyl benzoate was of analytical-reagent grade from Merck (Darmstadt, Germany), and was used without further purification.

Sodium *p*-nitrobenzoate was prepared by the addition of an ethanolic solution (200 ml) containing benzoic acid (3·3 g, 0·02 mol) to 10% NaOH solution (20 ml). After stirring, water was separated with a Dean and Stark tube, then the crude product was filtered, washed with EtOH and dried over P_2O_5 *in vacuo* to give pure sodium *p*-nitrobenzoate. Other sodium substituted benzoates were prepared by the same procedure.

Water for kinetics and analysis was obtained by distilling deionized water twice after oxidation by $KMnO_4$.

Acetone was purified as described previously.[11] Briefly, it was refluxed over $KMnO_4$ for 1 day, distilled, dried (K_2CO_3) for 3 days and fractionated by using a 50 cm Widmer distillation column.

The concentration of NaOH and HCl solutions was checked by titration against standard reagents. Measurements of pH were made with a Model 292 pH meter made (Fisher).

Kinetics. The kinetics of the alkaline hydrolysis of benzyl esters were determined in 80% (v/v) aqueous acetone at 20, 34 and 40 °C by means of acid–base titration. The procedure employed for this measurement was essentially as described.[8,12]

The reaction was started by mixing equimolar amounts of the solutions of ester and alkali to give an initial concentration of $(4·2 \pm 0·2) \times 10^{-3}$ mol l^{-1} in the mixture. Samples of 3 ml were withdrawn from the reaction flask at appropriate intervals, quenched with 4 ml of $(4·0 \pm 0·2) \times 10^{-3}$ mol l^{-1} HCl and 5 ml of acetone, and back-titrated with standardized $(4·0 \pm 0·2) \times 10^{-3}$ mol l^{-1} NaOH solution using bromothymol blue as indicator. The end-point was obtained by comparison with a colour standard of sodium benzoate in 80% (v/v) aqueous acetone containing the same amount of indicator as used in the titration. The initial titre, C_0, was determined using the alkaline solution alone. All runs which involved more than 12 measurements followed a second-order kinetic law, covering an 80% extent of reaction. The bimolecular rate constant, k_2, was obtained from the plot of time against $C_x/(C_x - C_0)C_0$, where C_x is the titre at $t = x$.

RESULTS AND DISCUSSION

The second-order rate constants for the alkaline hydrolysis of the substituted benzyl substituted benzoates are given in Table 1. The rate constants show that electron-withdrawing substituents in both the acyl and aryl moieties increase the rate. Since the rate of the reaction is determined largely by the rate of addition of hydroxide ion to the carbonyl group of the benzyl benzoate, electron-withdrawing substituents in the carbonyl group will increase the reactivity of the ester.

The Hammett ρ value is the most quantitative parameter for the measurement of this effect. A Hammett

Table 1. Rate constants ($k_2 \times 10^2$ l mol^{-1} s^{-1}) for alkaline hydrolysis of substituted (X) benzyl substituted (Z) benzoates in 80% (v/v) aqueous acetone at 34 °C

	X					
Z	*p*-CH_3O	*p*-CH_3	H	*p*-Cl	*m*-Br	*p*-NO_2
H	1·89	2·06	2·92	4·40	–	16·3
p-Cl	8·46	8·85	11·1	20·8	–	56·3
p-NO_2	123	140	172	278	360	692

	Z							
X=H	*p*-MeO	*p*-Me	*m*-Me	H	*p*-Cl	*m*-Cl	*m*-NO_2	*p*-NO_2
	1·32	1·76	1·88	2·92	11·1	13·5	38·9	172

Table 2. Hammett σ^0 plots for the alkaline hydrolysis of substituted (X) benzyl substituted (Z) benzoates in 80% (v/v) aqueous acetone at 34 °C

	Z		
Parameter	H	p-Cl	p-NO₂
ρ^0	0·938	0·858	0·763
R	0·996	0·999	0·998
Intercept	−0·039	0·012	−0·005

plot of the kinetic data for alkaline hydrolysis of the substituted benzyl benzoates in 80% aqueous acetone shows a good linear relationship with 0·938 for the ρ_x (ρ_{aryl}) value, holding the acyl moiety constant (Table 2). In dioxane-water (2 : 1), the ρ_x value[13] of the substituted benzyl benzoates is 0·91, which is not very different from our value given above. The values of ρ_x for substituted phenyl benzoates in both water and acetonitrile–water (1 : 2) were 1·10[5] and 1·275[14], respectively.

Additionally, slightly smaller ρ values for the same reactions are obtained in more polar solvents, where the medium is able to stabilize the transition state more effectively and therefore the response to electronic effects of the substituents is less critical.

The substituent effects in the acyl group are considerably larger than those described above for substitution in the aryl group. For example, all of the ρ_z (ρ_{acyl}) values for the alkaline hydrolysis of substituted benzyl substituted benzoates in 80% aqueous acetone at 34 °C are in the range of about 2·07–2·32, as shown in Table 3.

A comparison of ρ_x with ρ_z values in Tables 2 and 3 reveals that the rates of alkaline hydrolysis of benzyl esters are more sensitive to electron-attracting substituents in the acyl portion than in the benzyl oxygen group. This result is consistent with the view that when the substituent is closer to the acyl carbon atom of benzyl benzoates, larger values of ρ are to be expected. Published reports[3,4] on the rates of alkaline hydrolysis of methyl benzoates and phenyl acetates also showed larger ρ_{acyl} than ρ_{aryl} values. It was explained that the slow step for these reactions almost certainly involves the rate of addition of hydroxide ion to the acyl carbon atom, the carbonyl carbon being close to the acyl substituent than to the phenol. Kirsch *et al.*[14] also reported on the alkaline hydrolysis of acyl- and aryl-substituted phenyl benzoates in which the values of ρ_{acyl} (1·982–2·044) were found to be greater than those of ρ_{aryl} (1·181–1·278).

Table 3. Hammett ρ values for the alkaline hydrolysis of substituted (X) benzyl substituted (Z) benzoates in 80% (v/v) aqueous acetone at 34 °C

X	p-CH₃O	p-CH₃	H	p-Cl	p-NO₂
ρ_z	2·286	2·318	2·250	2·261	2·067

Further, in the case of substituted benzyl benzoates the Hammett plots are correlated better by σ^0 than σ in Figure 1. The excellent[15] fit to the σ^0 values of substituents in the aryl moieties may be due to the cancellation of the resonance interactions of substituents and the reaction centre between the initial and final states. In this system, through-conjugation with the reaction site is inhibited by an intervening methylene bond.

A general mechanism of carboxylic ester hydrolysis by hydroxide ion is well known to involve acyl–oxygen cleavage, which is second order in both ester and hydroxide concentration, so direct hydroxide ion attack is involved.

The alkaline hydrolysis of carboxylic esters is a nucleophilic substitution of the alkoxide group by hydroxide ion. It remains to be established whether the mechanisms of this reaction involve concerted one-step displacements or two steps with the intermediate formation of a tetrahedral compound. These alternative mechanisms were considered more or less equally likely until 1950, when elegant work on isotopic exchange was

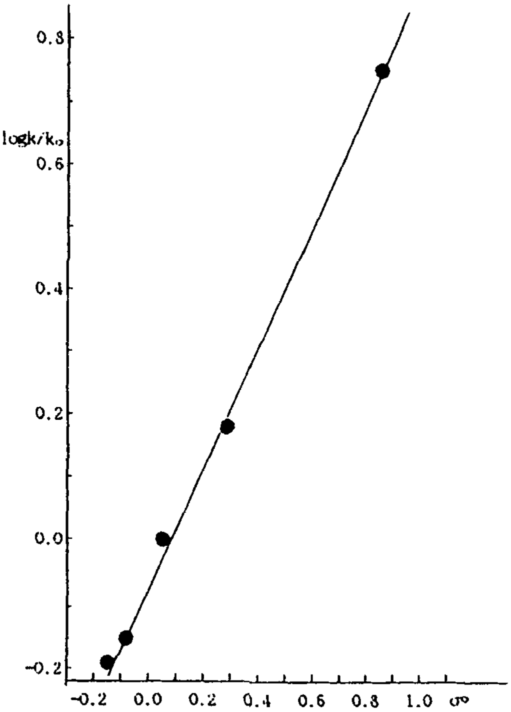
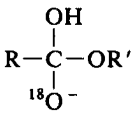


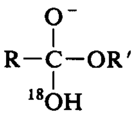
Figure 1. σ^0 plots for the alkaline hydrolysis of substituted benzyl benzoates in 80% (v/v) aqueous acetone at 34 °C

reported by Bender[16] with ^{18}O as tracer. He carried out alkaline hydrolyses of methyl, ethyl and isopropyl benzoates in which the esters were synthesized with the carbonyl oxygen labelled with ^{18}O, and focused, attention on the rectant. Bender[16] found that in alkaline solution the alkyl esters were undergoing not only hydrolysis but also exchange of the ^{18}O with unlabelled oxygen from the solvent. He determined the ratio of the rates of hydrolysis and oxygen exchange, k_h/k_{ex}. The results strongly supported the existence of a tetrahedral intermediate. In contrast to alkyl benzoates, the alkaline hydrolysis of substituted benzyl benzoates, expecially p-methoxybenzyl benzoates, showed large k_h/k_{ex} values. For instance, the k_h/k_{ex} values of methyl benzoate and p-methoxybenzyl benzoate were 5·8 and 192, respectively. The results do not necessarily mean that no tetracovalent intermediate is formed in the case of benzyl esters. The reason can tentatively be explained[6,16] that if the tetrahedral intermediate,



$$R-\overset{\displaystyle OH}{\underset{\displaystyle {}^{18}O^-}{C}}-OR'$$

or



$$R-\overset{\displaystyle O^-}{\underset{\displaystyle {}^{18}OH}{C}}-OR'$$

does not revert to the ester, but goes entirely to the acid, k_h/k_{ex} may be large even for the intermediate. In the case of substituted benzyl benzoates, the same results may be obtained because the formation of benzoic acid relieves steric hindrance.

From the above discussion, the rate of formation of the intermediate is affected by both electronic and steric factors. Even in those cases where oxygen change is not detected, we do not rule out the possibility of an intermediate; it may simply be that it is converted into hydrolysis products much faster than it does anything else.

The cleavage of the alkyl–oxygen bond by nucleophilic agents generally requires high temperatures and/or prolonged reaction times. These conditions would be too vigorous for highly sensitive molecules. Sheehan and Daves[17] reported that sodium thiophenoxide did not affect the cleavage of the less activated benzyl benzoates at 25 °C, but it was found to the extent of 64% at 100 °C, whereas the highly hindered *tert*-butyl ester was stable for 2 h at 100 °C. Less hindered phenacyl benzoates are more easily cleaved at the alkyl–oxygen bond by the action of sodium thiophenoxide below room temperature. It is suggested that sodium thiophenoxide does not affect the cleavage of the less activated benzyl benzoate and sterically hindered *tert*-butyl benzoate.

Table 4. Rate constants ($k_2 \times 10^2$ l mol^{-1} s^{-1}) for alkaline hydrolysis of benzyl substituted benzoates in aqueous acetone at 34 °C

	H_2O (%, v/v)				
Z	10	20	30	40	50
p-CH_3O	–	1·32	–	–	–
p-CH_3	–	1·76	–	–	–
H	4·54	2·92	1·84	1·38	0·911
p-Cl	20·7	11·1	8·65	6·71	4·26
p-NO_2	243	172	101	79·1	54·5
ρ	2·07	2·06	2·18	2·20	2·23
R	0·998	0·996	0·995	0·994	0·996

The rate constants for the alkaline hydrolysis of benzyl substituted benzoates decrease and the ρ_{acyl} values increase with increasing water content, as shown in Table 4. It is considered that the solvation of OH^- with increasing water content decreases the rate of addition of hydroxide anion to the carbonyl group. This result means that addition of hydroxide ion to the carbonyl carbon of the benzyl benzoate is the rate-determining step, because the rate decreases in more rather than less polar solvents. This result also agrees well with the results in Table 1. As shown in the Table 5, the rates and activation parameters are largely determined by the addition step.

Humffray and Ryan[12] determined the rate constants

Table 5. Kinetic data for the alkaline hydrolysis of substituted benzyl p-nitrobenzoates in 80% (v/v) aqueous acetone[a]

	$k_2 \times 10^2$ (l mol^{-1} s^{-1})					
X	25 °C	34 °C	40 °C	$\Delta H^{\neq}$ (kcal mol^{-1})	$-\Delta S^{\neq}$ (e.u.)	$\Delta G^{\neq}$ (kcal mol^{-1})
p-CH_3O	81·9	123	150	6·98	35·5	17·9
p-CH_3	90·0	140	170	7·33	34·1	17·8
H	108	172	205	7·45	33·3	17·7
p-Cl	179	278	338	7·38	32·6	17·4
p-NO_2	576	693	–	3·11	44·6	16·8

[a] All activation data were calculated at 34 °C. 1 kcal = 4·184 kJ.

Table 6. Application of Yukawa–Tsuno equation, $\log (k/k_0) = \rho(\sigma^0 + r\Delta\bar{\sigma}_{R^-} + r\Delta\bar{\sigma}_{P^+})$

Reaction	ρ	r	Ref.
Alkaline hydrolysis, $ArC(O)OCH_2C_6H_5$, 80% (v/v) aqueous acetone, 34 °C	1·72	0·49	This work
Alkaline hydrolysis, ArCOOEt, 85% (v/v) aqueous ethanol 25 °C	2·59	0·25	15
Alkaline hydrolysis, $ArCH_2C(O)OC_6H_5$, 70% (v/v) aqueous acetone, 25 °C	0·978	0·000	18
Solvolysis, ArCHMeCl, 80% (v/v) aqueous acetone, 45 °C	−4·96	1·16	19
Solvolysis, $ArCH_2OTs$, acetic acid, 40 °C	−3·71	1·65	20

Table 7. Brønsted β values for the alkaline hydrolysis of substituted benzoic acid esters[a]

Ester	β	R	Solvent	Temperature (°C)
Substituted benzyl benzoates	−0·678	0·996	80% (v/v) aqueous acetone	34
Substituted benzyl benzoates[6]	−0·668	0·994	Dioxane–water (1 : 2)	25
Substituted benzyl *p*-chlorobenzoates	−0·625	0·993	80% (v/v) aqueous acetone	34
Substitued benzyl *p*-nitrobenzoates	−0·553	0·998	80% (v/v) aqueous acetone	34
Substituted phenyl benzoates[14]	−0·450	0·975	33% (v/v) aqueous acetonitrile	25
Substituted phenyl acetates (general base catalysed)[21]	−0·406	0·963	Aqueous acetate buffer	25

[a] pK_a values of benzyl alcohols were evaluated by $pK_a = 15{\cdot}74 - 1{\cdot}32\sigma$.

for the hydrolysis of substituted phenyl acetates in the Yukawa–Tsuno equation, and found r values of 0·20 and 0·30. In the alkaline hydrolysis of substituted benzyl substituted benzoates in 80% aqueous acetone at 34 °C, we found that the rate constants are very well correlated by the Yukawa–Tsuno equation, $\log k/k_0 = 1{\cdot}72(\sigma^0 + 0{\cdot}49\Delta\bar{\sigma}_{R^-})$ (Table 6). This means that the addition of hydroxide anion to form a charged tetrahedron is consistent with the r values the given.

Brønsted β values of the leaving group for the alkaline hydrolysis of substituted benzyl benzoates are given in Table 7; they are very close to those in Bender's *et al.* work.[13] The values for the hydrolysis of three benzyl benzoates become more negative with introduction of more electron-withdrawing substituents into the acyl moieties. This result indicates that the substituents are able to stabilize the transition state, especially in the case of electron-withdrawing substituents.

These results indicate that the reaction involves a tight transition state or intermediate. Moreover, the large negative entropy values imply an intermediate rather than a transition state. Hence this reaction proceeds via an intermediate going into the substituent H to p-NO_2 in the acyl moieties. Overall, the results suggest that alkaline hydrolysis of benzyl esters proceeds through an unstable tetrahedral intermediate.[22]

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