

## Preparation, Physical Properties, and Kinetics of the Hydrolysis of Substituted $\alpha$ -Chlorobenzyl Benzoates

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There have been prepared 34  $\alpha$ -chlorobenzyl benzoates with substituents in the *para*- or *meta*-position of the acyl or/and benzyl group. Their physical properties have been determined and the kinetics of their hydrolysis in aqueous acetone, acetonitrile, and dioxane solutions has been investigated. The hydrolysis of the esters with substituents in the acyl group obey the Okamoto-Brown equation with  $\rho = -0.8$ . For the esters with substituents in the benzyl group the value of  $\rho$  is  $-2.8$  in 60 “%” acetone-water. The points for the *p*-methoxy-substituted compounds do not, however, lie on the line determined by the other substituents. These facts together with the values found for solvent and deuterium solvent isotope effects and for activation parameters show that the reaction is an  $S_N1$  solvolysis of the  $\alpha$ -chlorine in all the cases studied.

One of the present authors<sup>1,2</sup> has shown that the neutral hydrolysis of  $\alpha$ -haloalkyl esters may proceed either by general-base catalysed ester hydrolysis ( $B_{AC}3$ ) with water as the base or by a nucleophilic displacement ( $S_N$ ) of the  $\alpha$ -halogen atom. It is known that  $\alpha$ -chloroethyl acetate<sup>1</sup> and benzoate<sup>3</sup> are solvolysed by the  $S_N1$  mechanism and that  $\alpha$ -phenyl substituents facilitate the unimolecular solvolysis by resonance much more than alkyl groups do.<sup>4</sup> Therefore it is to be expected that at least  $\alpha$ -halobenzyl esters of acids without strongly electron-withdrawing substituents are solvolysed by the  $S_N1$  mechanism. This was shown to be true in the case of  $\alpha$ -chlorobenzyl acetate by Cleve and Euranto.<sup>5</sup> It was also found that  $\alpha$ -chlorobenzyl formate follows the same mechanism, but that  $\alpha$ -chlorobenzyl trifluoro- and trichloroacetates are hydrolysed by the  $B_{AC}3$  mechanism.<sup>5</sup> It is therefore probable that  $\alpha$ -chlorobenzyl benzoate follows the  $S_N1$  mech-

anism, but strongly electron-withdrawing substituents could possibly change the mechanism, which then could be seen as a deviation from linearity in the Hammett plot. A study of the hydrolysis of substituted  $\alpha$ -chlorobenzyl benzoates was performed to test the validity of these hypotheses. Also information about the transmission of substituent effects through the carboxylic group was thought to be desirable because the influence of structural changes in the acyl group of  $\alpha$ -haloethyl esters was earlier found to be relatively strong.<sup>6</sup>

Several  $\alpha$ -halobenzyl benzoates have already been prepared by the reaction of benzoyl halides with benzaldehydes.<sup>7-9</sup> The method was improved later.<sup>10,11</sup> Of the 34  $\alpha$ -chlorobenzyl benzoates now studied, only the unsubstituted<sup>7,10,11</sup> and three other esters<sup>8,9,12,13</sup> seem to have been prepared earlier. Of their physical properties, except melting points, only few data on their IR-spectra can be found in the literature.<sup>10,12</sup> To our knowledge, no quantitative kinetic investigations of their reactions have been performed earlier.

### EXPERIMENTAL

*Solvents.* The solvent mixtures used in the kinetic experiments were prepared as described earlier.<sup>1,14</sup> Weight percentages were employed in the case of dioxane-water mixtures. In the case of aqueous acetone (E. Merck AG, *pro analysi*) and acetonitrile (Fluka, AG, *purissimum*) solutions the symbol *p* “%” indicates that 100 cm<sup>3</sup> of the solvent mixture contained (100 - *p*) g of water. In the deuterium oxide (Norsk hydro-elektrisk kvaestofaktieselskab, 99.8 g D<sub>2</sub>O/100 g) solutions containing acetonitrile, the molarity of D<sub>2</sub>O was the same

as that of water in the corresponding ordinary water solutions.

**Esters.** The  $\alpha$ -chlorobenzyl benzoates were prepared from benzoyl chlorides and benzaldehydes under nitrogen with zinc chloride as catalyst.<sup>10</sup> After the reaction mixture was allowed to stand for 15 min to several days at room temperature, the ester was precipitated by adding hexane. Occasionally cooling was necessary for precipitation. In some cases the yield of the crystalline ester was low. Sometimes the formed ester could not be separated

from the reaction mixture at all. The esters were analysed by hydrolysing weighed amounts in acetone-water and titrating potentiometrically with standard sodium hydroxide and silver nitrate solutions. The IR-spectra were recorded in benzene solution on a Perkin-Elmer Model 337 Grating Infrared Spectrophotometer. The NMR-spectra were recorded on a 60 MHz Perkin-Elmer Model R 10 NMR Spectrometer in tetrahydrofuran solution using TMS as internal standard. The analytical results are given in Table 1.

Table 1. Analytical results, melting points, and spectral data for  $\alpha$ -chlorobenzyl benzoates Y-C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>CHClC<sub>6</sub>H<sub>4</sub>-Z.

Y	Z	Acid % <sup>a</sup>	Chlorine % <sup>a</sup>	Melting point °C	IR (in benzene) $\nu_{\text{C=O}}$ cm <sup>-1</sup>		$\nu_{\text{C-O-C}}$ cm <sup>-1</sup>	NMR (in THF) $\delta$ (benzylic H)
H	H	99.9	99.8	45–52	1746.2	1249	1077	1059
				51–52 <sup>11</sup>	1749.9 <sup>b</sup>	1251 <sup>b</sup>	1078 <sup>b</sup>	1059 <sup>b</sup>
H	<i>m</i> -Br	102.5	99.0	43–45	1742.6	1247	1073	1055
H	<i>p</i> -Br	84.5	75.3	80–85	1743.6	1247	1073	1057
				109–110 <sup>9</sup>				
H	<i>m</i> -Cl	104.4	98.1	45–65	1744.4	1247	1071	1054
H	<i>p</i> -Cl	99.2	99.5	75–78	1745.8	1249	1077	1060
H	<i>m</i> -NO <sub>2</sub>	103.9	102.6		1746.4	1247	1077	1060
H	<i>p</i> -NO <sub>2</sub>	103.2	98.1	90	1744.8	1247	1075	1058
H	<i>m</i> -CH <sub>3</sub>				1741.3	1247	1077	1059
H	<i>p</i> -CH <sub>3</sub>				1743.4	1250	1077	1058
H	<i>m</i> -OCH <sub>3</sub>				1741.6	1253	1077	1060
H	<i>p</i> -OCH <sub>3</sub>				1739.7	1251	1079	1060
<i>m</i> -Br	H			120–130	1744.4	1245	1066	1057
<i>p</i> -Br	H			85	1744.0	1243	1066	1057
<i>m</i> -Cl	H			82–84	1746.0	1247	1070	1055
<i>p</i> -Cl	H	99.3	92.3	70–75	1743.6	1249	1072	1055
<i>p</i> -Cl	<i>m</i> -NO <sub>2</sub>	96.5	93.9	ca. 100	1744	1240	1066	1055
<i>m</i> -NO <sub>2</sub>	H	103.5	79.1	60	1748.7	1240	1075	1058
				87–88 <sup>9</sup>				
<i>m</i> -NO <sub>2</sub>	<i>m</i> -NO <sub>2</sub>	97.4	101.4	106	1748	1232	1070	1053
<i>m</i> -NO <sub>2</sub>	<i>m</i> -CH <sub>3</sub>				1747.9	1253	1071	1055
<i>p</i> -NO <sub>2</sub>	H	101.7	102.4	130	1746.5	1249	1077	1055
				118–118.5 <sup>8</sup>				7.84
				119–120 <sup>12</sup>	1745 <sup>c,12</sup>			
				115–116 <sup>13</sup>				
<i>p</i> -NO <sub>2</sub>	<i>p</i> -OCH <sub>3</sub>	96.1	79.3		1742	1247	1077	
<i>m</i> -CH <sub>3</sub>	H	84.3	78.7	58–68	1740.0	1260	1084	1062
<i>m</i> -CH <sub>3</sub>	<i>m</i> -NO <sub>2</sub>			91–93	1745.4	1259	1081	1060
<i>p</i> -CH <sub>3</sub>	H	94.9	92.4	49–51	1740.1	1247	1066	1060
<i>m</i> -CF <sub>3</sub>	H				1747.9	1245	1064	1060
<i>m</i> -CF <sub>3</sub>	<i>m</i> -NO <sub>2</sub>	97.8	99.4	95	1748	1221	1064	1060
<i>p</i> -CF <sub>3</sub>	H				1748.9	1250	1077	1060
<i>m</i> -CH <sub>3</sub> O	H	99.8	94.9		1738.7	1257	1080	1071
<i>p</i> -CH <sub>3</sub> O	H	99.3	95.2	48	1737.3	1251	1069	1071
<i>p</i> -CH <sub>3</sub> O	<i>m</i> -Cl	98.9	97.9	60–65	1739.1	1247	1068	1071
<i>p</i> -CH <sub>3</sub> O	<i>p</i> -Cl			73–80	1731.2	1251	1069	1071
<i>p</i> -CH <sub>3</sub> O	<i>m</i> -NO <sub>2</sub>	99.8	99.6	90–94	1739.1	1249	1066	1071

<sup>a</sup> Percentages of the theoretical amounts of hydrolysable acids and chlorine according to the scheme RCO<sub>2</sub>CHClR' + H<sub>2</sub>O → RCO<sub>2</sub>H + HCl + R'CHO. <sup>b</sup> In 2,3-dimethylbutane. <sup>c</sup> In chloroform.

*Kinetic experiments.* The reaction rates were measured by a conductometric method employing a Philips PR 9501 or a Radiometer CDM 3 conductometer. The ester concentration was usually  $ca. 5 \times 10^{-3} \text{ mol dm}^{-3}$ , but in the case of the least soluble esters a saturated solution was used. The reactions followed first-order kinetics indicating that the hydrogen ion produced by the reaction did not catalyse it in these concentrations. In the case of the hydrolysis of  $\alpha$ -chlorobenzyl *p*-nitrobenzoate in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixtures the ester concentration was  $ca. 10^{-3} \text{ mol dm}^{-3}$  and the rate coefficients were calculated by Guggenheim's method. The hydrolysis of  $\alpha$ -chlorobenzyl benzoate in dioxane-water mixtures was studied also in solutions containing added electrolytes. The ester concentration was then 0.02 to 0.04  $\text{mol dm}^{-3}$  and the time-average  $\bar{v}_t$  of the hydrogen-ion

concentration and the rate coefficient  $k_0$  for zero acid concentration were calculated as described earlier.<sup>1</sup> The kinetic data are given in Tables 2-5.

*Errors.* Some of the esters contained appreciable amounts of impurities, which could not be removed. Benzoyl chlorides, if present, disturbed the kinetic determinations, because their hydrolysis rates sometimes were quite similar to those of the esters. In these cases, marked in Table 3, their hydrolysis rates were determined separately and appropriate corrections, not exceeding 18 %, were made in the conductivity values. Other impurities did not interfere with the spectral and kinetic determinations.

When the rate coefficients were calculated conventionally from the integrated first-order rate equation, their accuracy was estimated

Table 2. Kinetic data for the hydrolysis of  $\alpha$ -chlorobenzyl benzoate in *p* “%” acetone-water (A-W) or *p* wt. % dioxane-water (D-W).

<i>p</i>	Solvent	<i>t</i> °C	Added electrol. $\text{mol dm}^{-3}$	$\bar{v}_t$ $\text{mol dm}^{-3}$	<i>k</i> $10^{-3} \text{ s}^{-1}$	$\Delta H^\ddagger$ $\text{kJ mol}^{-1}$	$\Delta S^\ddagger$ $\text{J K}^{-1} \text{ mol}^{-1}$	
50	A-W	25	—	—	43.4	$66.8 \pm 1.5$	$-60 \pm 5$	
60	A-W	5	—	—	1.27			
		15	—	—	3.91			
		25	—	—	9.63			
		35	—	—	23.9			
67.5	A-W	25	—	—	3.65	$61$	$-87$	
75	A-W	25	—	—	1.09			
60	D-W	35	—	0	21.1 <sup>a</sup>			
			—	0.0124	21.8			
45	—	—	0.0527 $\text{HClO}_4$	0.0644	24.6			
			—	0	44.7 <sup>a</sup>			
			—	0.0081	41.4			
			—	0.0090	51.7			
			—	0.0527 $\text{HClO}_4$	0.0707			58.7
			—	0.0617 $\text{HClO}_4$	0.0801			62.1
70	D-W	45	—	0	10.0 <sup>a</sup>			
			—	0.0057	10.2			
			—	0.0068	10.2			
			—	0.0505 $\text{HClO}_4$	0.0595	12.2		
			—	0.050 $\text{NaClO}_4$	0.0044	12.0		
75	D-W	25	—	0.050 $\text{NaClO}_4$	0.0164	12.1		
			—	0	0.594			
		35	—	—	—	0.0051	0.628	
					—	0.0063	0.634	
					—	0.0069	0.595	
					—	0.0526 $\text{HClO}_4$	0.0639	0.857
					—	0	1.66	
					—	0.0031	1.77	
		45	—	—	—	0.0066	1.65	
					—	0.0526 $\text{HClO}_4$	0.0691	2.38
—	0				4.16			
—	0.0059				4.57			
—	—	—	—	0.0070	4.10			
			—	0.0529 $\text{HClO}_4$	0.0670	5.99		

<sup>a</sup> The value of the rate coefficient extrapolated to zero acid concentration.

as the standard deviation of the mean. The so estimated relative errors were found to vary only little, the average value being 0.75 %. When parallel runs were performed, the mean of their average deviations was found to be 0.95 %. The method of least squares was used when the rate coefficients were calculated by Guggenheim's method, when the extrapolated values at zero acid concentration were computed, and when the Arrhenius equation was applied. In the first case the average value of the relative standard deviations was found to be 0.58 %. The errors given for the parameters in the Arrhenius equation are standard deviations.

## DISCUSSION

*Physical properties.*  $\alpha$ -Chlorobenzyl benzoates in general, but especially those with electron-donating substituents in the benzyl group, are unstable and decompose partly during purification or when standing for a few hours or days even at a low temperature under nitrogen. However, esters with strong electron-withdrawing substituents are more stable.<sup>9</sup>

The IR-frequencies for the carbonyl group (1730–1750  $\text{cm}^{-1}$  in benzene solution, Table 1) and the  $-\text{CO}_2\text{C}-$  group (1221–1260 and one or two peaks at 1053–1084  $\text{cm}^{-1}$ ) vary only slightly with structure. The NMR signal for the benzylic proton ( $\delta$  7.77–7.87 in tetrahydrofuran) lies among those for the aromatic protons and could be identified sometimes only by the aid of the NMR spectra of the corresponding substituted benzyl benzoates. No clear correlation between the spectral data and various substituent constants could be found.

*Kinetics and mechanism of the hydrolysis of  $\alpha$ -chlorobenzyl benzoate.* The data (Table 2) from the kinetic runs carried out in dioxane-water solutions containing perchloric acid or sodium perchlorate show that both of these electrolytes increase the rate slightly and equally. The acceleration is thus a salt effect rather than acid catalysis and similar to that found in the case of  $\alpha$ -chloroethyl benzoate<sup>3</sup> and acetate.<sup>6</sup> The following facts show that the reaction mechanism is  $\text{S}_{\text{N}}1$  for the unsubstituted ester. The thermodynamic parameters of activation (Table 2) resemble closely those found for  $\alpha$ -chloroethyl benzoate in 75 wt. % dioxane-water ( $\Delta H^\ddagger = 82.1 \pm 0.8$  kJ/mol,  $\Delta S^\ddagger = -71 \pm 3$  J  $\text{K}^{-1}$  mol $^{-1}$ )<sup>3</sup> and for  $\alpha$ -chloroethyl acetate in 50 wt. % acetone-water ( $\Delta H^\ddagger =$

$74.8 \pm 0.2$  kJ/mol,  $\Delta S^\ddagger = -56 \pm 1$  J  $\text{K}^{-1}$  mol $^{-1}$ ), although the influence of different solvent composition has to be taken into account in the latter case.<sup>1</sup> Also the solvent effect is typical of  $\text{S}_{\text{N}}1$  reactions. Plots of  $\log k$  against  $\log c_{\text{H}_2\text{O}}$  for  $\alpha$ -chlorobenzyl benzoate (not shown) are slightly curved. Their slopes, 4.9 for 70 wt. % dioxane-water at 45 °C and 4.6 for 70 “%” acetone-water at 25 °C, compare with the values 4.4 for  $\alpha$ -chloroethyl benzoate and 4.3 for  $\alpha$ -chloroethyl acetate under corresponding conditions.<sup>3</sup>

Table 3. Rate coefficients  $k/10^{-3}$  s $^{-1}$  for the hydrolysis of  $\alpha$ -chlorobenzyl benzoates  $\text{Y-C}_6\text{H}_4\text{CO}_2\text{CHClC}_6\text{H}_4\text{-Z}$  in  $p$  “%” acetone-water mixtures at 25 °C.

Y	Z	$p = 60$	$p = 75$
H	H	9.63	1.09
H	<i>m</i> -Br	0.432	
H	<i>p</i> -Br	2.76	
H	<i>m</i> -Cl	0.465	
H	<i>p</i> -Cl	3.48	
H	<i>m</i> -NO <sub>2</sub>	0.110	
H	<i>p</i> -NO <sub>2</sub>	0.067	
H	<i>m</i> -CH <sub>3</sub>	12.8	1.52
H	<i>p</i> -CH <sub>3</sub>	75.6 <sup>a</sup>	12.8 <sup>a</sup>
H	<i>m</i> -CH <sub>2</sub> O	4.52	0.596
H	<i>p</i> -CH <sub>2</sub> O	74.5 <sup>a</sup>	6.12 <sup>a</sup>
<i>m</i> -Br	H	2.89	
<i>p</i> -Br	H	3.78	
<i>m</i> -Cl	H	2.71	
<i>p</i> -Cl	H	6.43	
<i>m</i> -NO <sub>2</sub>	H	1.89	
<i>p</i> -NO <sub>2</sub>	H	2.40	
<i>m</i> -CH <sub>3</sub>	H	9.98	
<i>p</i> -CH <sub>3</sub>	H	13.7	
<i>m</i> -CF <sub>3</sub>	H	2.28	
<i>p</i> -CF <sub>3</sub>	H	2.73	
<i>m</i> -CH <sub>2</sub> O	H	6.91	
<i>p</i> -CH <sub>2</sub> O	H	30.3	
<i>m</i> -NO <sub>2</sub>	<i>m</i> -NO <sub>2</sub>	0.0238	
<i>m</i> -NO <sub>2</sub>	<i>p</i> -CH <sub>3</sub>	2.76	
<i>m</i> -NO <sub>2</sub>	<i>p</i> -CH <sub>3</sub>	18.3	
<i>p</i> -NO <sub>2</sub>	<i>p</i> -CH <sub>3</sub>	28.7	
<i>p</i> -NO <sub>2</sub>	<i>p</i> -OCH <sub>3</sub>	25.9	
<i>p</i> -CH <sub>2</sub> O	<i>m</i> -Cl	1.52	
<i>p</i> -CH <sub>2</sub> O	<i>p</i> -Cl	9.44	
<i>p</i> -CH <sub>2</sub> O	<i>m</i> -NO <sub>2</sub>	0.326	
<i>p</i> -Cl	<i>m</i> -NO <sub>2</sub>	0.0848	
<i>m</i> -CH <sub>3</sub>	<i>m</i> -NO <sub>2</sub>	0.119	
<i>m</i> -CF <sub>3</sub>	<i>m</i> -NO <sub>2</sub>	0.0278	

<sup>a</sup> The reaction mixture contained benzoyl chloride; its hydrolysis was taken into account when calculating the rate coefficient.

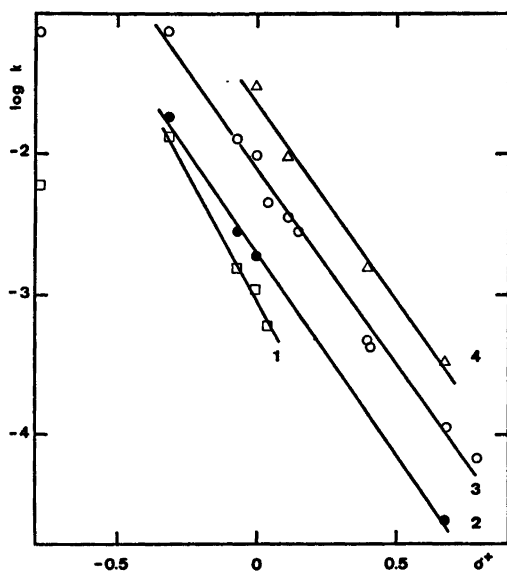


Fig. 1. The  $\sigma^+$  correlation for the hydrolysis rates of  $\alpha$ -chlorobenzyl benzoates  $Y-C_6H_4COOCHClC_6H_4-Z$  with variable substituents  $Z$  in the benzyl group. Solvent  $p$  “%” acetone-water; temperature 25 °C. The solid lines are the least-square fits for all other points than that for the  $p$ -methoxy compound. 1.  $Y = H$ ,  $p = 75$ ; 2.  $Y = m\text{-NO}_2$ ,  $p = 60$ ; 3.  $Y = H$ ,  $p = 60$ ; 4.  $Y = p\text{-CH}_3O$ ,  $p = 60$ .

The rate coefficients for  $\alpha$ -chlorobenzyl benzoate are on an average 120 times as great as those for  $\alpha$ -chloroethyl benzoate.<sup>3</sup> This is in accordance with the supposed  $S_N1$  mechanism for both esters and with the influence of this structural change. The rate difference is due to the lower activation enthalpy and

the less negative activation entropy of the  $\alpha$ -chlorobenzyl ester.

**Structural effects.** When substituents in the benzyl group were varied, the rate coefficients (Table 3) obeyed the Hammett equation  $\log k = \log k^0 + \rho\sigma$  (Fig. 1). Best correlation was obtained with  $\sigma^+$  substituent constants<sup>15</sup> (the Okamoto–Brown equation). The reaction constants  $\rho$  (Table 4) are negative as they ought to be for an  $S_N1$  reaction. They are, however, less negative than found for the solvolysis of tertiary halides in corresponding solvents; e.g., Okamoto and Brown<sup>16</sup> calculated for  $\rho$  the value  $-4.11$  for the hydrolysis of substituted benzhydryl chlorides in 70 % acetone-water and the value  $-4.62$  for that of phenyldimethylmethyl chlorides in 90 % acetone-water. The less negative values for  $\alpha$ -chlorobenzyl benzoates may be due to the fact that the positive charge of the supposed intermediate is not only on the benzylic carbon atom but partly on the etheral oxygen, cf. Ref. 17. In fact, similar values are found also for other reactions leading to oxonium-carbenium ions; as examples the following values can be presented:  $-1.9$  for the hydrolysis of  $\alpha$ -acetoxystyrenes in aqueous sulfuric acid,<sup>17</sup>  $-2.25$  for  $\alpha$ -methoxystyrenes<sup>18</sup> and  $-2.29$  for acetophenone dimethyl acetals<sup>19</sup> in 5 “%” dioxane-water.

$\alpha$ -Chloro- $p$ -methoxybenzyl benzoates are omitted from the above correlations because they essentially lower the correlation coefficients (see Fig. 1). The reason could be the inaccuracy of the rate measurements for these very fast reacting, thermally unstable esters, which could not be prepared free from impurities, especially from benzoyl chlorides. It is,

Table 4. Values of the reaction constants  $\rho$  for the hydrolysis of  $\alpha$ -chlorobenzyl benzoates in  $p$  “%” acetone-water at 25 °C.  $n$  = number of substituents,  $r^+$  = correlation coefficient for the presented  $\sigma^+$  correlation,  $r$  = correlation coefficient for the corresponding  $\sigma$  correlation.

Substrate	$p$	$n$	$\rho$	$r^+$	$r$
$C_6H_5CO_2CHClC_6H_4-Z$	75	4	$-3.67$	0.997	0.923
	60	10	$-2.80$	0.995	0.981
$p\text{-CH}_3OC_6H_4CO_2CHClC_6H_4-Z$	60	4	$-2.86$	0.995	0.982
$m\text{-NO}_2C_6H_4CO_2CHClC_6H_4-Z$	60	4	$-2.89$	0.999	0.980
$Y-C_6H_4CO_2CHClC_6H_5$	60	13	$-0.81$	0.967	0.938
$Y-C_6H_4CO_2CHClC_6H_4\text{-}m\text{-NO}_2$	60	6	$-0.82$	0.983	0.962

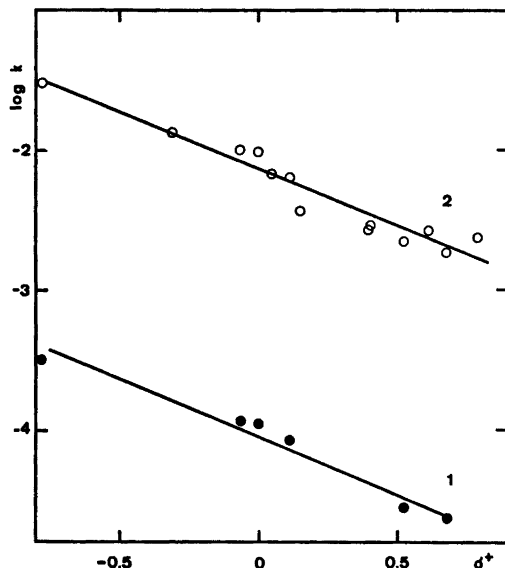


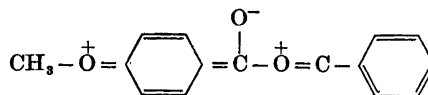
Fig. 2. The  $\sigma^+$  correlation for the hydrolysis rates of  $\alpha$ -chlorobenzyl benzoates  $Y-C_6H_4COOCHClC_6H_4-Z$  with variable substituents  $Y$  in the acyl group. Solvent 60 “%” acetone-water; temperature 25 °C. The solid lines are the least-square fits for all experimental points.

1.  $Z = m\text{-NO}_2$ ; 2.  $Z = H$ .

however, improbable that the exceptional rate coefficients are seriously wrong, because similar results were obtained under various conditions of the hydrolysis for two esters of several batches. In fact, *p*-methoxy-substituted compounds have been found to deviate downward in  $\sigma^+$  correlations also in several other cases.<sup>18–20</sup> Loudon and Berke<sup>19</sup> have examined this kind of substituent effect with the Yukawa-Tsuno relation and extended Hückel molecular orbital calculations. Their explanation, however, does not explain quantitatively the present case, because the points for the *p*-methyl-substituted esters lie on the lines fixed by the other substituents, thus requiring a value close to unity for Yukawa's and Tsuno's resonance parameter  $r$ . On the other hand, the *p*-methoxy-substituted compounds reacted in all cases studied at lower rates than the *p*-methyl compounds and require that  $r < 0.1$ . The deviating behaviour of the methoxyl group as substituent may reflect the partial oxonium-ion character

of the intermediate,<sup>20</sup> which makes its resonance effect less important.

When the variable substituent is in the acyl group, the correlation is worse (Fig. 2), but even then  $\sigma^+$ -values give better correlation than  $\sigma$  (Table 4). This is in contrast with the first expectation, because the substituent cannot be in direct resonance with the developing positive charge on the benzylic carbon atom. Resonance forms like



are, however, possible in the present case. If their contribution is sufficient, they may explain the observed correlation.

The values of the reaction constants  $\rho$  are lower in the latter case (Table 4), which evidently is due to the larger distance between the substituent and the reaction centre. The ratio of the reaction constants is about 0.3, which is larger than the corresponding ratio (about 0.2)<sup>21</sup> for two intervening methylene groups. This is a further indication that the transmission of electronic effects through the carboxylic group takes place easier than through a saturated hydrocarbon chain.<sup>6</sup>

*Hydrolysis mechanism of substituted  $\alpha$ -chlorobenzyl benzoates.* The structural effects considered above show that also substituted  $\alpha$ -chlorobenzyl benzoates obey the same  $S_N1$  mechanism as the unsubstituted ester. They thus confirm quantitatively the conclusion drawn by Filler and Miller on the basis of qualitative hydrolysis experiments which  $\alpha$ -chlorobenzyl benzoate and *p*-nitrobenzoate that “attack of water on the carbonyl carbon is not involved in the rate-determining step”.<sup>12</sup> A slight curvature, which possibly could be found in some of the Okamoto-Brown plots (Figs. 1 and 2), could be an indication of a shift from  $S_N1$  to  $B_{AC}3$  mechanism in the case of the most electronegative substituents. A rough estimation based on the known rate of the  $B_{AC}3$  hydrolysis of  $\alpha$ -chlorobenzyl trichloroacetate<sup>5</sup> and on reasonable structural and solvent effects gives for the rate coefficient of the hydrolysis of  $\alpha$ -chloro-*m*-nitrobenzyl *m*-nitrobenzoate in 60 “%” acetone-water at 25 °C a value of the order of  $10^{-6} \text{ s}^{-1}$ , whereas

Table 5. Kinetic data for the hydrolysis of  $\alpha$ -chlorobenzyl benzoates  $\text{Y-C}_6\text{H}_4\text{CO}_2\text{CH}(\text{Cl})\text{C}_6\text{H}_5$  in 22.20 M solutions of water (60 “%” acetonitrile-water) or its mixtures with deuterium oxide in acetonitrile at 25 °C.  $n$  = deuterium atom fraction.

Y	$n$	$k/10^{-3} \text{ s}^{-1}$	$k_n/k_0$
H	0.00	31.4	1.000
	1.00	21.3	0.678
$p$ -NO <sub>2</sub>	0.00	4.90	1.000
	0.30	4.26	0.869
	0.60	3.88	0.792
	0.80	3.58	0.731
	1.00	3.37	0.688

the experimental value is  $2.38 \times 10^{-5} \text{ s}^{-1}$ . This indicates that a change in the mechanism is possible. The change is, however, ruled out by the fact that no deviation can be observed in the case of the above-mentioned ester. This conclusion was confirmed by determining the temperature dependence of its rate. The obtained rate coefficients [ $2.38$  (Table 3),  $6.28$ ,  $16.6$ , and  $41.9 \times 10^{-5} \text{ s}^{-1}$  at  $24.98$ ,  $34.95$ ,  $45.01$ , and  $55.07$  °C, respectively] yield the values  $76.9 \pm 0.3 \text{ kJ/mol}$  for  $\Delta H^\ddagger$  and  $-76 \pm 1 \text{ J K}^{-1} \text{ mol}^{-1}$  for  $\Delta S^\ddagger$ . They differ only slightly from those found for the unsubstituted ester (Table 2) and show that the observed lower rate is due to both the higher activation enthalpy and the lower activation entropy. A significant contribution of ester hydrolysis should have produced a lower activation enthalpy. No change in mechanism could thus be found in the hydrolysis of the esters studied.

**Solvent isotope effects.** The deuterium solvent isotope effect  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 0.68$  (Table 5) found for the hydrolyses of both  $\alpha$ -chlorobenzyl benzoate and  $p$ -nitrobenzoate in acetonitrile-water mixtures is typical for an  $\text{S}_{\text{N}}1$  reaction in water.<sup>22</sup> Relatively small amounts of organic solvents have only a small influence on the isotope effect.<sup>23</sup> In the case of  $\alpha$ -chlorobenzyl  $p$ -nitrobenzoate also the rates in  $\text{H}_2\text{O}$ - $\text{D}_2\text{O}$  mixtures were measured. The plot (not shown) of  $k_n/k_{\text{H}}$  against  $n$  (the deuterium atom fraction) is slightly bent downward, but does not fit any simple equation based on the equilibrium theory of solvent isotope effects.<sup>23</sup>

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