Phenolic Esters. Part I. Rate of Hydrolysis of Phenyl, *p*-Tolyl, and *p*-Chlorophenyl Hydrogen Succinate

By **F. G. Baddar,*** (Mrs.) **S. Abdel Wahhab,** (Mrs.) **Boshra M. Awad,** and **Nabila M. Guindy,** A'in Shams University, Cairo, U.A.R.
M. Wahba (in part) and **Bakhoum A. Abdel Malek** (in part), Cairo University, Cairo, U.A.R.

The rates of hydrolysis of phenyl, *p*-tolyl, and *p*-chlorophenyl hydrogen succinate are determined at different pH values and temperatures. They follow the first-order rate equation, and decrease in the order *p*-chlorophenyl > phenyl > *p*-tolyl. The rate also decreases with decrease of pH, reaches a minimum at pH 2, then increases gradually and remains constant between pH 5·8 and 7·0. A mechanism involving the intermediate formation of succinic anhydride is discussed.

No kinetic study of the hydrolysis of aryl hydrogen succinates has been undertaken. This investigation was planned to study the effect of pH of the medium, the temperature, the solvent, and the water ratio on the rate of hydrolysis of some aryl hydrogen succinates in dioxan–water and in acetone–water mixtures.

EXPERIMENTAL

p-*Tolyl Hydrogen Succinate*.—*p*-Cresol (1 mol.) and succinic anhydride (1 mol.) were heated at 130—140° for 3 hr. The mixture was worked up as described by Baddar and El-Assal.[1] The product was crystallized from benzene–light petroleum (b.p. 40—60°) to give p-*tolyl hydrogen succinate*, m.p. 105—106° (Found: C, 63·3; H, 5·8. $C_{11}H_{12}O_4$ requires C, 63·4; H, 5·8%). *p*-Chlorophenyl hydrogen succinate had m.p. 106—108° (lit.,[2] 106°) (Found: C, 52·3; H, 4·0; Cl, 15·6. Calc. for $C_{10}H_9ClO_4$: C, 52·3; H, 4·0; Cl, 15·5%). The i.r. spectra of phenyl, *p*-tolyl, and *p*-chlorophenyl hydrogen succinate show a broad band with several maxima at 2930—3200 cm.$^{-1}$, characteristic of the bonded OH of carboxylic acids, and two bands at 1705 and 1660 cm.$^{-1}$ characteristic of the $\nu_{C=O}$ of phenolic esters [3a] and carboxylic acids,[3b] respectively. The lower stretching frequencies than expected may be due to hydrogen bonding.

Rate Measurements.—The rates of hydrolysis of phenyl, *p*-tolyl, and *p*-chlorophenyl hydrogen succinate were studied in mixtures of water with pure dioxan [4a] or pure acetone [4b] containing different buffers at different temperatures. The rate was followed by titration of the liberated succinic acid against alcoholic 0·02N-sodium ethoxide solution, prepared by dissolving pure sodium metal,[4c] with phenol red as indicator.

The buffer solution and the reaction flask (100 ml.) were placed in a thermostat bath at the appropriate temperature, and left to attain thermal equilibrium.

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[1] F. G. Baddar and L. S. El-Assal, *J. Chem. Soc.*, 1950, 3606.

[2] F. G. Baddar, E. Enayat, and S. M. Abdel Wahhab, *J. Chem. Soc. (C)*, 1967, 343.

[3] L. J. Bellamy, 'The Infrared Spectra of Complex Organic Molecules,' Methuen and Co. Ltd., London, 1960, (*a*) p. 179, (*b*) p. 162.

[4] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, Green and Co., London, (*a*) p. 175, (*b*) p. 189, (*c*) p. 164.

A known weight of the ester (1·0 g.) was rapidly dissolved in some of the buffer solution, and the ester solution made up to 100 ml., then immediately immersed in the thermostat bath. Aliquot portions (5 ml.) of the solution were pipetted out at suitable intervals, placed in a flask thoroughly cooled in an ice–salt bath, and titrated with the standard sodium ethoxide solution. The reaction was followed to at least 75% of the hydrolysis. Each run was repeated at least twice.

TABLE 1

	Composition of buffer	μ [a]	pH in water [b]	Dioxan–water mixture 3 : 7 (v/v)			Dioxan–water mixture 2 : 3 (v/v)			Dioxan–water mixture 1 : 1 (v/v)		
				pH [c]	k_1 (min.$^{-1}$)	log k_1	pH [c]	k_1 (min.$^{-1}$)	log k_1	pH [c]	k_1 (min.$^{-1}$)	log k_1
1	0·1M-KCl; 0·2086M-HCl	0·3036	1·10	1·10	$5·06 \times 10^{-4}$	$\bar{4}$·704				1·10	$1·80 \times 10^{-4}$	$\bar{4}$·255
2	0·1004N-H_2SO_4	0·1506	1·60	1·65	$9·02 \times 10^{-5}$	$\bar{5}$·955				1·60	$3·98 \times 10^{-5}$	$\bar{5}$·600
3	0·05M-KCl; 0·0106M-HCl	0 0606	2 00	2·00	$8·96 \times 10^{-5}$	$\bar{5}$·952	2·00	$4·96 \times 10^{-5}$	$\bar{5}$·696	2·05	$3·15 \times 10^{-5}$	$\bar{5}$·498
4	0·1M-KCl; 0·00212M-HCl	0·1021								3·00	$9·66 \times 10^{-5}$	$\bar{5}$·985
5	0·1M-Succinic acid	0·30	2·55	2·90	$4·69 \times 10^{-4}$	$\bar{4}$·670	3·00	$2·21 \times 10^{-4}$	$\bar{4}$·344			
6	0·1M-Succinic acid; 0·004M-sodium succinate	0·312	2·95							3·90	$5·13 \times 10^{-4}$	$\bar{4}$·710
7	0·1M-Succinic acid; 0·002M-sodium succinate	0·306		3·30	$1·04 \times 10^{-3}$	$\bar{3}$·017						
8	0·1M-Succinic acid; 0·006M-sodium succinate	0·318	3·10							4·17	$9·39 \times 10^{-4}$	$\bar{4}$·973
9	0·1M-Succinic acid; 0·008M-sodium succinate	0·324					4·15	$2·50 \times 10^{-3}$	$\bar{3}$·398			
10	0·1M-Succinic acid; 0·014M-sodium succinate	0·342	3·50	4·35	$9·43 \times 10^{-3}$	$\bar{3}$·975				4·85	$3·28 \times 10^{-3}$	$\bar{3}$·516
11	0·1M-Succinic acid; 0·015M-sodium succinate	0·345	3·60				4·70	$7·48 \times 10^{-3}$	$\bar{3}$·874			
12	0·1M-Succinic acid; 0·03M-sodium succinate	0·39	4·05 [d]							5·45	$1·09 \times 10^{-2}$	$\bar{2}$·037
13	0·1M-Succinic acid; 0·05M-sodium succinate	0·45	4·85							5·85	$2·10 \times 10^{-2}$	$\bar{2}$·322
14	0·05M-Succinic acid; 0·025M-sodium succinate	0·225					5·68	$3·02 \times 10^{-2}$	$\bar{2}$·480			
15	0·05M-Succinic acid; 0·05M-sodium succinate	0·30		5·50	$4·15 \times 10^{-2}$	$\bar{2}$·618						
16	0·05M-Succinic acid; 0·1M-sodium succinate	0·45		5·95	$4·29 \times 10^{-2}$	$\bar{2}$·633				6·30	$2·15 \times 10^{-2}$	$\bar{2}$·332
17	0·05M-Succinic acid; 0·046M-sodium succinate	0·288	5·80									
18	0·05M-Succinic acid; 0·15M-sodium succinate	0·60	5·90 [e]	6·25	$4·21 \times 10^{-2}$	$\bar{2}$·624	6·85	$3·22 \times 10^{-2}$	$\bar{2}$·508	6·85	$2·156 \times 10^{-2}$	$\bar{2}$·334
19	0·1M-Succinic acid; 0·32M-sodium succinate	1·26		6·80	$4·20 \times 10^{-2}$	$\bar{2}$·623						
20	0·2526M-KH_2PO_4 0·1516N-NaOH	1·6672								7·20	$2·43 \times 10^{-2}$	$\bar{2}$·385
21	0·1263M-KH_2PO_4 0·0758N-NaOH	0·8336	7·00	7·90	$1·46 \times 10^{-1}$	$\bar{1}$·164						
22	0·067M-Succinic acid; 0·067M-borax	0·402	7·05							8·05	$5·61 \times 10^{-2}$	$\bar{2}$·749

[a] Ionic strength of salts of buffer. [b] Average pH of the buffer solution after the immediate addition of ester and at complete hydrolysis. The difference usually does not exceed ±0·2. [c] All pH values are measured with a pH meter. [d] pH in 51 : 49 acetone–water (v/v) mixture = 5·3. [e] pH in 51 : 49 acetone–water (v/v) mixture = 6·35.

The amount of unhydrolysed ester ($a - x$) at time t is equivalent to the volume of standard ethoxide which is required to neutralize the acid in the buffer and the completely hydrolysed ester in a known volume minus the volume of the ethoxide solution required to neutralize the same volume of ester solution at time t. However, with *p*-chlorophenyl hydrogen succinate, since the completely hydrolysed ester required a volume of sodium ethoxide higher than the calculated value because *p*-chlorophenol behaves as a weak acid, a correction was made for each titration by the use of correction curve (straight line), constructed by plotting the volume of the standard sodium ethoxide solution required to neutralize known volumes of a solution of *p*-chlorophenol (0·5627 g.; the amount liberated from 1·0 g. of the ester) in 100 ml. of the buffer. The volume of ethoxide equivalent to *p*-chlorophenol liberated at time t is calculated from the slope of the curve, and subtracted from the volume of ethoxide equivalent to the amount of ester hydrolysed at time t.

The rates of hydrolysis of the esters were determined at pH 1·0—6·85. Plotting log ($a - x$) against t gave good straight lines, which indicated that the hydrolysis was of the first order.

It was not possible to determine the rate of hydrolysis at pH above 7, since it was too rapid.

Degree of Ionization of Aryl Hydrogen Succinate.—The electrical resistance of solutions of different concentrations of the esters in 1 : 1 (v/v) dioxan–water mixtures was measured, then the equivalent conductance as well as the ionization constant and pK_a values were calculated at the given concentrations.[5]

RESULTS AND DISCUSSION

The rate of hydrolysis of phenyl hydrogen succinate (0·19 g. in 100 ml.) at 25° was measured in buffer solu-

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[5] S. Glasstone, ' Textbook of Physical Chemistry,' MacMillan and Co. Ltd., London, 1953, p. 889.

tions at different pH in 1 : 1, 2 : 3, and 3 : 7 (v/v) dioxan–water mixtures (Table 1). The rates for *p*-tolyl and *p*-chlorophenyl hydrogen succinate (1·0 g. in 100 ml.) at 35° in 1 : 1 (v/v) dioxan–water mixtures at different pH are reported in Table 2.

TABLE 2

Relation between log k_1 and pH at 35°

Buffer no.[a]	pH	*p*-Tolyl hydrogen succinate k_1 (min.$^{-1}$)	*p*-Tolyl hydrogen succinate log k_1	*p*-Chlorophenyl hydrogen succinate k_1 (min.$^{-1}$)	*p*-Chlorophenyl hydrogen succinate log k_1
2	1·60	$1{\cdot}080 \times 10^{-4}$	$\bar{4}{\cdot}0334$	$1{\cdot}621 \times 10^{-4}$	$\bar{4}{\cdot}2098$
3	2·05	$7{\cdot}311 \times 10^{-5}$	$\bar{5}{\cdot}8640$	$8{\cdot}529 \times 10^{-5}$	$\bar{5}{\cdot}9309$
4	3·00	$1{\cdot}894 \times 10^{-4}$	$\bar{4}{\cdot}2774$	$2{\cdot}468 \times 10^{-4}$	$\bar{4}{\cdot}3924$
8	4·17	$1{\cdot}706 \times 10^{-3}$	$\bar{3}{\cdot}2319$	$3{\cdot}071 \times 10^{-3}$	$\bar{3}{\cdot}4873$
13	5·75	$4{\cdot}516 \times 10^{-2}$	$\bar{2}{\cdot}6548$	$9{\cdot}870 \times 10^{-2}$	$\bar{2}{\cdot}9943$
18[b]	6·65	$5{\cdot}116 \times 10^{-2}$	$\bar{2}{\cdot}7089$	$14{\cdot}056 \times 10^{-2}$	$\bar{1}{\cdot}1479$

[a] See Table 1. [b] The pH is slightly lower than that found for phenyl hydrogen succinate in the same buffer.

When log k_1 (at 25°) for phenyl hydrogen succinate (0·19 g. in 100 ml.) in the three dioxan–water mixtures were plotted against pH, the curves shown in Figure 1 were obtained. At a fixed pH the rate of hydrolysis increases with increase in water concentration. Figure 2 shows the same relation for log k_1 (at 35°) for *p*-tolyl and *p*-chlorophenyl hydrogen succinate (1·0 g. in 100 ml.).

These curves also show that the rate of hydrolysis first decreases with increase of pH, becoming a minimum at about pH 2, and then increases regularly reaching a value at which the rate becomes independent of pH over a short range (from about pH 5·8—7·0).

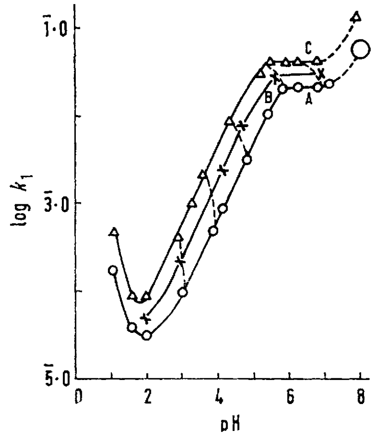


FIGURE 1 log k_1 as a function of apparent pH. A, 1 : 1; B, 2 : 3; and C, 3 : 7 dioxan–water

Effect of Buffer Salts.—In the present investigation most of the buffers used consisted of succinic acid (*i.e.*, the acid liberated by the hydrolysis of the ester), and sodium succinate in different proportions. However, the rate of hydrolysis of phenyl hydrogen succinate at 25° in 1 : 1 (v/v) dioxan–water mixture was determined at pH 3 and 6·85 with different buffers. The values of k_1 were practically the same in the different buffers (Table 3). This indicates that no salt effect is encountered in the hydrolysis of this ester, and the rate is independent of the ionic strength.

Effect of Dielectric Constant on the Rate of Hydrolysis.—The rate of hydrolysis of phenyl hydrogen succinate (0·19 g. in 100 ml. buffer) at 25° was compared at the same pH (measured) in acetone–water and dioxan–water mixtures either having the same dielectric constant but different water concentrations, or having the same water concentration but different dielectric constant.

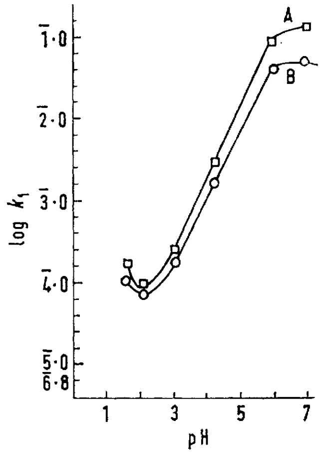


FIGURE 2 log k_1 as a function of apparent pH. A, *p*-Chlorophenyl hydrogen succinate and B, *p*-tolyl hydrogen succinate

TABLE 3

The rate of hydrolysis of phenyl hydrogen succinate (0·19 g. in 100 ml.) in different buffers with the same pH

Buffer no.	Composition of buffer	Measured pH	k_1 (min.$^{-1}$)	μ
4	0·1M-KCl, 0·00212M-HCl	3·00	$9{\cdot}66 \times 10^{-5}$	0·10212
5	0·2M-Succinic acid	3·05	$9{\cdot}96 \times 10^{-5}$	0·20
	0·025M-Succinic acid; 0·075M-sodium succinate	6·85	$2{\cdot}15 \times 10^{-2}$	0·30
18	0·05M-Succinic acid; 0·15M-sodium succinate	6·85	$2{\cdot}15 \times 10^{-2}$	0·20
	0·1M-Succinic acid; 0·3M-sodium succinate	6·85	$2{\cdot}15 \times 10^{-2}$	0·42
	0·054M-Succinic acid; 0·046M-borax	6·80	$2{\cdot}16 \times 10^{-2}$	0·30

In preparing such mixtures, use was made of the dielectric constant data of Akerlof [6] for aqueous acetone and of Akerlof and Short [7] for aqueous dioxan.

The rate of hydrolysis was measured in 51 : 49 (v/v) acetone–water mixture, such composition giving the same dielectric constant (51·4) as 3 : 7 (v/v) dioxan–water mixture. Two buffers (Nos. 12 and 18, Table 1) were used in the acetone solution, which gave pH values of 5·30 and 6·35, respectively. The experimental values of k_1 in the 51 : 49 (v/v) acetone–water mixture are compared with the interpolated values (Figure 1)

[6] Gosta Akerlof and Oliver A. Short, *J. Amer. Chem. Soc.*, 1936, **58**, 1241.

[7] Gosta Akerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

of k_1 in 3 : 7 (v/v) dioxan–water, as shown in Table 4 (Nos. 1 and 2). Table 4 shows that the values of k_1 are greater in the dioxan solution which has a higher water concentration than in the acetone solution with the same dielectric constant.

TABLE 4

	pH	Composition of liquid mixture (v/v)	Dielectric constant of liquid mixture (without buffer)	k_1 (min.$^{-1}$)
1	5·30	51A : 49W *	51·4	1·14 × 10^{-2}
	5·30	30D : 70W		3·63 × 10^{-2}
2	6·35	51A : 49W	51·4	2·48 × 10^{-2}
	6·35	30D : 70W		4·17 × 10^{-2}
	5·30	51A : 49W	51·4	1·14 × 10^{-2}
3	5·30	50D : 50W	33·6	8·32 × 10^{-3}
	5·50 †	50D : 50W	33·6	1·20 × 10^{-2}
	4·25	30A : 70W	63·8	8·85 × 10^{-3}
4	4·25	30D : 70W	51·4	7·41 × 10^{-3}
	4·40 †	30D : 70W	51·4	9·55 × 10^{-3}

* A, D, and W stand for acetone, dioxan, and water, respectively. † pH of D–W mixture containing the same buffer as the corresponding A–W mixture.

The results also show that k_1 is nearly independent of the dielectric constant (Table 4, Nos. 3 and 4), and this indicates that the rate of hydrolysis is pseudo-first-order.

Better agreement of the values of k_1 in the acetone–water and dioxan–water mixtures with the same water concentration is obtained if, instead of being compared at the same measured pH, they are compared in the different liquid mixtures containing the same buffer (Table 4). Thus k_1 in 51 acetone : 49 water (v/v) at pH 5·30 is in better agreement with k_1 in 1 : 1 dioxan–water containing the same buffer (pH 5·50) than at pH 5·30 (the same buffer but only different concentrations) (Table 4, No. 3).

Such agreement may indicate that a given buffer in dioxan–water or acetone–water mixtures with the same water concentration gives the same rate of hydrolysis of phenyl hydrogen succinate irrespective of the slight difference in the measured pH of the two solutions. This may mean that the change of pH of a given buffer with the organic component of the liquid mixture is more apparent than real.

Order of the Reaction with Respect to Water.—The molecular concentration of water in the solution used being very high relative to the molecular concentration of the ester (about 3000 : 1), the water concentration may be considered constant and k_2 will be equal to k_1/C_w. Table 5 shows the calculated values of k_2 for phenyl hydrogen succinate at 25° in the three dioxan–water mixtures. The values of k_1 at different pH are either obtained experimentally (Table 1) or interpolated from Figure 1. In calculating C_w account was made for volume contraction on mixing dioxan and water, amounting to 15—17 ml. per litre of mixture. For example, with 1 : 1 (v/v) dioxan–water, one litre consisted of 507·5 ml. of each of the two liquids at 25°, so that $C_w = (507{\cdot}5 \times 0{\cdot}997)/18 = 28{\cdot}12$ moles/l. Similarly, C_w amounted to 33·76 moles/l. in 2 : 3 and 39·40 moles/l. in 3 : 7 dioxan–water mixtures.

Table 5 shows that the values of k_2 at a fixed pH are not equal at different water concentrations, but still increase with increase in water concentration although not at the same rate as k_1. Moreover, the increase of k_2, like k_1, with water concentration is different at different ranges of pH. Thus, the ratio between the values of k_2 in 3 : 7 and in 1 : 1 dioxan–water mixtures (Table 5) amounts to *ca.* 2 below pH 3, and *ca.* 5 in the pH range 3—5. However, it is 1·4 in the pH range 5·8—7·0 (*i.e.*, the horizontal part of the plots of log k_1 against pH). In the plot of log k_2 against pH (Figure 3), the curves A, B, and C are less widely spaced especially at the low and high pH values than the same curves in Figure 1 (log k_1 against pH).

TABLE 5

Dioxan–water mixtures (v/v)

	1 : 1		2 : 3		3 : 7			
pH	k_2 *	log k_2	k_2	log k_2	k_2	log k_2	$\frac{k_1(3:7)}{k_1(1:1)}$	$\frac{k_2(3:7)}{k_2(1:1)}$
1·1	6·40 × 10^{-6}	$\bar{6}$·8065			1·29 × 10^{-5}	$\bar{5}$·1093	2·8	2·0
1·6	1·42 × 10^{-6}	$\bar{6}$·1450			2·29 × 10^{-6}	$\bar{6}$·3594	2·3	1·6
2·0	1·12 × 10^{-6}	$\bar{6}$·0496	1·47 × 10^{-6}	$\bar{6}$·1679	2·27 × 10^{-6}	$\bar{6}$·3566	2·8	2·0
3·0	3·24 × 10^{-6}	$\bar{6}$·5112	6·54 × 10^{-6}	$\bar{6}$·8157	1·42 × 10^{-5}	$\bar{5}$·1523	6·1	4·4
4·0	2·24 × 10^{-5}	$\bar{5}$·3512	5·15 × 10^{-5}	$\bar{5}$·7118	1·11 × 10^{-4}	$\bar{4}$·0440	6·9	4·9
5·0	1·59 × 10^{-4}	$\bar{4}$·2014	3·81 × 10^{-4}	$\bar{4}$·5809	7·00 × 10^{-4}	$\bar{4}$·8451	6·1	4·4
5·9—6·8	7·52 × 10^{-4}	$\bar{4}$·8762	8·94 × 10^{-4}	$\bar{4}$·9513	1·07 × 10^{-3}	$\bar{3}$·0294	2·0	1·4

* $k_2 = k_1/C_w$ where k_1 is taken from Table 1; see text for C_w. All values are in l. mole^{-1} min.$^{-1}$.

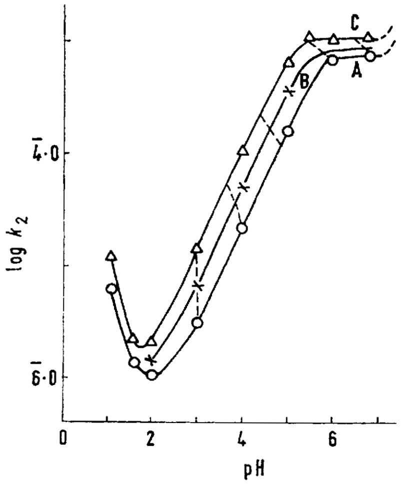


FIGURE 3 log k_2 as a function of apparent pH. A, 1 : 1; B, 2 : 3; and C, 3 : 7 dioxan–water

However, if we consider that the pH of any buffer at a given concentration in a dioxan–water mixture is that of the buffer in pure water and plot k_2 against the pH in water (Figure 4) we obtain curves which are much closer to each other but are still far from coinciding. This result indicates that water does not only act as one reactant in the bimolecular hydrolysis but also seems to catalyse the reaction over the whole experimental pH range, apart from the catalysis by hydrogen ion over the low pH range.

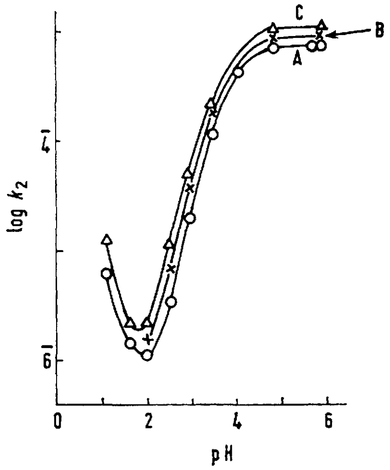


FIGURE 4 log k_2 as a function of real pH. A, 1 : 1; B, 2 : 3; and C, 3 : 7 dioxan–water

In the horizontal portions of the curves of log k_2 against pH, if the values of k_2 are again divided by the molarities of water to give the termolecular rate constant k_3, then these become identical at different water concentrations.

In this respect it has been found by Archer and Hudson [8] that the rate of hydrolysis of benzoyl chloride in acetone–water mixtures is approximately a linear function of C_w^{2} and $C_w^{7\cdot5}$ in the range 5—30 and 50—70% water, respectively.

TABLE 6

T (°K)	$\frac{1}{T}$	log k_1 Phenyl	*p*-Tolyl	*p*-Chlorophenyl	
	pH	6·65	6·65	6·65	1·6
295	0·003390			$\bar{2}$·5329	
296	0·003378		$\bar{2}$·0693		
299	0·00330	$\bar{2}$·5482			$\bar{5}$·5384
300	0·003333		$\bar{2}$·2653	$\bar{2}$·6686	
303	0·003300	$\bar{2}$·6794		$\bar{2}$·7505	$\bar{5}$·8474
308	0·003246	$\bar{2}$·8834	$\bar{2}$·7089		$\bar{4}$·2098
311	0·003215	$\bar{2}$·9644			
Slope		3·23 $\times 10^3$	4·84 $\times 10^3$	2·44 $\times 10^3$	6·82 $\times 10^3$
E^* (kcal. mole^{-1})		14·78	22·14	11·16	31·20
ΔH^* (kcal. mole^{-1})		14·19	21·55	10·66	30·61
ΔS^* (cal. deg.$^{-1}$ mole^{-1})		−17·87	+5·43	−29·40	+24·44

Energies and Entropies of Activation.—The rate of hydrolysis of the three esters (0·00438 mole in 100 ml. buffer) was determined in 1 : 1 dioxan–water mixtures at different temperatures. Results are in Table 6. Plotting log k_1 against $1/T$ gave good straight lines. The activation energies at pH 6·65 for the three esters and that for *p*-chlorophenyl hydrogen succinate at pH 1·6 were calculated from the relation (1). The energies

$$E^* = \text{slope of the straight line} \times 2\cdot303 \times \boldsymbol{R} \qquad (1)$$

of activation were used to calculate the entropy of activation at 25° from the equations [9] (2) and (3). The

$$\Delta H^* = E^* - \boldsymbol{R}T \qquad (2)$$

$$\Delta S^* = \boldsymbol{R}\left(2\cdot303 \log_{10}k_1 - 2\cdot303 \log_{10}\frac{\boldsymbol{R}T}{Nh}\right) + \frac{\Delta H^*}{T} \qquad (3)$$

values of ΔH^* and ΔS^* are reported in Table 6.

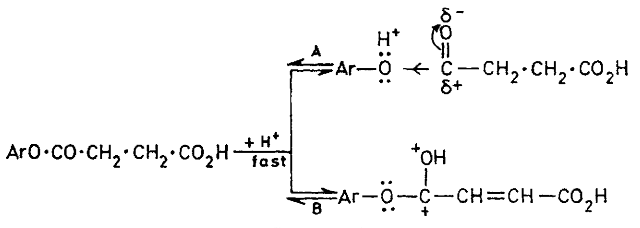
Effect of Structure.—When log k_1 at 35° for phenyl, *p*-tolyl, and *p*-chlorophenyl hydrogen succinate in buffer solutions of pH values 1·35 and 6·70 (Table 7) were plotted against σ values for the corresponding substituted benzoic acids,[10] straight lines were obtained. The slopes give the parameters ρ, which have positive values and are 1·66 and 1·20, respectively.

TABLE 7

Ester	Mole/l.	pH	k_1 (min.$^{-1}$)	log k_1	σ
p-Chlorophenyl hydrogen succinate	0·0438 0·0240	6·7 1·35	14·06 × 10^{-2} 11·515 × 10^{-5}	$\bar{1}$·1479 $\bar{4}$·0615	+0·227
Phenyl hydrogen succinate	0·0438 0·0240	6·7 1·35	7·165 × 10^{-2} 4·265 × 10^{-5}	$\bar{2}$·8558 $\bar{5}$·6299	0·0
p-Tolyl hydrogen succinate	0·0438 0·0240	6·7 1·35	4·606 × 10^{-2} 2·399 × 10^{-5}	$\bar{2}$·6634 $\bar{5}$·3802	−0·17

Mechanism of Hydrolysis.—In the pH range below 2 the hydrolysis is bimolecular and appears to proceed by the $A_{AC}2$ mechanism.

The molecule contains two centres of attack for the proton, *viz.*, the phenolic oxygen atom and the oxygen atom of the CO of the carboxy-group. These can be attacked by the proton according to Scheme 1. However, route B is more probable. The hydrolysis at pH below 2 appears to proceed according to Scheme 2.



SCHEME 1

Since the rate of hydrolysis increases with increase of water concentration at a fixed pH, water must play an important role in the rate-determining step.[11] It

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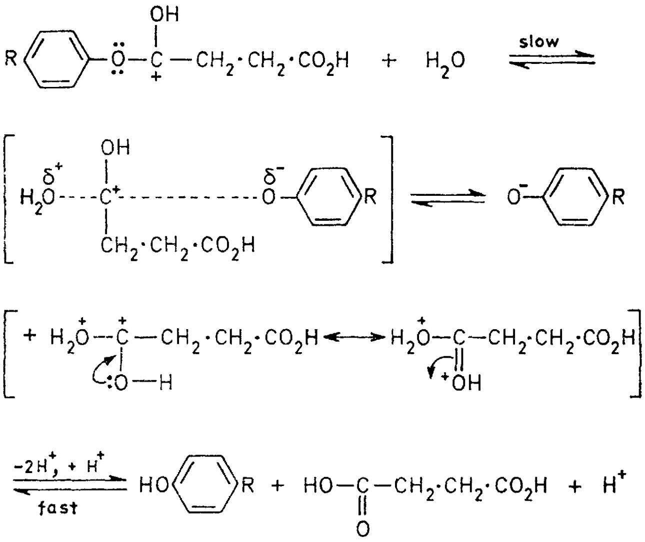
[8] B. L. Archer and R. F. Hudson, *J. Chem. Soc.*, 1950, 3259.

[9] H. Eyring, *J. Chem. Phys.*, 1935, **3**, 107.

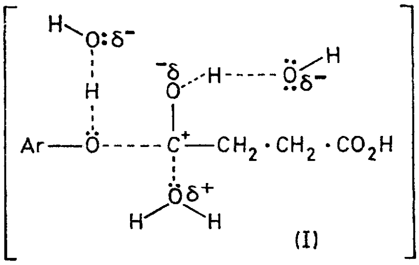
[10] L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill Book Co., New York, 1940, p. 184.

[11] S. V. Anantakrishnan and P. S. Radhakrishnamurti, *Indian J. Chem.*, 1965, **3**, 336.



Scheme 2

appears, however, that at pH below 2, the reaction is catalysed by water molecules besides its catalysis by H$^+$ (*cf.* transition state (I). This may explain why the rate of hydrolysis increases in certain pH regions faster than C_{w}^2, but does not exclude the simultaneous catalytic effect of H$^+$.

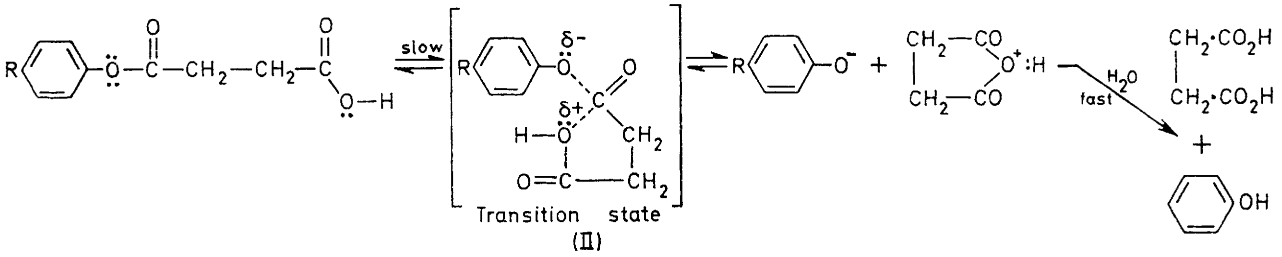


(I)

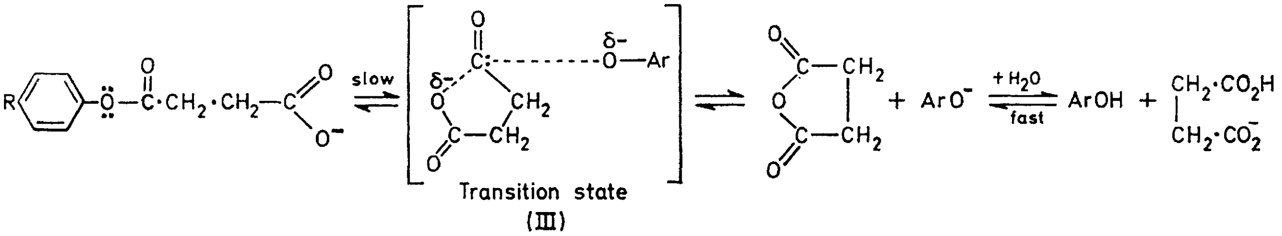
Electron-withdrawing groups (*e.g.*, Cl) increase the rate of hydrolysis by facilitating the cleavage of the aryloxy–carbonyl bond.

The Anchimeric Assistance of the Carboxy-group and Carboxylate Ion.—The increase of the rate of hydrolysis by increase of pH above 2 and the tendency of the rate to become constant at pH 5·8—7 was similar to the finding of Chanley *et al.*[12] for the hydrolysis of acetylsalicylic acid. He explained this behaviour by assuming the formation of a cyclic intermediate.

Thus, a similar mechanism could be suggested for the hydrolysis of aryl hydrogen succinates in pH > 2 (Scheme 3). Thus, the increase of the rate of hydrolysis by increase of pH may be attributed to the increase in the ionization of the carboxy-group of the half-ester. The carboxylate ion, being more nucleophilic than the carboxylic group, together with the fact that the transition state (II) in Scheme 3 involves charge separation, whereas in (III) (Scheme 4) it involves charge distribution, may explain the increase in the rate of hydrolysis by increase of the ionization of the half-ester.



Scheme 3



Scheme 4

This does not exclude the catalytic effect of H$^+$ (Scheme 2) and water molecules (*cf.* I) as stated before, *i.e.*, all three mechanisms may operate side by side.

In Scheme 4 the formation of the transition state and not the hydrolysis of the formed succinic anhydride is the rate-determining step, since the rate of hydrolysis of succinic anhydride was found to be about 100 times that of the ester at the same pH and the same temperature.

The formation of a cyclic intermediate in the hydrolysis of these esters in the pH range 2—6·65 is supported by the fact that the entropy of activation for *p*-chloro-

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[12] J. D. Chanley, E. M. Gindler, and H. Sobatka, *J. Amer Chem. Soc.*, 1952, **74**, 4347.

TABLE 8

Ester	pH in 1 : 1 (v/v) D–W	Concn. (mole/l.)	Temp.	k_1 (min.$^{-1}$)
p-Chlorophenyl	1·6	0·0131	35°	$3{\cdot}54 \times 10^{-5}$
	1·6	0·0451	35	$3{\cdot}58 \times 10^{-5}$
	1·6	0·0910	35	$3{\cdot}43 \times 10^{-5}$
Phenyl	5·85	0·0098	25	$2{\cdot}44 \times 10^{-2}$
	5·85	0·0437	25	$1{\cdot}40 \times 10^{-2}$
p-Tolyl	6·70	0·0240	25	$2{\cdot}512 \times 10^{-2}$
	6·70	0·0438	25	$1{\cdot}818 \times 10^{-2}$

phenyl hydrogen succinate at pH 6·65 is —29·40 cal. deg.$^{-1}$ mole^{-1} which is very small compared with that at pH 1·6 (+24·44). At this low pH no cyclic intermediate is possible owing to the protonation of the carboxy-group when the medium is strongly acidic.

TABLE 9

Equiv./100 ml.	Equiv. conductivity (ohm^{-1} cm.^{2})	Λ_∞ (ohm^{-1} cm.^{2})	α	α^2	$\alpha^2 c$	$k_a = \dfrac{\alpha^2 c}{1-\alpha}$	pK_a
			Phenyl				
0·0322	0·6240	1·03	0·605	0·366	0·0118	0·0299	1·524
0·0530	0·4600		0·446	0·199	0·01055	0·01905	1·720
0·1173	0·2795		0·271	0·0735	0·00860	0·01180	1·928
0·3131	0·1436		0·139	0·0193	0·00604	0·00703	2·152
			p-Tolyl				
0·0345	0·5171	0·81	0·638	0·407	0·01405	0·0388	1·411
0·1112	0·2648		0·327	0·107	0·0119	0·0177	1·752
0·1233	0·2623		0·324	0·105	0·0129	0·0191	1·719
0·2670	0·1564		0·193	0·037	0·0096	0·0119	1·928
			p-Chlorophenyl				
0·0309	0·7654	1·25	0·612	0·375	0·0116	0·0300	1·523
0·0549	0·4929		0·394	0·156	0·0086	0·0142	1·854
0·1204	0·2740		0·219	0·048	0·0053	0·0074	2·131
0·2620	0·1879		0·151	0·023	0·0060	0·0070	2·155

The low entropy of activation at pH 6·65 indicates that the rate-determining step involves a more organized transition state (fewer degrees of freedom) than that at pH 1·6. The organized transition state can be arrived at by the formation of such a cyclic intermediate.

The positive ρ-values (+1·2, +1·66) for this reaction supports the suggested mechanism, because it indicates that the rate-determining step involves the attack of a nucleophilic reagent on a centre with low electron density,[10] *i.e.*, the reaction is enhanced by electron-withdrawing groups. However, the magnitude of ρ indicates that the reaction is not highly sensitive to the polar character of the substituents in the phenyl group.

Effect of Concentration.—Further evidence in support of the anchimeric assistance of the carboxylate ion is the fact that the rate of hydrolysis at pH > 2 was found to be decreased by increase of the ester concentration, whereas at pH < 2 the rate was independent of ester concentration (Table 8).

This could be easily explained by the fact that the degree of ionization of the investigated half-esters was found to decrease with increase of ester concentration (Table 9). This can be taken as evidence that the rate of hydrolysis at pH > 2 is proportional to the degree of ionization of the half-ester, *i.e.*, to the concentration of the carboxylate ion.

[9/404 *Received, March 7th,* 1969]