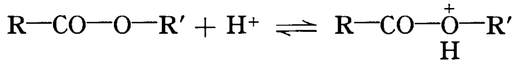
224. *A Kinetic Study of the Hydrolysis and Alcoholysis of Phenyl Acetate.*

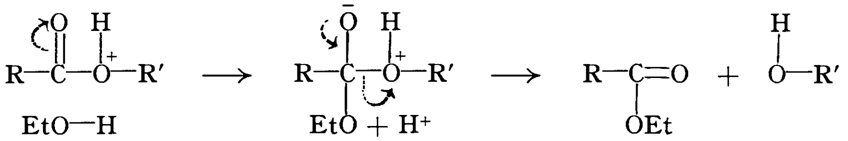
By William A. Waters.

Several recent communications in the *Journal* have dealt with the kinetics of esterification and hydrolysis catalysed by acids, but in none of them has any experimental attempt been made to distinguish between the rôle of the solvent and that of the catalyst. For instance, Hinshelwood and Legard (J., 1935, 587) have made a statistical investigation based upon the conception that the esterification process involved collision between molecules of a carboxylic acid and solvent molecules with which are associated the catalyst, in the form of complexes such as $CH_3{\cdot}OH_2^+$. On the other hand, Lowry (J., 1925, **127**, 1380) had, from analogy with the mechanism of mutarotation, previously suggested that the processes of hydrolysis and esterification involved, in acid media, the initial union of proton with the ester molecule :



$$R{-}CO{-}O{-}R' + H^+ \rightleftharpoons R{-}CO{-}\underset{H}{\overset{+}{O}}{-}R'$$

followed by reaction of the carbon atom of the carbonyl group in this complex kation with a solvent molecule (cf. Lowry and Smith, J., 1927, 2530). Thus, in a case of alcoholysis there might occur :



The same conclusion as to the rôle of proton as catalyst has also been reached independently by Berger and Olivier (*Rec. trav. chim.*, 1927, **46**, 861) from a prolonged study of the polar effects of substituents upon the rates of hydrolysis of esters, acid anhydrides, and acid chlorides.

In order to test the detailed mechanism of esterification and hydrolysis suggested by Lowry, the decomposition of phenyl acetate by ethyl alcohol–water mixtures of known composition, containing hydrogen chloride, was studied. It was found by preliminary experiments that the reactions

$$CH_3{\cdot}CO_2Ph + EtOH \longrightarrow CH_3{\cdot}CO_2Et + Ph{\cdot}OH \quad . \ . \ . \ . \ . \ . \quad (1)$$

and

$$CH_3{\cdot}CO_2Ph + H_2O \longrightarrow CH_3{\cdot}CO_2H + Ph{\cdot}OH \quad . \ . \ . \ . \ . \ . \quad (2)$$

proceeded simultaneously at comparable rates (k_1 and k_2), which could easily be followed by measuring the rates of liberation of (*a*) phenol and (*b*) acetic acid, by means of titration with bromine and alkali respectively. Unfortunately, the alkali titration yields data which are complicated by the fact that, consecutive with reactions (1) and (2), the interconversion (3) sets in :

$$CH_3{\cdot}CO_2Et + H_2O \rightleftharpoons CH_3{\cdot}CO_2H + EtOH \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence the rate of hydrolysis (k_2) could only be estimated from titrations made at the initial stages of the decomposition of the phenyl acetate, or by extrapolation processes, and so may be subject to an error of up to 10% in the data recorded below. In contrast, the rate of liberation of phenol followed very closely the usual unimolecular equation in all experiments, the average deviation of any one observation from the mean being rarely more than 2% over the whole range from 10% to 90% conversion of phenyl acetate into other products. There was no evidence of any reverse reaction to either (1) or (2).

The quantitative irreversible formation of phenol, and of no other aromatic product such as phenetole, provides the strongest support for Lapworth's conclusions (J., 1912, **101**, 273; compare Ingold and Ingold, J., 1932, 756) that carboxylic esters undergo acid hydrolysis and alcoholysis by the fission of an alkoxy-group (A) and not an alkyl group (B).

R·CO—⁝—O·R′ (A.)
HO—⁝—H

R·CO·O—⁝—R′ (B.)
H—⁝—OH

FIG. 1.

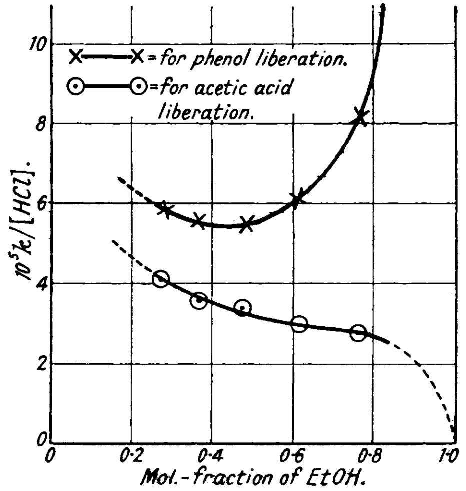
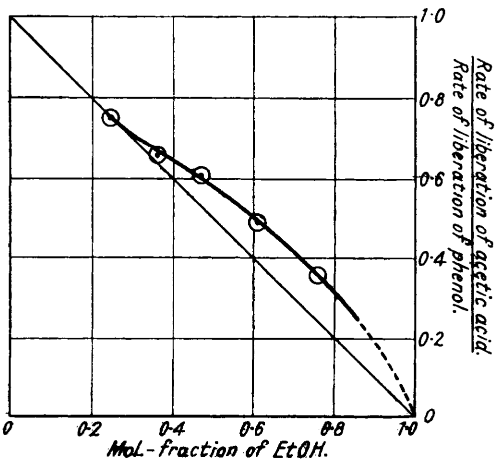


FIG. 2.



The decomposition of esters by acids in alcohol or water is therefore quite different from the reaction in glacial acetic acid solution (Tronov and Ssibgatullin, *Ber.*, 1929, **62**, 2850), in which phenyl acetate is not decomposed by an acid catalyst.

Ethyl alcohol–water mixtures containing 50, 60, 70, 80, 90, and 95% of ethyl alcohol by weight were prepared and used as solvents. Hydrogen chloride was added in the form of the dried gas, and the rate of reaction was followed for each solvent, a series of acid concentrations between 0·01 and 0·4*N* and at least two different temperatures being employed in each case.

It was found that, in general, the rates of both reactions (1) and (2) were proportional to the concentrations of the acid catalyst. With the 95% alcohol, however, the rate increased with hydrogen chloride concentration in more than linear proportion, and a similar slight deviation from proportionality was found in all other solvent mixtures, decreasing in extent with increase in the water content of the solvent. Since one must regard the relationship between the rate of hydrolysis of an ester and the acidity of the solution as being, in full, represented by a catenary curve, this upward trend is not unexpected. The fact that it is the more pronounced in the alcohol mixture containing the least water indicates, however, that there is a decided change in the activity of hydrogen ion in passing from water to alcohol as a solvent.

The results of the reaction velocity measurements at 25° are shown in Fig. 1, in which

(Rate of reaction)/(HCl normality) is plotted against the molar composition of the solvent. It will be seen that the rate of liberation of phenol is practically unchanged in passing from the 50% to the 70% alcohol and increases at higher concentrations of alcohol, whilst the rate of liberation of acetic acid falls off progressively.

By applying the Arrhenius equation $k = A \, . \, e^{-E/RT}$ to all the experimental results it was found that :

(i) The critical increment, E, for phenol liberation is constant at 16,320 ± 200 cals. between 50% and 90% alcohol, though it seems to fall to about half in the 95% alcohol, for which, however, the rate of reaction is not proportional to the acidity.

(ii) The critical increment, E', for the acetic acid liberation is almost identical, being evaluated as 16,600 ± 1000 cals. over the same range of solvents. The complications arising from the occurrence of reaction (3) made it impossible to achieve greater accuracy.

(iii) The variations of reaction velocity with solvent composition can practically all be expressed as changes in the reaction constant A. In particular, the constant for the acetic acid liberation decreases as the percentage of water is diminished in a manner closely corresponding to the decrease in the molar fraction of water in the solvent (Fig. 2). Moreover, the ratio

$$\frac{\text{Rate of reaction of phenyl acetate with water}}{\text{Total rate of reaction of phenyl acetate}} = \frac{k_2}{k_1 + k_2}$$

does not noticeably vary with temperature.

TABLE I.

Solvent, EtOH,		Phenol liberation.		HOAc liberation.			Ratio of rates	
					$A' \times 10^{-7}$			
as wt. %.	as mol.-fractn.	E, cals.	$A \times 10^{-7}$.	E', cals.	from E'.	* from E.	from A'^*/A.	from $k_2/(k_1+k_2)$.
50	0·2787	16,320	5·25	16,800	5·0	3·7	0·70	0·72
60	0·3689	16,360	5·02	16,300	4·4	3·3	0·65	0·65
70	0·4772	16,320	4·95	16,600	4·1	3·1	0·62	0·60
80	0·6103	16,330	5·6	17,700	3·8	2·7	0·48	0·48
90	0·7612	16,100	7·3	15,600	3·4	2·5	0·35	0·36
95	0·8839	6,500						

Before suggesting any theoretical implications of these results, it is necessary to point out that the accuracy of the figures given above varies greatly. The reaction velocity measurements for the phenol liberation have been evaluated with a computed error of the mean of less than 0·5%, but, in consequence of the deviation from linear relationship of the function $k = k_0[\text{HCl}]$, the values of k_0 used in calculating E and A may be 3% in error. For the liberation of acetic acid the error is about ten times as large, with corresponding errors in the values of A' (for which the range of possibilities is given).

The last column of Table I gives, to an accuracy of 5%, the mean value of the ratio between the rates of liberation of acetic acid and of phenol, calculated directly from the reaction velocity measurements at all temperatures, whilst the preceding column gives the same ratio calculated from the reaction constants A and A'.

The general order of accuracy attained is admittedly low, but reference to the experimental section will show that the experimental measurements themselves are quite comparable in accuracy with the great majority of those used previously for theoretical calculation by other workers in this field.

DISCUSSION.

Although the results reported in the previous section relate to only a small temperature range, they indicate without doubt that the functions of the ester and of the reacting solvent are quite separable. A very small change in the polar character of an acid molecule undergoing esterification, or of an ester molecule undergoing hydrolysis, results in a relatively large change (*ca.* 2000 cals.) in the energy of activation of the chemical change (compare *inter alia* Hinshelwood and Legard, J., 1935, 587), but, as shown by the present experiments, a change in the nature of the reacting alcohol molecule results, in an acid solution, in a change of E which, if not actually zero, must be less than the experimental error (*ca.* 300 cals.) involved in the calculations made from the measurements of the rate of liberation of phenol (Table I, col. 3). This conclusion is supported, not merely by the approximate measurement of E' for the acetic acid liberation, which is identical with E to well within the experimental error, but also by the evaluation of the ratio $k_2/(k_1 + k_2)$, *i.e.*, of the ratio between the rates of liberation of acetic acid and of phenol. This ratio has been calculated from the reaction velocity measurements to an accuracy of 5%, and does not appear to change with temperature over the range 20—40°. Since a difference of energy between E and E' of 2000 cals. would produce about a 10% alteration in this ratio for a 10° change of temperature, one must again conclude that E and E' cannot differ appreciably, and that the ratio found is probably that of the two reaction constants A and A'.

Hence it is possible that the activated entities in the chemical changes (1) and (2) may be identical, not involving either the alcohol or the water molecules. This is acceptable in Lowry's scheme for esterification, in which one assumes that there occur :

(*a*) Reversible formation of an ester–proton complex

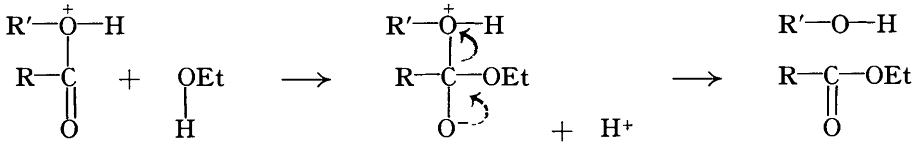
$$R{\cdot}CO{\cdot}OR' + H_3O^+ \rightleftharpoons R{\cdot}CO{\cdot}\overset{+}{O}(H){\cdot}R' + H_2O$$

(*b*) activation of this complex; followed by

(*c*) collision with a normal solvent molecule, which may react *either* so as to produce a molecular interchange

$$R'{\cdot}\overset{+}{O}(H){\cdot}CO{\cdot}R + EtOH \longrightarrow Et{\cdot}\overset{+}{O}(H){\cdot}CO{\cdot}R + R'{\cdot}OH$$

or by anion donation, with simultaneous liberation of proton :



The same conclusion may be expressed perhaps more concisely in the terminology of Hughes and Ingold (J., 1935, 244) by stating that ester hydrolysis or alcoholysis in acid solution appears to be unimolecular, belonging to the category $S_N(1)$.

Thus acid hydrolysis may be regarded as a nucleophilic reaction of the type $R—\overset{+}{X} \longrightarrow \overset{+}{R} + X$, in which $R = CH_3{\cdot}CO$ and $\overset{+}{X} = \overset{+}{O}(H){\cdot}Ph$, the rate-determining stage (*b*) being the decomposition of the complex kation $= CH_3{\cdot}CO{\cdot}\overset{+}{O}(H){\cdot}Ph$.

Other possible implications of this experimental work, however, are revealed by applying the kinetic theories of Moelwyn-Hughes ("Kinetics of Reactions in Solution," Oxford Univ. Press, 1933; *Phil. Mag.*, 1932, **14**, 112) and evaluating the data of Table I, not in the form $k = Ae^{-E/RT}$, but in the form $k = PZe^{-E'/RT}$ in which Z is a collision frequency and E' is the activation energy corrected by allowing for the change of viscosity of the solution with temperature, as indicated by Jowett (*Phil. Mag.*, 1929, **8**, 1059). The experimental figures recalculated in this manner are given in Table II, in which η represents the viscosity at 25°.*

TABLE II.

EtOH, wt. %.	$10^3\eta$.	E, cals.†	E', cals.	$PZ \times 10^{-11}$. (Phenol liberation.)	$PZ \times 10^{-11}$. (Acid liberation.)
50	23·6	5926	22,250	11·5	7·9
60	22·3	5679	22,140	9·1	5·9
70	20·2	5306	21,630	3·8	2·5
80	17·4	4800	21,130	1·9	0·9
90	14·2	4100	20,200	0·5	0·2

* From the International Critical Tables.

† Energy correction calculated from viscosities at 20° and 40°.

Two alternative methods are available for calculating the collision number Z.

(i) For the *total* number of collisions between a solute molecule and solvent molecules, Moelwyn-Hughes (J., 1932, 96) deduced the formula

$$Z = 8N\eta\sigma(M_1 + M_S)/M_1M_S = 5{\cdot}1 \times 10^{24}\eta\sigma(M_1 + M_S)/M_1M_S$$

where M_1 and M_S = molecular weight of the solute and the solvent molecules respectively, and σ = diameter of the solute = $1{\cdot}33 \times 10^{-8}(V_m)^{1/3}$ (Moelwyn-Hughes's alternative formula does not take into account the molecular dimensions of the solvent molecules).

(ii) For *an aqueous solution* in which all the hydrogen ions are assumed to be present as H_3O^+, the formula $Z' = 3\pi N\sigma\eta/2M_S[H_2O]$, in which $[H_2O]$ is the number of g.-mols. of water per litre, gives the number of collisions between ester molecules and H_3O^+ kations (Moelwyn-Hughes, *Phil. Mag.*, *loc. cit.*).

The equations of (i) and (ii) above may be adapted to the case of the alcohol–water mixtures by substituting for M_S the mean molecular weight of the mixture, and for $[H_2O]$ the number of solvent molecules present per litre of pure solvent [S].

We then find the theoretical figures given in Table III. Both Z and Z' are nearly constant, whereas PZ (Table II) decreases progressively as the alcohol content of the solvent rises.

TABLE III.

EtOH, wt. %.	M_S.	[S].	$Z_{\text{total}} \times 10^{-14}$.	$Z'_{\text{with H}^+} \times 10^{-11}$.
50	26·32	34·57	3·64	9·6
60	28·38	31·36	3·24	10·0
70	31·36	27·53	2·70	10·3
80	35·09	23·92	2·11	10·2
90	39·82	20·43	1·57	9·7

Values of P have been calculated from Tables II and III by using Z_{total} for each solvent, and are given in Table IV. Since any theoretical errors in the computation of Z by this method will be practically identical for all the solvent mixtures, one would be forced to conclude that, as the alcohol content of the solvent increases, a progressively smaller fraction of the activated collisions between ester and solvent molecules results in chemical change.

TABLE IV.

EtOH, wt. %	50	60	70	80	90
$P \times 10^3$ (phenol liberation)	3·2	2·8	1·5	0·9	0·3
$P \times 10^3$ (acetic acid liberation)	2·2	1·8	0·9	0·4	0·1
Ratio	0·69	0·65	0·63	0·46	0·24

If the mechanism of ester hydrolysis is treated from the theoretical viewpoint of Moelwyn-Hughes, according to which reaction occurs on activated collision between molecules of ester and of proton–solvent complexes (*i.e.*, between Ac·OPh and $EtOH_2^+$), then, since Z' of Table III should give the frequency of this type of collision, one would have to conclude that the percentage of suitably oriented solvent–proton complexes falls as the alcohol content of the solution increases, being 100% in the case of 50% alcohol, and 10% in the case of 90% alcohol. This change, however, cannot be accomplished by any shift of the equilibrium $H_3O^+ + EtOH \rightleftharpoons H_2O + EtOH_2^+$, since this would alter the ratios of rates of formation of acetic acid and phenol in a way not corresponding to that found. The change of ratio is, it must be stressed, quite close to that of the molar composition of the mixed solvent (Fig. 2).

On the other hand, if changes in P are considered from Lowry's theory, according to which $k_0 = k/[HCl]$ (as used in all the above calculations) measures the rate at which, in N-acid the activated complex (Ester, H^+) collides with a *normal* solvent molecule, then P becomes a measure of the basicity of the ester relative to that of the solvent.

Since Ester + $H_3O^+ \rightleftharpoons$ (Ester,H^+) + H_2O, we have $[\text{Ester,H}^+]/[\text{Ester}] = C[H_3O^+]/[H_2O]$; hence, as P is calculated from the reaction velocity in N-acid, P =

$C/([S] - 1)$, where [S] has values as in Table III. The values thus calculated for the equilibrium constant C are:

EtOH, % by weight	50	60	70	80	90
C	0·106	0·086	0·039	0·020	0·007

indicating that the order of affinity for proton is HOEt>HOH>ROAcyl>(HOAcyl)—exactly what one would anticipate from inspection of the polar effects that must be operating in oxonium kation formation.

It is of theoretical significance that the particular conclusions reached by the above analysis, and given in Tables II—IV, all result from the introduction of the viscosity of the solvent, and its change with temperature. The viscosity correction of the E term, in fact, converts steady values of both E and A ($= PZ$) into progressively changing ones.

The experimental determinations of A need not, however, be interpreted solely by the one theoretical concept that has been employed by Moelwyn-Hughes. In contrast, Bradley (J., 1934, 1910), with others, has pointed out that it is not necessary to believe that viscosity enters explicitly into the theory, since "it would seem incorrect to apply the diffusion theory of colloidal particles, in so far as it embodies Stokes's law, to molecular diffusion." An entirely different approach to the calculation of theoretical rates of reaction in solutions is possible. The alternative formula proposed by Bradley for a unimolecular reaction, *viz.*, $k = (v/a)(\frac{3}{2}\pi)^{\frac{1}{2}}(E/RT)e^{-E/RT}$, where v^2 is the mean square velocity and a the mean double amplitude of oscillation of a molecule, is one in which the collision frequency is independent of the viscosity, and varies much more slightly with temperature than it does in Moelwyn-Hughes's formula. It would therefore lead to an entirely different interpretation of the experimental figures given in Table I. In particular, the correction to be applied to E (*i.e.*, $\frac{3}{2}RT$) is the *same* constant for each solvent mixture (890 cals. at 25°), with the result that the calculated PZ term would have a much more steady value, and, consequently, the deductions made above upon the hypothesis of a varying P factor would no longer be valid. Unfortunately, the selection of the term a is in any case somewhat arbitrary, and hence any attempt to compute its magnitude in a complicated mixed solvent would be very speculative.

Although the author, therefore, does not wish to attach any vital significance to measurements of the "collision rate" and of the "probability factor" for the unimolecular reaction which he has studied, he considers that his experimental results have served to emphasise the contrasting features of the theories of Bradley and of Moelwyn-Hughes.

The general conclusion, that ester hydrolysis in acid solution is a unimolecular reaction occurring between activated ester–proton complexes and normal solvent molecules, is based upon energy considerations, and is not dependent upon any abstruse physical concepts. The conclusion, however, cannot be considered other than as provisional, since the reactions of several esters in a wide range of solvent mixtures need to be studied before the speculations can be adequately confirmed or disproved.

EXPERIMENTAL.

Materials.—The phenyl acetate was purified by shaking for some time with iodine in presence of sodium bicarbonate, and, after removal of the excess iodine with sodium thiosulphate, was dried and fractionally distilled three times in a vacuum, large head and tail fractions being rejected.

The alcohol was boiled with silver nitrate and a large excess of caustic potash, in order to remove aldehydes, carefully fractionated through a 3′ column, and diluted with freshly distilled conductivity water until of the correct density for the required solvent mixture. All densities were measured at 20° by means of a Westphal balance, and the resulting error in the composition of the solvent was not more than 0·05%.

Analytical Procedure.—10 C.c. portions of the reacting solutions were removed in standard pipettes, kept at the temperature of the thermostat, and added to an equal volume of cold alcohol. For estimation of the acetic acid, sodium hydroxide (0·02—0·05N) and phenolphthalein were employed.

For estimation of the phenol, the portions were treated with a known volume of a standard (*ca.* $N/3$) solution of bromine in acetic acid containing an excess of sodium acetate, stoppered, shaken, and after $\frac{1}{2}$ minute treated with an excess of a potassium iodide solution. The liberated iodine was titrated by thiosulphate, with starch, a few c.c. of chloroform being added when necessary in order to dissolve any tribromophenol. Preliminary tests of this procedure showed that phenyl acetate reacted at a negligible rate with bromine solutions if buffered to p_H 3 or more (compare Gibby and Waters, J., **1932**, 2643), whereas phenol instantly gave tribromophenol. By using sodium acetate as a buffer salt, the continued decomposition of the phenyl acetate was instantly checked and constant phenol titres were obtained. Tests with pure phenol showed that the reaction was quantitative, and that, during the time occupied in a titration, the alcohol used as solvent had no appreciable reaction with bromine. A typical bromine reagent contained 10 c.c. of bromine, 100 c.c. of glacial acetic acid, and 50 g. of sodium acetate per litre; it was prepared at least a day before use, and was restandardised every few hours.

Preparation of Reaction Mixtures.—Phenyl acetate was weighed into a standard flask, dissolved in the required solvent, and diluted to the required volume whilst immersed in the thermostat. Another portion of the solvent was treated with dry hydrogen chloride, prepared from A.R. reagents, and also brought to the reaction temperature. Known volumes of both solutions, together with more solvent if required, were then pipetted into dry flasks having standard ground-glass stoppers: N.P.L. standard flasks and pipettes were used throughout. Various ester concentrations between 0·1 and 0·2*N* were employed, and the acid concentrations were chosen so that even with the most rapid reactions a series of titrations could be made at half-hour intervals. To minimise unconscious prediction of titre results, no attempt was made to adjust the concentrations of any solutions to predetermined values. It was found that the values obtained for (Rate of reaction)/(HCl normality) were not noticeably influenced by the initial concentration of the ester.

Calculation of Results.—All reaction velocities were calculated as g.-mol./l./second. The usual unimolecular equation was used for the phenol liberation. For the liberation of acetic acid, no unimolecular constant can be calculated (see p. 1015). Following the procedure of Dawson and Lowson (J., **1927**, 2107; **1928**, 2146), however, an approximate constant $k_2 = y/t(a - x)$ (where y = acid liberated and x = phenol liberated) can be calculated from the initial readings. In alcohol–water mixtures of 60—80% EtOH content, this equation gave fairly steady values until $x > 0{\cdot}3a$. Approximations were made in other cases by graphical extrapolation of observations.

The following data, obtained in a typical experiment, illustrate the procedure.

Experiment No. 54. 70% EtOH by weight. Temp. = 35°.

Initial concns.: ester = 0·1815*N*; HCl = 0·1186*N*.

Time, mins.	PhOH liberated, x (mols.).	HOAc liberated, y (mols.).	$k \times 10^5$ (phenol).	$k_2 \times 10^6$.	Time, mins.	PhOH liberated, x (mols.).	HOAc liberated, y (mols.).	$k \times 10^5$ (phenol).	$k_2 \times 10^6$.
175	0·0261	0·0160	1·48	9·8	360	0·0493	0·0275	1·47	9·6
210	0·0308	0·0187	1·48	9·8	420	0·0560	0·0312	1·47	9·9
240	0·0351	0·0202	1·49	9·6	480	0·0620	0·0351	1·46	10·1
270	0·0386	0·0219	1·48	9·4	500	0·0644	0·0348	1·46	9·9
300	0·0418	0·0236	1·48	9·4	520	0·0644	0·0348	1·45	9·7
330	0·0458	0·0260	1·47	9·7	535	0·0683	0·0365	1·48	10·0

$k \times 10^5 = 1{\cdot}470 \pm 0{\cdot}01$ (12 values); $k_2 = 9{\cdot}8 \times 10^{-6}$.

Summarised Experimental Results.

A. *Liberation of phenol.*

I. 50% EtOH by weight. Mol.-fraction of EtOH = 0·2787.

(*a*) Temp. = 20°.

Expt. No.	HCl, *N*.	$k \times 10^6$.	No. of values.	$10^5k/[\text{HCl}]$.	Expt. No.	HCl, *N*.	$k \times 10^6$.	No. of values.	$10^5k/[\text{HCl}]$.
23	0·0234	0·786	4	3·34 ± 0·8	25	0·219	8·23	10	3·76 ± 0·04
21	0·0372	1·27	10	3·43 0·02	24	0·284	10·54	11	3·72 0·03
22	0·0747	2·52	10	3·39 0·01	26	0·419	16·65	8	3·98 0·02

Weighted mean: $k/[\text{HCl}] = 3{\cdot}645 \times 10^{-5}$ (49 values).

(*b*) Temp. = 25°.

30	0·0129	7·32	14	5·68 ± 0·04	32	0·387	23·5	13	6·08 ± 0·03
31	0·258	14·7	9	5·70 0·01					

Weighted mean: $k/[\text{HCl}] = 5{\cdot}829 \times 10^{-5}$ (36 values).

(*c*) Temp. = 30°.

Expt. No.	HCl, *N*.	$k \times 10^6$.	No. of values.	10^5k/[HCl].	Expt. No.	HCl, *N*.	$k \times 10^6$.	No. of values.	10^5k/[HCl].
38	0·148	11·7	10	7·89 ± 0·05	39	0·296	14·97	10	8·45 ± 0·10

Weighted mean : k/[HCl] = 8·17 × 10^{-5}.

(*d*) Temp. = 35°.

63	0·0717	8·92	15	12·44 ± 0·03	61	0·157	18·6	13	11·87 ± 0·03
60	0·0784	9·44	14	12·03 0·02	65	0·175	20·9	17	11·93 0·09
64	0·1434	17·4	12	11·98 0·06	62	0·235	27·5	7	11·7

Weighted mean : k/[HCl] = 12·02 × 10^{-5} (78 values).

(*e*) Temp. = 40°.

72	0·0145	3·13	13	21·6 ± 0·10	75	0·2861	64·2	10	22·13 ± 0·07
73	0·0218	4·59	13	21·07 0·05	76	0·429	99·8	12	23·24 0·03
74	0·143	31·1	16	22·26 0·05					

Weighted mean : k/[HCl] = 21·78 × 10^{-5} (51 values).

II. 60% EtOH by weight. Mol.-fraction of EtOH = 0·3689.

(*a*) Temp. = 25°.

35	0·133	7·22	12	5·42 ± 0·05	33	0·320	18·2	12	5·69 ± 0·03
34	0·267	13·1	10	5·66 0·03					

Weighted mean : k/[HCl] = 5·583 × 10^{-5} (34 values).

(*b*) Temp. = 40°.

77	0·0628	12·98	11	20·66 ± 0·04	79	0·154	32·4	13	21·08 ± 0·08
78	0·1356	26·4	11	21·06 0·06					

Weighted mean : k/[HCl] = 20·94 × 10^{-5} (35 values).

III. 70% EtOH by weight. Mol.-fraction of EtOH = 0·4772.

(*a*) Temp. = 20°.

14	0·0319	1·12	13	3·53 ± 0·01	15	0·366	13·5	10	3·69 ± 0·01
10	0·0870	3·09	5	3·55	11	0·529	20·4	12	3·87 0·02
9	0·173	5·91	7	3·41	13	0·639	27·0	6	4·23
12	0·265	9·95	10	3·75 0·07	16	1·225	52·5	12	4·29 0·02

Weighted mean : k/[HCl] = 3·689 × 10^{-5} (50 values).

(*b*) Temp. = 25°.

20	0·0445	2·32	5	5·20	28	0·275	16·05	9	5·84 ± 0·01
19	0·0808	4·58	7	5·67 ± 0·05	18	0·2975	16·44	9	5·53 0·04
27	0·1375	7·44	12	5·41 0·01	29	0·550	36·4	8	6·62
17	0·149	8·18	9	5·50 0·06					

Weighted mean : k/[HCl] = 5·534 × 10^{-5} (51 values).

(*c*) Temp. = 30°.

46	0·0130	1·10	11	8·47 ± 0·01	45	0·265	24·5	7	9·26 ± 0·03
47	0·0392	3·30	11	8·41 0·03	43	0·397	35·4	11	8·40 0·04
44	0·1986	17·2	9	8·65 0·15					

Weighted mean : k/[HCl] = 8·481 × 10^{-5} (42 values).

(*d*) Temp. = 35°.

57	0·0756	9·08	15	12·0 ± 0·02	59	0·1513	18·0	14	11·9 ± 0·04
58	0·1134	13·5	15	11·9 0·03	55	0·2373	30·0	10	12·6 0·02
54	0·1186	14·7	11	12·4 0·02	56	0·356	46·4	14	13·0 0·04

Weighted mean : k/[HCl] = 12·25 × 10^{-5} (79 values).

(*e*) Temp. = 40°.

66	0·0364	7·63(−)	7	20·9	68	0·1093	22·3	8	20·4 ± 0·08
67	0·0729	15·0	14	20·6 ± 0·06	70	0·1681	36·2	12	21·5 0·05
69	0·0841	17·8	12	21·1 0·09	71	0·2103	45·2	9	21·5 0·05

Weighted mean : k/[HCl] = 21·03 × 10^{-5} (62 values).

IV. 80% EtOH by weight. Mol.-fraction of EtOH = 0·6103.

(*a*) Temp. = 25°.

86	0·0677	4·06	12	5·99 ± 0·01	84	0·1806	11·2	13	6·22 ± 0·01
83	0·0903	5·45	14	6·04 0·01	88	0·2030	12·9	11	6·35 0·02
87	0·1354	8·40	11	6·19 0·01	85	0·2710	18·0	12	6·63 0·01

Weighted mean : k/[HCl] = 6·190 × 10^{-5} (73 values); by zero extrapolation, 6·074 × 10^{-5}.

(*b*) Temp. = 35°.

Expt. No.	HCl, *N*.	$k \times 10^6$.	No. of values.	$10^5k/[HCl]$.	Expt. No.	HCl, *N*.	$k \times 10^6$.	No. of values.	$10^5k/[HCl]$.
80	0·1201	18·2	11	15·1 ± 0·01	82	0·2402	39·3	12	16·3 ± 0·06
89	0·1547	23·4	10	15·1 0·03	90	0·2707	43·7	12	16·2 0·02
81	0·1802	28·1	12	15·6 0·06					

Weighted mean : $k/[HCl] = 15·70 \times 10^{-5}$ (57 values) ; by zero extrapolation, $14·65 \times 10^{-5}$.

V. 90% EtOH by weight. Mol.-fraction of EtOH = 0·7612.

(*a*) Temp. = 25°.

94	0·0431	3·27	13	7·58 ± 0·04	92	0·1103	8·92	12	8·09 ± 0·01
91	0·0551	4·38	13	7·94 0·02	93	0·1654	13·9	16	8·43 0·02
95	0·0861	6·58	13	7·64 0·04	96	0·2585	23·2	16	8·99 0·04

Weighted mean : $k/[HCl] = 8·155 \times 10^{-5}$ (83 values) ; lowest values, $7·610 \times 10^{-5}$ (39 values) ; graphical zero, $7·26 \times 10^{-5}$.

(*b*) Temp. = 35°.

99	0·0198	3·64	10	18·41 ± 0·02	97	0·0660	13·1	12	19·79 ± 0·08
100	0·0395	7·15	12	18·09 0·03	98	0·1322	26·7	12	20·21 0·08
101	0·0593	11·0	14	18·61 0·05					

Weighted mean : $k/[HCl] = 19·03 \times 10^{-5}$ (60 values) ; lowest values, $18·37 \times 10^{-5}$ (36 values). graphical zero, $17·5 \times 10^{-5}$.

VI. 95% EtOH by weight. Mol.-fraction of EtOH = 0·8839.

(*a*) Temp. = 24·35°.

8	0·00748	1·39	7	18·6 ± 0·3	5	0·2618	60·5	14	23·1 ± 0·4
4	0·1353	27·6	18	20·4 0·3	6	0·3926	110·9	13	28·2 0·6

Zero extrapolation : $k/[HCl] = 18·30 \times 10^{-5}$.

(*b*) Temp. = 35°.

102	0·0323	8·41	14	26·0	103	0·0646	18·6	16	28·8
105	0·0266	7·27	13	27·3	107	0·0797	22·8	16	28·6
106	0·0531	14·8	12	26·7	104	0·0968	18·5	13	29·4

Zero extrapolation : $k/[HCl] = 25·8 \times 10^{-5}$.

B. *Liberation of acetic acid.*

(Figures in parentheses are obtained by graphical extrapolation.)

I. 50% EtOH by weight. Mol.-fraction of EtOH = 0·2787.

(*a*) Temp. = 25°.

Expt. No.	HCl, *N*.	$k_2 \times 10^6$.	k_2/k.	$10^5k_2/[HCl]$.	Expt. No.	HCl, *N*.	$k_2 \times 10^6$.	k_2/k.	$10^5k_2/[HCl]$.
30	0·1289	5·1	0·69	3·9	31	0·2578	10·9	0·74	4·25

(*b*) Temp. = 35°.

63	0·0717	7·15 (6·7)	0·80 (0·75)	9·97	64	0·1434	14·9	0·86 (0·72)	10·4
60	0·0784	7·66	0·77 (0·69)	9·77					

(*c*) Temp. = 40°.

71	0·00727	1·14	0·67	15·7	74	0·1431	22·6	0·73	15·8
72	0·0145	2·31 (2·25)	0·74 (0·68)	15·9	75	0·2861	48·6	0·76 (0·60)	15·8
73	0·0218	3·44	0·75	15·8					

$k_{acid}/k_{phenol} = 0·724$ (mean of 10 best values).

II. 60% EtOH by weight. Mol.-fraction of EtOH = 0·3689.

(*a*) Temp. = 25°.

35	0·1332	4·85	0·67 (0·65)	3·65	33	0·3199	11·3	0·62	3·52
34	0·2665	9·75	0·65	3·66					

(*b*) Temp. = 40°.

77	0·0628	8·67 (8·28)	0·67 (0·63)	13·8	79	0·1535	20·8	0·64	13·5
78	0·1256	17·2	0·65	13·6					

$k_{acid}/k_{phenol} = 0·65$.

III. 70% EtOH by weight. Mol.-fraction of EtOH = 0·4772.

Expt. No.	HCl, *N*.	$k_2 \times 10^6$.	k_2/k.	10^5k_2/[HCl].	Expt. No.	HCl, *N*.	$k_2 \times 10^6$.	k_2/k.	10^5k_2/[HCl].
(*a* Temp. = 25°.									
27	0·1375	4·51	0·61	3·3	28	0·2751	11·1 (7·5)	0·69	4·0
(*b*) Temp. = 30°.									
44	0·1986	10·2	0·59	5·1	43	0·3972	22	0·61	5·5
45	0·2648	14·2	0·58	5·3					
(*c*) Temp. = 35°.									
57	0·0756	6·3 (5·2)	0·69 (0·57)	8·34	55	0·2373	18·6 (18·2)	0·62 (0·61)	7·84
54	0·1186	9·8 (8·9)	0·66 (0·61)	8·25	56	0·3559	19·6 (28·0)	0·64 (0·60)	8·32
(*d*) Temp. = 40°.									
66	0·0366	4·65	0·61	12·77	69	0·0841	10·7 (9·9)	0·60	12·77
67	0·0729	9·25 (9·16)	0·61	12·66	70	0·1680	21·6	0·60	12·86

$k_{\text{acid}}/k_{\text{phenol}}$ = 0·603 (mean of 11 best values).

IV. 80% EtOH by weight. Mol.-fraction of EtOH = 0·6103.

(*a*) Temp. = 25°.									
86	0·0677	1·96	0·48	2·89	84	0·1806	5·58	0·50	3·09
83	0·0903	2·68	0·49	2·97	88	0·2030	5·98	0·46	2·94
87	0·1354	3·96	0·47	2·93					
(*b*) Temp. = 35°.									
80	0·1201	9·9 (9·8)	0·54	8·30	82	0·2402	19·8	0·50	8·25
89	0·1547	11·3	0·48	7·33	90	0·2702	21	0·48	7·72
81	0·1802	14·2	0·50	7·90					

$k_{\text{acid}}/k_{\text{phenol}}$ = 0·484 (mean of 9 values).

V. 90% EtOH by weight. Mol.-fraction of EtOH = 0·7612.

(*a*) Temp. = 25°.									
94	0·0431	1·23 (1·31)	0·38 (0·40)	2·86	92	0·1103	3·37	0·38	3·05
91	0·551	1·57	0·36	2·85	93	0·1654	4·93 (5·01)	0·35 (0·36)	2·98
95	0·0862	2·18 (2·26)	0·33 (0·34)	2·52					
(*b*) Temp. = 35°.									
99	0·0198	1·34	0·37	6·76	97	0·0661	4·91	0·38	7·44
100	0·0395	2·41 (2·46)	0·34	6·11	98	0·1322	9·23	0·35	6·98
101	0·0593	3·59	0·33	6·06					

$k_{\text{acid}}/k_{\text{phenol}}$ = 0·357 (mean of 10 values).

Measurement of the rate of liberation of acid in 95% EtOH was impracticable; from the initial titre the ratio k_2/k may be about 0·25—0·3, but it falls rapidly, even when less than 0·1 of the phenyl acetate has been attacked.

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