130. *The Factors determining the Velocity of Reactions in Solution. Molecular Statistics of the Esterification of Carboxylic Acids.*

By C. N. Hinshelwood and A. R. Legard.

As is now generally recognised, there are well-marked correlations between the energy of activation of a gaseous reaction and the absolute rate, which can, indeed, not infrequently be calculated fairly accurately from the simple formula $Ze^{-E/RT}$, Z being the collision number ("Kinetics of Chemical Change," Oxford, 1933, Chap. 3). Christiansen (*Z. physikal. Chem.*, 1924, **113**, 35) applied the formulæ of the kinetic theory to a few bimolecular reactions in solution and found that the rates calculated on the basis of analogy with the simplest gas reactions were several powers of ten greater than those observed. He mentioned as one possibility that the solvent exercised a specific deactivating influence, an idea which was taken up by Norrish and Smith (J., 1928, 129). Moelwyn-Hughes and Hinshelwood (J., 1932, 230) showed that certain typically slow reactions in solution did not take place any faster in the absence of the solvent, and, moreover, that the decomposition of chlorine monoxide (*Proc. Roy. Soc.*, 1931, *A*, **131**, 177), which has a normal rate in the gas phase (Hinshelwood and Hughes, J., 1924, **125**, 1841), takes place at the same rate and with the same activation energy in carbon tetrachloride solution. Thus the slowness of the reactions discussed by Christiansen must be inherent in their chemical nature rather than a function of the solvent. This idea is supported by the existence of a few examples of gas reactions with rates much smaller than the activation rate indicated by the simple formula (*e.g.*, Kistiakowsky and Nelles, *J. Amer. Chem. Soc.*, 1932, **54**, 2208). The work on chlorine monoxide showed that the formulæ for collisions between gas molecules could be applied with reasonable accuracy to the calculation of collisions between molecules of a solute, since it is very unlikely that such a compensation of effects would occur as to leave both the rate of reaction and the activation energy unchanged, if the collision number had been seriously changed by the solvent.

Moelwyn-Hughes ("Kinetics of Reactions in Solution," Oxford, 1933) then found in the literature a number of examples of reactions in solution where the rate is in fact given quite closely by the simplest formula, and it was pointed out by Grant and Hinshelwood (J., 1933, 258) that, of the known examples, nearly all which satisfy this formula are reactions in which an ion takes part. They suggested the desirability of exploring the hypothesis that in the expression $P \cdot Z \cdot e^{-E/RT}$ the value of P approaches unity when one of the reacting species is an ion, but tends to be several powers of ten smaller for reactions between undissociated molecules. Following this up, they found that for the reactions (*ibid.*) of ethyl chloride, bromide, or iodide with potassium hydroxide P is nearly unity, while for the benzoylation of aniline it is very much smaller (*ibid.*, p. **1351**). Williams and Hinshelwood (J., **1934**, 1079) later showed that this conclusion still held even if the reaction of the amine with the acid chloride is a termolecular change involving a molecule of the solvent.

Quantum mechanics predicts the possibility, though not the inevitability, of chemical reactions with rates governed by transformation probabilities independent of temperature but profoundly modifiable by perturbing forces of an electrical nature. This suggested (J., **1933**, 1357) that it might be profitable to explore the question of how far variations in E represented the operation of classical factors on reaction velocity, and variations in P that of quantum mechanical factors; *e.g.*, how far the high value of P in ionic reactions, or the influence of polar solvents, might depend upon the modification of a transformation probability by an electric field. Pursuing this idea, Williams and Hinshelwood (J., **1934**, 1079) studied the influence of polar substituents in aniline and in benzoyl chloride on the rate of benzoylation, to find out whether the electron-displacement effects of organic chemistry would be represented by large changes in P. They found, however, a rather striking correlation between the changes in rate and the changes in E, in spite of the fact that P was as small as 10^{-7}. This was in agreement with Bradfield (*Chem. and Ind.*, 1932, **51**, 254), who had concluded that, in aromatic substitution, changes in activation energy were the important factors governing the rate. It seemed, therefore, that the smallness of P in the benzoylation reaction might be more reasonably attributed to the necessity for some very precise orientation of the molecules at the moment of reaction, but no definite conclusion could be reached without further evidence. On the other hand, marked variations in P came to light in the study of catalytic reactions. Rolfe and Hinshelwood (*Trans. Faraday Soc.*, 1934, **30**, 935) found that for the reaction of methyl alcohol with acetic acid catalysed by undissociated molecules of acetic acid P was of the order 10^{-7}, while Williamson and Hinshelwood (*ibid.*, p. 1145) found a value of 10^{-3} when the catalyst was the ion $CH_3{\cdot}OH_2^+$. This led to the more extended investigation of the variations of P and E in esterification reactions, which is the subject of the experimental part of this paper. During the course of the work a paper by Smith (J., **1934**, 1744) appeared dealing with the acetone–iodine reaction. He finds that the value of P for various acid catalysts is a function of their acid strength, an observation which seems analogous to that of the contrast between the molecule of acetic acid and the ion $CH_3{\cdot}OH_2^+$, but, as will appear, the analogy does not prove to be as complete as might have been expected.

Kinetics of Esterification.—Esterification is, as far as we know, always a catalytic process, and is complicated kinetically by the fact that several of the molecular or ionic species present may be exerting independent catalytic effects. In the examples which we shall consider, the principal terms in the velocity equation are $-d[HX]/dt = k_0[HX][ROH_2^+] + k_1[HX]^2$, the alcohol, ROH, being the solvent and therefore of practically constant concentration. For a weak acid in presence of added hydrogen chloride, the first term so far outweighs the second that k_1 may be neglected and k_0 determined directly; k_1 can be determined by working in the absence of added hydrions at a fairly high temperature. In some of the examples, the reaction under these conditions becomes bimolecular with respect to the acid, and shows practically no retardation by small amounts of the sodium salt of the acid. The contribution of the hydrion-catalysed reaction must then be negligible, and k_1 is obtainable directly. When the addition of salt reveals an appreciable contribution from the hydrion-catalysed reaction, the appropriate corrections can be made by a suitable series of experiments with buffer solutions of varying concentration. At higher salt concentrations there may be an acceleration of the reaction in virtue of the catalytic effect of the anions. This, however, we are not directly concerned with. In general, there is little difficulty in isolating k_0 by working with added hydrogen chloride in the range 0—60°, and k_1 by working without added hydrions in the range 120—200°. It should be mentioned that the reaction between hydrogen chloride and aliphatic alcohols is rapid above 60°, having an energy of activation much higher than that with most organic acids. This fact limits the utility of hydrogen chloride as a catalyst, a matter which does not appear always to have been taken into account in the earlier work on esterification.

The method of measurement was that described by Rolfe and Hinshelwood and by

Williamson and Hinshelwood (*locc. cit.*). When k_1 is obtainable directly, it is calculated from the formula

$$kt = 1/(a - x) - 1/a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and k_0 is obtained from the Goldschmidt formula

$$kct = (1 + a/r) \log_e a/(a - x) - x/r \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the units being g.-mols. per litre and seconds, and the subscripts being omitted since both k's are essentially the constants of a bimolecular process; r is a constant which allows for the retardation of the hydrion-catalysed reaction by water. The values for different temperatures used are those found by Williamson and Hinshelwood, Goldschmidt having shown that, for a given temperature, r is a function only of the alcohol and not of the acid; a is the initial concentration of the organic acid and c that of the hydrogen chloride. All concentrations were corrected for the expansion of the solvent, data from the International Critical Tables being used.

EXPERIMENTAL.

Preparation of Materials.—The alcohols were always used as the solvent. Methyl alcohol was prepared by the method of Hartley and Raikes (J., 1925, **127**, 524), involving dehydration by aluminium amalgam; benzyl and *iso*propyl alcohols were prepared by careful fractionation of the purest obtainable commercial products, and *tert.*-butyl alcohol was purified by freezing out five times from the melt and discarding the mother-liquor. Acetic acid was purified by repeated freezing out, trichloroacetic acid by distillation (distillation in a vacuum or at normal pressure gave the same result), and other acids by recrystallisation to correct m. p. and titre. For the specimen of 2 : 4 : 6-trimethylbenzoic acid we are very much indebted to Professor Robinson. Each reaction presents certain special problems, so that a separate note on each is necessary, but the final velocity constants for the different temperatures are all collected together in Table I. In all the systems the Arrhenius equation is followed within the limits of experimental error.

Reaction Catalysed by Undissociated Acid.—*Acetic acid and methyl alcohol.* This has already been studied by Rolfe and Hinshelwood (*loc. cit.*). Special means were adopted to isolate k.

Acetic acid and benzyl alcohol. This gives bimolecular constants. A typical series at 154·0° for a solution 1·00*N* at 25° is as follows:

t (mins.)	30	60	120	180	240
Change, %	13·5	23·4	37·8	48·3	54·4
$k \times 10^5$	8·67	8·47	8·44	8·65	8·28

The mean, $8{\cdot}50 \times 10^{-5}$, corrected for the expansion of the solvent, becomes $9{\cdot}49 \times 10^{-5}$. As might be expected from the minuteness of the dissociation of carboxylic acids in benzyl alcohol, the hydrion effect is negligible. Buffer solutions of *N*/100-sodium acetate produced no retardation, but a slight acceleration, of the reaction, amounting to 6·0% at 154° and to 3·5% at 100°.

Acetic acid and iso*propyl alcohol.* The buffer effect was very small, and constants could be calculated directly by formula (1). At 100°, *N*/100-salt caused retardation by 4·0% for *N*-acid.

Acetic acid and tert.*-butyl alcohol.* This reaction presents special difficulties. It is very slow except at temperatures within measurable distance of the critical temperature of the alcohol. The practical difficulty of the high pressure developed was overcome by the use of small, stout, sealed tubes, but a further complication arose from the fact that above 200° the reaction came to equilibrium when less than 10% of the acid was esterified, a fact which seemed strange, since with other alcohols the reaction went almost to completion. Moreover, the equilibrium constant seemed to change with temperature more rapidly than corresponded to the van 't Hoff equation unless an improbably high value were assumed for the heat of reaction. When, however, it was realised that the critical temperature of the solvent was being approached, and that the latent heat of one of the reactants was therefore tending to zero, it became clear that rapid changes in the heat of reaction itself were to be expected, and abnormal displacements of equilibrium would result, which would, indeed, be in the sense observed. The procedure adopted was therefore to measure very carefully the progress of the reaction up to about 10%, and to find the initial rate by drawing tangents. Thence k can be calculated. It is easy to show from the kinetic equations that the early attainment of equilibrium does not introduce any inaccuracy into the initial rate method, since the curves start with the right slope and only begin to suffer rapid changes of curvature when equilibrium is fairly closely approached. Even at 100°, the buffer influence was small.

Benzoic acid and methyl alcohol. The contribution from the hydrion-catalysed reaction is smaller than with acetic acid. With N-solutions practically no correction is required over the range 100—150°. Bimolecular constants are obtained. These rise somewhat when the initial concentration is reduced to $N/5$ or to $N/20$. In the diluter solutions small concentrations of benzoate cause some retardation, and larger concentrations an acceleration.

	Initial concn.				Initial concn.		
Temp.	Acid.	Benzoate.	$k \times 10^{7}$.	Temp.	Acid.	Benzoate.	$k \times 10^{7}$.
153·1°	1·00	nil	111·2	100·0°	1·00	nil	5·11
	0·20	nil	123·9		0·20	nil	5·7
	0·05	nil	154·0				
	1·00	0·01	120·2		1·00	0·01	4·70

The following figures show the increase in speed produced by benzoate at higher concentrations, with $N/5$-acid : b = concentration of benzoate, v = initial rate, %, per 10^3 hours, and v' % per 10^3 minutes.

	100·0°.			
b	0·005	0·025	0·05	0·10
v	27·2	33·2	40·0	55·0

	153·1°.				
b	0·0	0·005	0·025	0·05	0·10
v'	10·5	10·5	15·0	24·0	36·3

By extrapolating the rising part of the curve of rate against benzoate concentration to zero concentration, we obtain the rate corrected for the hydrion effect. Further correcting this for expansion of the solvent, we find a value of 18,500 cals. for E. The effect of the buffer on the N-solutions is so small that the Arrhenius equation may be applied directly to the data in Table I, and a value 18,300 is found. The latter is adopted as the better value, since the experiments with N-solutions were more numerous, more accurate, and needed no extrapolation.

Benzoic acid and iso*propyl alcohol.* The influence of the sodium salt being small with acetic acid in *iso*propyl alcohol, and smaller with benzoic acid than with acetic acid in methyl alcohol, it was considered justifiable to make direct measurements with N-solutions.

Benzoic acid and tert.*-butyl alcohol.* The same special methods were necessary as with acetic acid and this alcohol.

Benzoic acid and benzyl alcohol. The temperature coefficient was determined directly with N-solutions. Sodium benzoate produces an acceleration.

o-*Nitrobenzoic acid and methyl alcohol.* The contribution of the hydrion-catalysed reaction here becomes considerable. Initial rates were measured for $N/5$-solutions with varying amounts of the sodium salt. At 153·7° :

Benzoate	0·0	0·0025	0·005	0·02	0·05	0·10
Relative initial rate	1·0	0·954	0·954	1·032	1·326	1·578

Extrapolating the rising part of the curve to zero concentration, we obtain a value of 0·92. The total velocity corresponds to a constant of $1{\cdot}32 \times 10^{-5}$. Thus the corrected constant is $1{\cdot}21 \times 10^{-5}$. A similar procedure at 100·0°, where the buffer influence is greater, gives a constant of $3{\cdot}54 \times 10^{-7}$, whence $E = 20{,}700$. This value is less reliable than those obtainable more directly.

Diphenylacetic acid and benzyl alcohol. Since none of the other acids showed an important hydrion effect in benzyl alcohol, a series of direct readings were made with N-solutions.

Trichloroacetic acid in benzyl alcohol. Although it is a strong acid in water, trichloroacetic acid is extremely weak in benzyl alcohol, and catalysis by hydrions is very small compared with that by undissociated molecules. The reaction is much faster than with the other acids studied, and conveniently measurable over the range 20—80°. To leave no doubt about the mechanism of the process measured, rather fuller data are given. Variation of the initial concentration over a wide range shows the reaction to be bimolecular with respect to the acid. Thus at 35·1° we have :

a	1·224	0·791	0·443	0·318	0·170	0·0900	0·0503
$k \times 10^{6}$	7·34	6·70	6·30	6·37	6·38	6·66	6·80

For $a = 0{\cdot}1634$ and sodium trichloroacetate = 0·01, $k \times 10^{6}$ was 6·20, and for $a = 0{\cdot}1763$ and sodium trichloroacetate = 0·02, $k \times 10^{6}$ was 6·50. For a given initial concentration, the bimolecular formula gives constant values of k over a considerable range; they fall away only when a rather high concentration of reaction product is reached. Thus at 35·1° the following typical results were obtained (a = 0·4426) :

Hours …………………	7·3	12·0	22·25	34·6	53·6	78·2	102·8
Change, % …………..	6·88	10·80	18·1	26·0	34·8	43·4	49·5
$k \times 10^6$ ………………	6·35	6·33	6·23	6·37	6·25	6·15	5·99

The values of k tabulated in Table I are mean values taken over the first third of the reaction. On account of the slight dependence on the initial concentration, values were found at each temperature for at least two concentrations, and that for a 0·50N-solution calculated by interpolation. The variation of k, however, is much too small to be of serious significance.

2 : 4 : 6-*Trimethylbenzoic acid in benzyl alcohol.* At first, it appeared that no measurements would be possible, since the pure molten acid suffered extensive decarboxylation at temperatures high enough to give a measurable rate of esterification. In benzyl-alcoholic solutions, however, the decarboxylation appeared to be negligible compared with that occurring in the pure state, since no pressure of carbon dioxide developed in the small sealed tubes used, no smell of mesitylene was observed, and the reaction was of the second order. Decarboxylation reactions are known in many examples, including that of the analogous 2 : 4 : 6-trinitrobenzoic acid (*Proc. Roy. Soc.*, **1931**, *A*, **131**, 186), to be of the first order. Thus we conclude that the actual rate of esterification is indicated by the rate of disappearance of the acid.

Temp. 279°	a ………..	0·713	0·356	0·238
	$k \times 10^5$ …	16·0	16·3	19·0

Temp. 240°	a ………..	0·713	0·356
	$k \times 10^5$ …	1·98	2·10

Reactions catalysed by Added Hydrions from Hydrogen Chloride.—Benzoic acid and methyl alcohol. The applicability of formula (2), already extensively tested by Goldschmidt, appears from the following figures for 25·0° :

a = 0·100, c = 0·020, r = 0·22; t' = time in minutes.

t' ………………	0	230	1175	1670	3120	4605	7270
$(a - x)$………..	0·0996	0·0946	0·0768	0·0694	0·0511	0·0402	0·0258
$k \times 10^4$ ……..	—	1·89	2·00	1·93	1·99	1·89	1·91

Of the mean values given in Table I, that for the highest temperature had to be corrected for a small disappearance of hydrogen chloride by reaction with the alcohol during the course of the experiment.

Diphenylacetic acid and methyl alcohol. The course of the reaction is given by (2).

TABLE I.

Mean velocity constants at various temperatures.

Acetic acid.
Benzyl alcohol.
a = 1·00.

Temp.	$k \times 10^6$.
154·0°	94·9
140·3	58·2
119·2	20·8
100·6	7·10

Acetic acid.
*iso*Propyl alcohol.
a = 1·00.

Temp.	$k \times 10^6$.
183·6°	72·9
154·4	23·2
139·2	11·9
118·6	4·49
100·5	1·65

Acetic acid.
tert.-Butyl alcohol.
a = 1·00.

Temp.	$k \times 10^7$.
211·0°	83·5
182·6	18·1
153·7	5·95
140·3	2·86
100·4	0·25

Benzoic acid.
Methyl alcohol.
a = 1·00.

Temp.	$k \times 10^7$.
153·1°	111·2
138·7	56·1
120·3	17·1
100·0	5·11

Benzoic acid.
*iso*Propyl alcohol.
a = 1·00.

Temp.	$k \times 10^7$.
210·8°	404
183·3	91·2
153·4	17·0
139·2	8·49

Benzoic acid.
tert.-Butyl alcohol.
a = 1·00.

Temp.	$k \times 10^8$.
211·1°	88·5
194·4	31·0
182·8	14·9

Benzoic acid.
Benzyl alcohol.
a = 1·00.

Temp.	$k \times 10^7$.
153·7°	119·2
138·9	54·6
121·0	17·1
100·0	4·24

Diphenylacetic acid.
Benzyl alcohol.
a = 1·00.

Temp.	$k \times 10^6$.
183·1°	108·2
154·6	38·0
140·1	18·1
119·1	6·73
100·7	2·06

Trichloroacetic acid.
Benzyl alcohol.
a = 0·500.

Temp.	$k \times 10^6$.
78·2°	91·5
65·4	47·3
52·95	21·1
35·1	6·42
24·2	2·94

2 : 4 : 6-Trimethylbenzoic acid.
Benzyl alcohol.
a = 0·587.

Temp.	$k \times 10^7$.
277·2°	1460
237·2	177
211·0	37·6
183·3	7·7

Benzoic acid.
Methyl alcohol.
Hydrogen chloride.

Temp.	a.	c.	$k \times 10^5$.	Temp.	a.	c.	$k \times 10^5$.
0·2°	0·100	0·0100	1·67	50·6°	0·100	0·0100	152
25·0	0·100	0·0100	19·0		0·100	0·0200	157
	0·100	0·0200	19·4	60·3	0·100	0·0100	303
40·0	0·100	0·0100	65·6				
	0·100	0·0200	65·0				

Diphenylacetic acid.
Methyl alcohol.
Hydrogen chloride.

Temp.	Mean $k \times 10^4$.
0·0°	3·63
24·05	19·0
34·0	33·6
44·0	55·4
54·14	106·6

DISCUSSION.

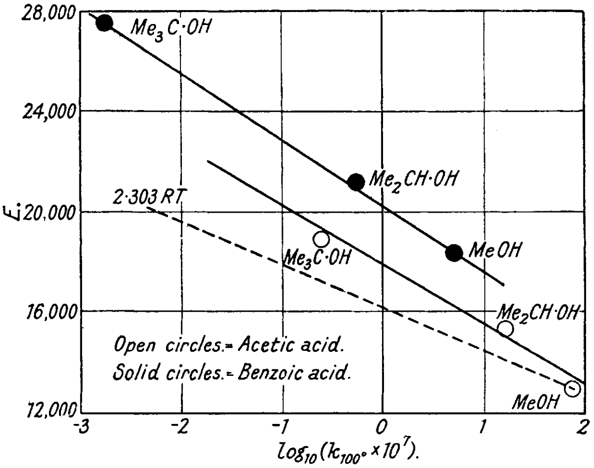
General.—The values of the constants in the formula $\log_e k = A - E/RT$, together with the calculated values for the velocity constant at 100·0°, are given in Table II.

TABLE II.

Acid.	Alcohol.	Catalyst.	*A*.	*E*.	$k_{100°} \times 10^7$.
$CH_3{\cdot}CO_2H$	$CH_3{\cdot}OH$	$CH_3{\cdot}CO_2H$	5·817	13,000	76·4
$C_6H_5{\cdot}CO_2H$	$CH_3{\cdot}OH$	$C_6H_5{\cdot}CO_2H$	10·282	18,300	5·07
o-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$	$CH_3{\cdot}OH$	o-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$	13·20	20,700	3·54
$C_6H_5{\cdot}CO_2H$	$C_6H_5{\cdot}CH_2{\cdot}OH$	$C_6H_5{\cdot}CO_2H$	12·054	19,750	4·19
$CH_3{\cdot}CO_2H$	$(CH_3)_3C{\cdot}OH$	$CH_3{\cdot}CO_2H$	7·943	18,830	0·24
$CH_3{\cdot}CO_2H$	$C_6H_5{\cdot}CH_2{\cdot}OH$	$CH_3{\cdot}CO_2H$	8·942	15,350	72·1
$CHPh_2{\cdot}CO_2H$	$C_6H_5{\cdot}CH_2{\cdot}OH$	$CHPh_2{\cdot}CO_2H$	9·061	16,350	21·0
$CH_3{\cdot}CO_2H$	$(CH_3)_2CH{\cdot}OH$	$CH_3{\cdot}CO_2H$	7·434	15,330	16·4
$C_6H_5{\cdot}CO_2H$	$(CH_3)_2CH{\cdot}OH$	$C_6H_5{\cdot}CO_2H$	11·879	21,150	0·528
$C_6H_5{\cdot}CO_2H$	$(CH_3)_3C{\cdot}OH$	$C_6H_5{\cdot}CO_2H$	14·745	27,500	0·00171
2 : 4 : 6-$C_6H_2Me_3{\cdot}CO_2H$	$C_6H_5{\cdot}CH_2{\cdot}OH$	$C_6H_2Me_3{\cdot}CO_2H$	16·481	27,700	0·00741
$CCl_3{\cdot}CO_2H$	$C_6H_5{\cdot}CH_2{\cdot}OH$	$CCl_3{\cdot}CO_2H$	9·580	13,130	2760
$CH_3{\cdot}CO_2H$	$CH_3{\cdot}OH$	$CH_3{\cdot}OH_2^+$	14·448	10,200	$1·89 \times 10^7$
$C_6H_5{\cdot}CO_2H$	$CH_3{\cdot}OH$	$CH_3{\cdot}OH_2^+$	18·039	15,700	$4·0 \times 10^5$
$CHPh_2{\cdot}CO_2H$	$CH_3{\cdot}OH$	$CH_3{\cdot}OH_2^+$	12·067	10,800	$7·8 \times 10^6$

The most convenient way of obtaining a general view of the changes in *E* and *P* from one reaction to another is to plot *E* against log *k* for a standard temperature. Since (number of molecules reacting) $= P\,.\,Z\,.\,e^{-E/RT}$, $\log_e k = \log_e C + \log_e P + \log_e Z - E/RT$, where *C* is a universal constant, for conversion of units. For the series of reactions under consideration, the variations of $\log_e Z$ will be neglected in a preliminary survey, since they depend upon changes in square roots of functions of the molecular weights and upon variations in molecular diameters, two factors which are small compared with others and partly compensate one another. Thus, if the difference in speed of two reactions is due entirely to changes in *E*, the two points on the graph will be connected by a line of slope 2·303*RT*. The actual slope of the line shows how far the changes in speed are due to changes in *E* and how far to changes in *P*.

FIG. 1.

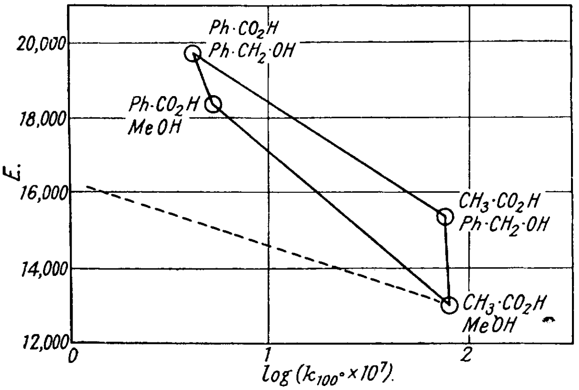


In Fig. 1 the results for the reactions of acetic and benzoic acids severally with a primary, secondary, and tertiary aliphatic alcohol are shown. When change of alcohol decreases the velocity of esterification, whether of acetic or of benzoic acid, there is an increase in the activation energy even greater than that corresponding to the line of slope 2·303*RT*. Thus *P* is actually greater for the slower reactions.

Fig. 2 reveals a similar increase both in *E* and in *P* on passing from methyl to benzyl alcohol, which is parallel with the increase in both factors on passing from acetic to benzoic acid.

Fig. 3 represents the results for a series of acids in benzyl alcohol, increases in E on passing from trichloroacetic acid through acetic acid to diphenylacetic acid almost entirely accounting for the changes in speed. For benzoic and trimethylbenzoic acids the values

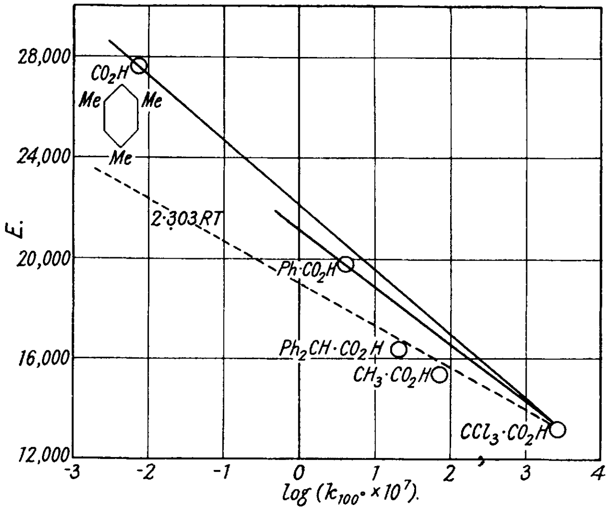
FIG. 2.



of E are again greater than corresponds to the decreased rates, so that P must have increased.

Fig. 4 shows the increase in P by several powers of ten when the hydrion replaces the undissociated acid molecule as the catalyst. Benzoic and acetic acids show nearly the same difference, the four points in the figure forming an approximately true parallelogram. The dotted lines have the slope $2{\cdot}303RT$.

FIG. 3.



Processes involved in Ester Formation.—There is good evidence that when an ester is formed the hydroxyl and not the hydrogen of the carboxylic acid is replaced (cf. Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508). On the other hand, catalysis by another acid molecule may depend upon the transfer of a proton from the catalyst at some stage of the reaction. Rate of esterification might, therefore, be a function of the readiness with which the dismemberments (1), (2), and (3) occur. (2) and (3), involving the movement of a proton only, might depend upon a quantum-mechanical transition probability.

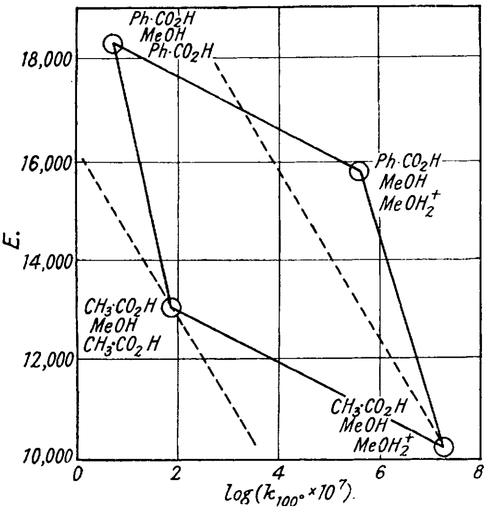
In so far as this was a controlling factor, the slowest reactions would be determined by small values of *P* rather than by large values of *E*. In fact, the reverse is found, as has just

$$\underset{(1)}{\mathrm{R{\cdot}CO\,|\,OH}} \qquad \underset{(2)}{\mathrm{R{\cdot}O\,|\,H}} \qquad \underset{(3)}{\mathrm{R{\cdot}COO\,|\,H}}$$

been shown. If, therefore, the processes (2) and (3) determine the rate, their ease appears to be measured by the activation energy.

When the catalyst is a second molecule of the reacting acid, (1) and (3) will be oppositely influenced by polar substituents. Thus, with trichloroacetic acid, (3) occurs more readily than with acetic acid, and (1), it may be presumed, correspondingly less readily. Hence compensation may be expected, though to an unpredictable extent. Actually, the reaction of trichloroacetic acid is more rapid than that of acetic acid. It is important to observe, however, that the compensation reflects itself in the not very different value of *E*. We do not find, as we might have done, that increased difficulty of (1) is reflected in an increased *E* while the increased ease of (3) leads to a correspondingly greater *P*.

FIG. 4.



So far, therefore, there is no positive evidence of the control of this reaction by quantum-mechanical transition probabilities. Nor do the foregoing results correspond to those found by Smith for the influence of different acid catalysts on the rate of enolisation of acetone, there being little sign of a correlation between the values of *P* of the acids and their acid strengths in water. We do, however, find that in the extreme case of replacement of the undissociated molecule by the hydrion, *P* increases by about 10^4. Whether this really depends upon the greater ease of proton transfer or whether it depends upon the powerful orientating influence of the charged ion in contrast with the undissociated molecule, is a matter for further experiment.

Absolute Magnitude and Nature of P.—The foregoing conclusions are to a large extent independent of the absolute value of *P*. To determine this it is necessary to satisfy ourselves that collision numbers in solution can be calculated correctly, at least as regards order of magnitude, and to know what correction, if any, must be applied to the observed energy of activation to allow for the variation with temperature of solvent–solute collisions. Under the conditions of these experiments, acid and catalyst must meet in presence of a suitable solvent molecule. That the ordinary formulæ for collisions between gas molecules are applicable, at least approximately, to the collisions between two solute molecules is indicated both by theoretical considerations and by the experimental results for chlorine monoxide (see p. 587). Collisions between solute and solvent are more difficult to treat. The number diminishes as the temperature rises, on account of the relatively rapid increase in the free space in the liquid as the total volume expands. The decrease in viscosity with rise in temperature runs parallel with this and may be due partly to the same cause. According to Jowett's formula (cf. Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1933, p. 159), the appropriate correction to make to the observed value of *E* is to add *Q* obtained from the formula $-\,d\log_e\eta/dT = Q/RT^2$. How far this correction is valid in general, or necessary in the present example, is a matter of some uncertainty, but when it is applied, the absolute value of *P* for the reaction between acetic acid and methyl alcohol catalysed by undissociated acetic acid is found to be of the order 10^{-7}. If the correction is omitted, the value is between 10^{-8} and 10^{-9}. Since *Z* will not vary seriously,

$\log_e P$ will be proportional to A of Table II, whence we find that the greatest value of P, for methyl alcohol, benzoic acid, and hydrion, is about 3×10^{-2}, with the viscosity correction (and 10—10^2 times smaller without). The other values range between the above limits. The highest values of P could quite easily be accounted for by the necessity for a correct orientation of the molecules at the time of reaction. The lowest are perhaps surprisingly small to be accounted for in this way, although the three molecules of alcohol, acid, and catalyst may have to arrange themselves in a delicately adjusted geometrical pattern before reaction can occur (and this adjustment may be rendered much easier by the presence of a charged ion).

Correlation between P *and* E.—Figs. 1—3 all show a quite definite increase of P with E. The slowest reactions are not slow because P is small, but because E is large, and indeed, when E is large P is also large. For systems, therefore, which only become reactive when supplied with a large excess of energy, the factor which normally renders the collisions inefficient appears to control the situation to a much smaller extent. Possible explanations are not difficult to invent. When a molecule is dislocated by violent internal vibrations, its exact orientation may well become of less consequence. Or again, a high degree of activation may cause such electrical polarisation that a transition probability, otherwise small, tends towards unity. Choice among these and other possibilities must await further experiment.* (It may be pointed out that the viscosity corrections for methyl, *iso*propyl, *tert.*-butyl, and benzyl alcohols are respectively 2480, 5100, 6500, and 5050 calories, and, if they were applied to the values in Figs. 1—3, they would exaggerate rather than explain away the correlation between high E and high P values.)

Nature of Steric Hindrance.—The diminution in rate on passing from primary through secondary to tertiary alcohols, from methyl to benzyl alcohol, from acetic to benzoic acid, and especially from benzoic acid to 2 : 4 : 6-trimethylbenzoic acid, exemplifies what is often called steric hindrance. It is of interest to note that the diminution is not due to decrease of P. Hence steric hindrance is energetic rather than geometrical in nature. The only example among those studied where there is not an actual increase in P for the sterically hindered reaction is on passing from acetic to diphenylacetic acid with hydrion as a catalyst in methyl alcohol : E increases by 600 cals. and P decreases by about one power of ten.

Conclusion.—In conclusion, it may be useful to summarise some information now available about the factor P for reactions in solution.

(1) It varies over the range 10^{-9} to unity. (2) When one of the reacting species is a charged ion, it tends to approach unity, sometimes rather closely. (3) There are examples, though rather less common than might have been expected, where it rises much above unity, on account, presumably, of the participation of internal degrees of freedom, as with unimolecular gas reactions of complex molecules. These cases do not seem to be common enough to invalidate the statement that unity is the limiting value for an important class. (4) Polar substituents in the benzene ring may produce great changes in velocity by changing the activation energy without affecting P to a degree comparable in importance,

---

* If the energy of activation is distributed among many degrees of freedom, P may assume a value far greater than unity ("Kinetics of Chemical Change in Gaseous Systems," 3rd edition, p. 187). On the other hand, the necessity for the redistribution of the energy to the appropriate parts of the molecule tends to reduce P. With unimolecular gas reactions, the first factor nearly always seems to predominate, but in certain circumstances the second might. If we had a change in mechanism from one involving direct activation in, say, one degree of freedom to one involving several degrees of freedom and an internal redistribution, then we might easily have an increase in E and a corresponding increase in P. Something of this kind is observed in certain catalytic reactions (*op. cit.*, p. 227). Where the collisions are such as to place the energy directly in the vital bond we have the low-E type, but where the vital bond is, as it were, shielded, much more energy must be put into the molecule, in order that some of it may find its way to the right place. But the increased variety of activated states now possible increases P very greatly. This effect might be superimposed on a geometrical condition making P tend to be small, and we should have the state of affairs under consideration in the present paper. The part which such factors may play in reactions in solution is under experimental investigation, but for the moment it seems preferable to see how much progress can be made without introducing this complication.

even when P itself is very small. (5) Steric hindrance depends upon E rather than upon P. In esterification, (6) changes in the alcohol or the reacting acid modify the rate according to their effect on E, (7) P tends to increase with E, (8) on changing from a non-ionic catalyst to the hydrion, P increases by about 10^4, but differences between undissociated acid catalysts seem to depend mainly upon E, in contrast with what has been found for the enolisation of acetone.

SUMMARY.

From the study of the rates and energies of activation of 15 esterification reactions, the following conclusions are reached.

(1) For a series of alcohols, changes in rate are determined by variations in the activation energy, not by the constant P in the formula : Rate $= P \,.\, Z \,.\, e^{-E/RT}$.

(2) Similarly, for a series of acids, those which react most slowly correspond to the highest values of E.

(3) In general, there is a correlation between large values of E and large values of P and *vice versa.*

(4) On changing from a non-ionic catalyst to the hydrion, there is an increase of P of about 10^4, but differences between various non-ionic catalysts seem rather to depend upon the values of E itself.

(5) Steric hindrance appears to depend upon high activation energy, rather than to be of a purely geometrical character.

(6) The results provide no positive evidence that the rate of esterification reactions depends upon quantum-mechanical transition probabilities, or that the smallness of P in such reactions is connected with the smallness of such probabilities, rather than with the necessity for a delicately adjusted orientation of the molecules at the moment of reaction.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE, OXFORD.

[*Received, March 7th,* 1935.]