

381. *Heats of Activation of the Acetone-Iodine Reaction.*

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FOR acid- and base-catalysed reactions very little information is available as to the dependence of the activation energy on the catalytic environment, measurements of the heats of activation relating to a series of different catalysts having been made only for the mutarotation of glucose (Kilpatrick and Kilpatrick, *J. Amer. Chem. Soc.*, 1931, **53**, 3698) and the enolisation of ethyl acetoacetate (Pedersen, *J. Physical Chem.*, 1934, **38**, 601). It was obviously desirable that the observations should be extended to include other reactions of this type.

The reaction investigated was that between acetone and iodine, the heat of activation for which when catalysed by strong acids had already been obtained by Rice and Kilpatrick (*J. Amer. Chem. Soc.*, 1923, **45**, 1401) and by Rice and Lemkin (*ibid.*, p. 1896). The

latter workers also showed that, on replacing the strong acid by a weak acid as catalyst, the heat of activation of the reaction is diminished, but the numerical results quoted are of no great value, since the heats of activation here are composite quantities relating to the solution of the weak acid as a whole and not to any specific catalyst present. In the present experiments two basic and five acid catalysts have been employed, and from measurements of reaction velocity at 0° and 25°, the heat of activation relative to each catalyst has been deduced.

(1) *Catalyst: Hydrochloric Acid.*—The acetone was 0.270*M*, and the acid was varied from 0.008 to 0.04*M*. The mean values of the ratio V/c_{HCl} at 0° and 25° respectively were 1.82×10^{-5} and 4.46×10^{-4} (l./g.-mol./min.). Since in a dilute solution of a strong acid the observed catalytic effect is due almost entirely to hydrion, any effect due to hydroxyl ion or undissociated molecules of acid being negligible, the above values represent the catalytic coefficients of the hydrion at the two temperatures, and hence for catalysis by this ion the ratio ${}_{25}k_{\text{h}}/{}_0k_{\text{h}} = 24.5$, which gives $E = 20,680$ cals. These values agree closely with those obtained by Rice and Kilpatrick (*loc. cit.*), *viz.*, 24,517 and 20,695 respectively.

In experiments with other and less efficient catalysts it was necessary to increase the concentration of acetone from 0.270 to 0.677*M*, since otherwise the reaction at 0° was inconveniently slow; this does not, however, in any way interfere with the strict comparability of the results for the various catalysts, for it was found that with hydrochloric acid as catalyst the ratio V/c_{acetone} , and hence the ratio ${}_{25}k_{\text{h}}/{}_0k_{\text{h}}$, was quite unaltered.

(2) *Catalyst: 0.1*M*-Acetic Acid + c*M*-Sodium Acetate.*—In aqueous mixtures of a weak acid and its sodium salt, the effective catalysts, besides the hydrion, are the undissociated acid molecule and the acid anion, and in order to evaluate the heat of activation corresponding with each of these catalysts, an obvious procedure would be to determine, by the methods already developed (Dawson and Carter, *J.*, 1926, 2282; Dawson and Dean, *ibid.*, p. 2872), the catalytic coefficients k_{m} and k_{a} at the two temperatures, and thus obtain the ratios ${}_{25}k_{\text{m}}/{}_0k_{\text{m}}$ and ${}_{25}k_{\text{a}}/{}_0k_{\text{a}}$. An alternative method of treatment has, however, been preferred, which has the advantage of allowing of the evaluation of the required velocity ratios directly, without the necessity for the intermediate step of the determination of the catalytic coefficients k_{m} and k_{a} at either temperature.

(a) *Evaluation of ${}_{25}k_{\text{a}}/{}_0k_{\text{a}}$.* The velocities in mixtures corresponding with the above series will, in general, be given by the equation

$$V_{\text{obs.}} = V_{\text{h}} + V_{\text{m}} + V_{\text{a}} = V_{\text{h}} + k_{\text{m}}c_{\text{m}} + k_{\text{a}}c_{\text{a}}$$

and, writing $V_{\text{obs.}} - V_{\text{h}} = V_{\text{corr.}}$, we have for the velocity at t° :

$$tV_{\text{corr.}} = t k_{\text{m}}c_{\text{m}} + t k_{\text{a}}c_{\text{a}}$$

Considering now any given mixture at 0° and 25°, we have

$$\frac{{}_{25}k_{\text{a}}c_{\text{a}}}{{}_0k_{\text{a}}c_{\text{a}}} = \frac{{}_{25}V_{\text{corr.}} - {}_{25}k_{\text{m}}c_{\text{m}}}{{}_0V_{\text{corr.}} - {}_0k_{\text{m}}c_{\text{m}}}$$

or putting ${}_{25}k_{\text{a}}/{}_0k_{\text{a}} = R_{\text{a}}$, and similarly for R_{m} , and ${}_{25}V_{\text{corr.}}/{}_0V_{\text{corr.}} = R_{\text{obs.}}$, it follows that ${}_{25}V_{\text{corr.}} - {}_{25}k_{\text{m}}c_{\text{m}} = R_{\text{a}} \frac{{}_{25}V_{\text{corr.}}}{R_{\text{obs.}}} - R_{\text{a}} \frac{{}_{25}k_{\text{m}}c_{\text{m}}}{R_{\text{m}}}$ which reduces to

$$\frac{1}{R_{\text{obs.}}} = \frac{1}{R_{\text{a}}} - \frac{1}{{}_{25}V_{\text{corr.}}} \left\{ \frac{{}_{25}k_{\text{m}}c_{\text{m}}}{R_{\text{a}}} - \frac{{}_{25}k_{\text{m}}c_{\text{m}}}{R_{\text{m}}} \right\} \dots \dots \dots (1)$$

The product ${}_{25}k_{\text{m}}c_{\text{m}}$ may be regarded as having an identical value for each mixture in the series, since c_{m} is sensibly constant throughout, and the value of ${}_{25}k_{\text{m}}$ is quite unaffected by the presence of considerable salt, in the case of sodium chloride even up to a concentration of 2*M* (Dawson and Key, *J.*, 1928, 1248). It follows that on plotting $1/R_{\text{obs.}}$ for the various mixtures against the corresponding value of $1/{}_{25}V_{\text{corr.}}$, a straight line will be obtained, the intercept of which on the $1/R$ axis gives the value of $1/R_{\text{a}}$. In Table I, equation (1) is applied to the data for mixtures in which the salt concentration is varied from 0.0085 to 0.3*M*.

TABLE I.

0.1M-Acetic acid + cM-sodium acetate; acetone, 0.677M.

c	0.300	0.200	0.100	0.0150	0.0100	0.00850
${}_{25}V_{\text{obs.}} \times 10^7$	33.7	23.5	13.45	6.17	6.25	6.40
${}_{25}V_{\text{h}} \times 10^7$	0.1	0.15	0.28	1.44	2.08	2.41
${}_{25}V_{\text{corr.}} \times 10^7$	33.6	23.35	13.17	4.73	4.17	3.99
${}_0V_{\text{obs.}} \times 10^7$	1.043	0.742	0.446	0.249	0.260	0.265
${}_0V_{\text{h}} \times 10^7$	0.005	0.005	0.011	0.059	0.085	0.098
${}_0V_{\text{corr.}} \times 10^7$	1.038	0.737	0.435	0.190	0.175	0.167
$1/R_{\text{obs.}}$	0.0309	0.0315	0.0330	0.0402	0.0410	0.0418
$1/R_{\text{obs.}}$ (calc.)	0.0309	0.0315	0.0331	0.0397	0.0411	0.0416
c_{a}	0.300	0.200	0.100	0.0151	0.0102	0.00873
$1/R_{\text{obs.}}$ (calc.)	0.0309	0.0315	0.0331	0.0401	0.0413	0.0418

In the first row is given the salt concentration, and in rows 2 and 5 respectively the observed velocities at 25° and 0°. The values of V_{h} (rows 3 and 6) are derived from the values of k_{h} and K_{a} appropriate to the salt concentration (Dawson and Key, J., 1928, 1239; Dawson and Lowson, J., 1929, 1217). In salt-free solutions, K_{a} has been taken as 1.85×10^{-5} and k_{h} at 25° and 0° respectively as 11.15×10^{-4} and 0.455×10^{-4} . In the absence of any reliable data to the contrary in each case the same value has been assigned to K_{a} at 0° and at 25°. Recent work (Harned and Ehlers, *J. Amer. Chem. Soc.*, 1934, 55, 665) would indicate that K_{a} is probably slightly smaller at the lower temperature, but the difference, if real, would be too small appreciably to affect the present results. The resulting values for $V_{\text{corr.}}$ (rows 4 and 7) give the values of $1/R_{\text{obs.}}$ recorded in row 8. These, when plotted against $1/{}_{25}V_{\text{corr.}}$ give the straight line $1/R_{\text{obs.}} = 0.02945 + 4.85 \times 10^{-9}/{}_{25}V_{\text{corr.}}$. The numbers calculated by means of this equation are given in row 9. It is clear that the equation reproduces closely the variation of $1/R_{\text{obs.}}$ with increasing salt concentration. The resulting value of R_{a} is $1/0.02945 = 34.0$, which gives $E = 22,800$ cal. for catalysis by the acetate ion.

(b) *Evaluation of R_{m} .* On substituting ${}_{25}V_{\text{corr.}} - {}_{25}k_{\text{a}}c_{\text{a}}$ for ${}_{25}k_{\text{m}}c_{\text{m}}$ in (1) and rearranging, one obtains

$$\frac{1}{R_{\text{obs.}}} = \frac{1}{R_{\text{m}}} + \frac{c_{\text{a}}}{{}_{25}V_{\text{corr.}}} \left\{ \frac{{}_{25}k_{\text{a}}}{R_{\text{a}}} - \frac{{}_{25}k_{\text{a}}}{R_{\text{m}}} \right\} \dots \dots \dots (2)$$

For salt concentrations up to 0.3M it is justifiable to regard ${}_{25}k_{\text{a}}$ as a constant (Dawson and Key, *loc. cit.*), and hence the plot of $1/R_{\text{obs.}}$ against $c_{\text{a}}/{}_{25}V_{\text{corr.}}$ will give a straight line, the intercept of which on the zero ordinate gives $1/R_{\text{m}}$. The relevant data are given in the last two lines of Table I. The values of c_{a} allow for the ionisation of the acetic acid in the solutions of smaller salt concentrations; and the values in the last row are calculated by means of the equation $1/R_{\text{obs.}} = 0.0453 - 1.617 \times 10^{-7} c_{\text{a}}/{}_{25}V_{\text{corr.}}$. Hence R_{m} for acetic acid is $1/0.0453 = 22.1$, which gives $E = 20,010$ cal.

(3) *Catalyst: 0.1M-Propionic Acid + cM-Sodium Propionate.*—The treatment was exactly similar to that adopted in the previous case.

(a) R_{a} for the propionate ion. The data are recorded in Table II, in which the arrangement is similar to that in Table I.

TABLE II.

0.1M-Propionic acid + cM-sodium propionate; acetone, 0.677M.

c	0.300	0.200	0.100	0.0200	0.0150	0.00850
${}_{25}V_{\text{obs.}} \times 10^7$	44.8	30.8	16.9	6.30	5.90	5.74
${}_{25}V_{\text{h}} \times 10^7$	0.09	0.12	0.23	0.83	1.08	1.81
${}_{25}V_{\text{corr.}} \times 10^7$	44.7	30.7	16.7	5.47	4.82	3.93
${}_0V_{\text{obs.}} \times 10^7$	1.352	0.946	0.549	0.248	0.240	0.245
${}_0V_{\text{h}} \times 10^7$	0.004	0.005	0.009	0.034	0.044	0.074
${}_0V_{\text{corr.}} \times 10^7$	1.348	0.941	0.540	0.214	0.196	0.171
$1/R_{\text{obs.}}$	0.0301	0.0307	0.0323	0.0391	0.0407	0.0435
$1/R_{\text{obs.}}$ (calc.)	0.0302	0.0307	0.0323	0.0392	0.0405	0.0432
c_{a}	0.300	0.200	0.100	0.0201	0.0151	0.00866
$1/R_{\text{obs.}}$ (calc.)	0.0301	0.0307	0.0323	0.0391	0.0407	0.0435

In the calculation of V_h (rows 3 and 6), K_a has been taken as 1.38×10^{-5} in salt-free solution. The values of $1/R_{obs.}$ given in line 9 are calculated by means of the equation $1/R_{obs.} = 0.0289 + 5.60 \times 10^{-9}/_{25}V_{corr.}$, from which R_a for the propionate ion is $1/0.0289 = 34.6$, which gives $E = 22,910$ cals.

(b) R_m for propionic acid. The effect of increasing the salt concentration on the value of $1/R_{obs.}$ can be represented by the equation $1/R_{obs.} = 0.0500 - 2.963 \times 10^{-7} c_a/_{25}V_{corr.}$, which gives $R_m = 1/0.0500 = 20.0$, or $E = 19,370$ cals. The additional data are at the foot of Table II. The numbers given in the last line are calculated by means of the equation given above.

(4) Catalyst: Chloroacetic Acid.—Measurements were made in solutions of chloroacetic acid of concentrations between 0.01 and 0.5M. The only effective catalysts in such solutions will be the hydrion and the undissociated acid molecule, any effect due to the acid anion being negligible owing to its feeble catalysing power and its small concentration in these solutions. Hence the observed velocity is given by $V_{obs.} = V_h + V_m = V_h + c_m k_m$, and comparing the velocities at the two temperatures for solutions of the same concentration and writing $_{25}V_{obs.}/_0V_{obs.} = R_{obs.}$ we have, by similar reasoning to that on p. 1745,

$$\frac{1}{R_{obs.}} = \frac{1}{R_m} - \frac{_{25}V_h}{_{25}V_{obs.}} \left\{ \frac{1}{R_m} - \frac{1}{R_h} \right\} \dots \dots \dots (3)$$

The plot of $1/R_{obs.}$ against $_{25}V_h/_{25}V_{obs.}$ will thus give a straight line, the intercept of which on the $1/R$ axis gives $1/R_m$, and which, for $_{25}V_h/_{25}V_{obs.} = 1 (c = 0)$, gives $1/R_{obs.} = 1/R_h$. The data are recorded in Table III.

TABLE III.

Chloroacetic acid; acetone, 0.677M.

c	0	0.0100	0.0200	0.0500	0.100	0.200	0.500
$_{25}V_{obs.} \times 10^6$		3.99	6.30	11.50	18.05	28.9	56.2
$_0V_{obs.} \times 10^6$		0.169	0.272	0.502	0.802	1.318	2.58
$c_h \times 10^3$		3.204	4.792	7.970	11.55	16.64	26.73
$_{25}V_h \times 10^6$		3.57	5.34	8.89	12.88	18.85	29.80
$_{25}V_h/_{25}V_{obs.}$	1.00	0.895	0.848	0.773	0.713	0.642	0.530
$1/R_{obs.}$	0.0408	0.0424	0.0432	0.0437	0.0445	0.0456	0.0459
$1/R_{obs.}$ (calc.)	0.0415	0.0425	0.0429	0.0437	0.0442	0.0450	0.0460

In the first row is given the concentration of the chloroacetic acid; in rows 2 and 3 respectively the observed velocities at 25° and 0°, and in row 7 the corresponding values of $1/R_{obs.}$. In the calculation of c_h (row 4), K_a has been taken as 1.51×10^{-3} , the value given by Dawson, Hall, and Key (J., 1928, 2844) for concentrations between 0.005 and 0.5M. The numbers given in the last line are those calculated by means of the equation $1/R_{obs.} = 0.0510 - 0.0095_{25}V_h/_{25}V_{obs.}$, which is seen to reproduce quite closely the change in $1/R_{obs.}$ on passing through a series of solutions in which the catalytic activity of the hydrion falls from 100% to only 53% of the total catalytic effect. From the equation, $R_m = 1/0.0510 = 19.6$, and $E = 19,230$ cals.

(5) Catalyst: Dichloroacetic Acid.—A similar procedure to the foregoing was adopted. Velocity measurements were made in solutions of concentrations ranging from 0.002 to 0.1M. The data are given in Table IV. On the provisional assumption that K_a is independent of dilution and has the value 5.0×10^{-2} (Drucker, Z. physikal. Chem., 1904, 49, 563), the values of c_h given in the fourth row are obtained. The corresponding values of

TABLE IV.

Dichloroacetic acid; acetone, 0.677M.

c	0	0.00200	0.00500	0.0100	0.0200	0.0500	0.100
$_{25}V_{obs.} \times 10^6$		2.20	5.55	10.61	20.38	46.7	87.2
$_0V_{obs.} \times 10^6$		0.091	0.233	0.451	0.879	2.033	3.850
$c_h \times 10^3$		1.925	4.575	8.54	15.30	30.9	50.0
$_{25}V_h \times 10^6$		2.13	5.08	9.48	17.03	34.6	56.25
$_{25}V_h/_{25}V_{obs.}$	1.00	0.968	0.915	0.889	0.836	0.741	0.645
$1/R_{obs.}$	0.0408	0.0414	0.0420	0.0425	0.0431	0.0435	0.0442
$1/R_{obs.}$ (calc.)	0.0410	0.0414	0.0419	0.0421	0.0426	0.0436	0.0445

${}_{25}V_h$ and ${}_{25}V_h/{}_{25}V_{obs.}$ are given in lines 5 and 6. The values of $1/R_{obs.}$ in the last line are derived from the equation $1/R_{obs.} = 0.0508 - 0.00976{}_{25}V_h/{}_{25}V_{obs.}$.

Although this equation reproduces the experimental data as closely as can be expected, this cannot necessarily be taken as evidence for the exactness of this particular value of K_a , or as a justification for the assumption of a constant K_a for these solutions, since the calculated value of $1/R_{obs.}$ is relatively insensitive to a moderate alteration in the values of c_h and V_h ; but conversely, an appreciable alteration in the values to be assigned to c_h would have little effect on the resulting value of $1/R_m$. This is shown to be the case by the following data, where alternative values are taken for K_a based on the data of Dawson and Lowson (*loc. cit.*) for the ionisation of dichloroacetic acid in sodium chloride solutions.

c	0	0.00200	0.00500	0.0100	0.0200	0.0500	0.100
μ		0.004	0.0075	0.0115	0.018	0.034	0.054
$K_a \times 10^2$		5.0	5.1	5.2	5.3	5.55	5.8
$c_h \times 10^3$		1.925	4.585	8.585	15.48	31.80	52.5
${}_{25}V_h \times 10^6$		2.13	5.09	9.53	17.22	35.6	59.05
${}_{25}V_h/{}_{25}V_{obs.}$	1.00	0.968	0.922	0.898	0.845	0.763	0.677
$1/R_{obs.}$	0.0408	0.0414	0.0420	0.0425	0.0431	0.0435	0.0442
$1/R_{obs.}$ (calc.)	0.0410	0.0413	0.0418	0.0421	0.0426	0.0435	0.0444

In the second line is given the ionic strength of the solutions derived from the approximate c_h of the solutions and the concentration of potassium iodide. The values of K_a (row 3) have been deduced on the assumption that K_a will be identical in the solution of ionic strength μ and in a sodium chloride solution of the same ionic strength. The values of $1/R_{obs.}$ given in the last line are obtained by means of the equation $1/R_{obs.} = 0.0515 - 0.0105{}_{25}V_h/{}_{25}V_{obs.}$. Both equations reproduce the experimental results almost equally well, although the former, perhaps, leads to rather smaller deviations. Both lead to very similar values for $1/R_m$, to which, therefore, the value 0.051 may be assigned with some confidence. Hence $R_m = 19.6$, and $E = 19,230$ cal.

Discussion of Results.

As has recently been pointed out (Williams and Hinshelwood, this vol., p. 1079), the velocity of a bimolecular reaction in solution can be expressed by an equation of the form

$$k = PZe^{-E/RT} \dots \dots \dots (4)$$

where Z is the collision frequency and P a probability factor. In a series of very similar bimolecular reactions, as in the present case, Z cannot differ appreciably for the various catalysed reactions, and hence any difference in the value of k must be associated with a difference either in E or in P , or in both simultaneously. Which of these three possibilities actually obtains can be seen from a comparison of the values of k and E . The relevant data are given in Table V. The catalytic coefficients given in col. 3 are, with one exception, obtained from the values recorded by Dawson, but have been converted from mins.⁻¹ and 0.270M-acetone into secs.⁻¹ and 1M-acetone. No value for the propionate ion was available, and hence the catalytic coefficient was evaluated from the data given in Table II, by the usual method (Dawson and Carter, *loc. cit.*). The resulting value for k_a is 3.5×10^{-7} , which is roughly comparable with the values for the other catalysts. On the assumption that the numbers given in col. 2 represent the true heats of activation, the values of P given in col. 4 have been calculated by means of equation (4), Z being taken as 2.8×10^{11} (Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 1933, p. 247); its exact value is not of great importance in the present instance, since it is the relative values of P , rather than the absolute values, which are of interest.

TABLE V.

Catalyst.	E .	${}_{25}k \cdot 10^7$.	$P \cdot 10^4$.	$K_a \cdot 10^4$.	$P/\sqrt{K_a}$.
Hydron	20,680	287	1500	555,000	0.021
Dichloroacetic acid	19,230	123	57	500	0.025
Chloroacetic acid	19,230	13.7	6.4	15.1	0.016
Acetic acid	20,010	0.83	1.4	0.185	0.033
Propionic acid	19,370	0.68	0.40	0.138	0.011
Propionate ion	22,910	3.5	820		
Acetate ion	22,800	2.5	480		

Discussion in the first instance may be limited to acid catalysis. Here the most noteworthy feature is that while the heats of activation do not differ very markedly there are very pronounced variations in the values of P ; *e.g.*, when hydrion is the catalyst, 1 in 6 or 7 collisions between activated molecules is effective, but with chloroacetic acid only 1 in about 1600, and with propionic acid only 1 in about 27,000 is effective. For the series of acids the values of P run parallel with the values of k , and the variations in the latter are clearly determined chiefly by the alteration in P , and to a much less extent by the changes in E .

It is apparent that there is a remarkably close relation between the value of P and the acidic strength of the catalyst. In col. 5 are given the acid dissociation constants, which range from 55.5 for hydrion (Bronsted, *J. Physical Chem.*, 1926, **30**, 776) to 1.38×10^{-5} for propionic acid. Further, it is found that P is closely proportional to $\sqrt{K_a}$, as shown in col. 6, the extreme values of the ratio $P/\sqrt{K_a}$ differing by a factor of only 3 as compared with one of 10^3 in the ratio P/K_a and one of 4×10^6 in the values of K_a . It thus follows that the order of magnitude of P can be defined by the relation $P \approx \text{const.} \times K_a^n$, where the constant is approximately 0.02 and $n = 0.5$. Taking this relation in conjunction with (4), one obtains $k \approx \text{const.} \cdot K_a^n \cdot Z \cdot e^{-E/RT}$. The significant feature of this relation is that it implies that in a collision involving molecules of catalyst and reactant in which the necessary energy conditions are satisfied, the probability that chemical action will occur is limited almost exclusively by a factor which is expressible as a simple function of the dissociation constant of the acid catalyst.

In an attempt to interpret the physical significance of this factor, it may be suggested that the acid catalyst facilitates the reaction, which consists essentially in a prototropic change, by itself undergoing ionisation (compare Lowry, *J.*, 1927, 2554). On this view, the probability that a collision between the activated molecules will be effective is limited by the probability of the simultaneous ionisation of the catalyst molecule. The latter probability will presumably increase with increasing acidic strength of the catalyst, and it is not unreasonable to suppose that it will be measured by an expression of the above type.

In the results for basic catalysts, the predominant feature is the much higher heat of activation than that for acid catalysis, the difference being 2000—3500 cal. It is unlikely that, in itself, the mere substitution of a basic for an acid catalyst would account for this difference, since in the mutarotation of glucose (Kilpatrick and Kilpatrick, *loc. cit.*) the heat of activation for acetate ion catalysis (19,100 cal.) is almost identical with that for hydrion catalysis (19,300 cal.); it is more probable that the difference represents the difference in energy associated with the acetone molecule in the two types of catalysis.

For both the basic catalysts, P is larger than for any of the acid catalysts with the exception of the hydrion. This is not unintelligible if, as is likely, basic is analogous to acid catalysis in that the value of P is largely determined by the basic strength of the catalyst; for the propionate ion and the acetate ion are both strong bases, and hence values of P of the order of magnitude observed might reasonably be anticipated.

EXPERIMENTAL.

Kinetic Measurements.—The procedure followed that previously developed in this laboratory for the determination of the initial velocity of reaction.

Purification of Materials.—The acetic and propionic acids were distilled from chromic anhydride and were then stable to iodine during the period of the experiments. Chloroacetic acid was distilled under reduced pressure, *m. p. ca.* 61°; and was then repeatedly fractionally frozen until the *f. p.* was constant at 62.4°. Mixtures of the acid and its sodium salt were quite stable to iodine.

Dichloroacetic acid as purchased had *m. p. ca.* 10.5° (Kendall, *J. Amer. Chem. Soc.*, 1914, **36**, 1230, gives —4.1° and 9.7°) but was obviously not pure. It was subjected to 15 fractional freezings and then had *m. p.* 13.50°, unaltered by additional freezings. As no special precautions were taken to exclude atmospheric moisture during the operations, the true value may be higher.

SUMMARY.

1. The heats of activation of the acetone-iodine reaction with five acid and two basic catalysts have been evaluated from velocity measurements at 25° and 0°.

2. It is shown that for acid catalysis the factor P in the equation $k = P \cdot Z \cdot e^{-E/RT}$ is functionally related to the acid strength of the catalyst by an expression of the form $P \approx \text{const. } K_a^n$.

3. It is suggested that this result is intelligible on the assumption that an essential condition for a fruitful collision between catalyst and reactant molecule is the simultaneous ionisation of the catalyst molecule.

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