219. *The Kinetics of Decarboxylation of Certain Organic Acids.*

By R. A. FAIRCLOUGH.

The rates of decarboxylation of the ions of three monobasic acids and of malonic acid have been measured at several temperatures. In each case the reaction is kinetically of the first order, and a mechanism is proposed for the monobasic acids in which the rate-determining step is the rupture of a carbon–carbon bond. This mechanism yields a simple explanation of the correlation between E and log PZ which is found to occur with these acids. Comparison of the results obtained for sodium hydrogen malonate with those of Bernoulli and Wege for malonic acid leads to the conclusion that the decomposition of malonic acid proceeds by a different mechanism, and is a more complex reaction.

THESE experiments were undertaken in the hope that the study of a unimolecular reaction might yield further general information as to the factors determining the rates of reactions in solution, and as to the reasons for the occurrence of the correlation, frequently observed and recently discussed (Fairclough and Hinshelwood, J., 1937, 538), between the activation energy and log PZ in the modified Arrhenius equation $\log k = \log PZ - E/\mathbf{R}T$. In order to isolate the reaction of the ion of the acid from any possible reaction of the undissociated molecule, aqueous solutions of the sodium salts were used. In the case of malonic acid, however, the disodium salt was found not to react under the conditions of experiment, and sodium hydrogen malonate was therefore used.

Quantitative measurements were made with trichloroacetic, tribromoacetic, phenylpropiolic, and malonic acids, and qualitative information of the behaviour of *p*-nitrophenylacetic, 2 : 4-dinitrophenylacetic, tri-iodoacetic, and dibromogallic acids was also obtained.

EXPERIMENTAL.

Under the conditions employed, the decarboxylation produced sodium bicarbonate, and this was used in the estimation of the extent to which the reaction had proceeded in a given time. Portions of 5 c.c. of N/2-solutions of the sodium salts of the acids were sealed up in small soft-glass tubes and immersed in the thermostats. After a suitable time a tube was removed, and its contents were transferred to the burette tube of a Lunge nitrometer, being washed in with sufficient boiled-out distilled water to make the volume of liquid up to 7 c.c. Carbon dioxide was then liberated from the bicarbonate by the addition of 1 c.c. of concentrated hydrochloric acid, leaving 8 c.c. of approximately N-acid above the mercury of the nitrometer. The burette tube was then thoroughly shaken, the pressure adjusted to atmospheric, and the volume of gas and the temperature of the mercury noted. The use of this standard procedure made it a simple matter to add to the observed volume a correction for the gas dissolved in the aqueous layer, the Bunsen solubility coefficient in N-hydrochloric acid being obtained from I.C.T. The amount of bicarbonate formed in the reaction was then calculated from the total volume of carbon dioxide reduced to *S.T.P.*

The thermostats were vapour baths for the higher temperatures, but for 40° and 47° electrically controlled thermostats were used. All solutions were made up in distilled water boiled free from carbon dioxide.

Trichloroacetic Acid.—The rate was measured at five temperatures, and satisfactory first-order constants were obtained at each temperature. The values obtained for the individual rate constants, and for E and log PZ are in agreement with those previously obtained by Verhoek (*J. Amer. Chem. Soc.*, **1934**, **56**, 571), which is considered a confirmation of the accuracy of the technique used here. The rate constants found for the various temperatures are shown below. (Throughout this paper all values of k are expressed in sec.$^{-1}$.)

Temp.	44·0°	60·8°	76·4°	76·6°	85·9°	99·8°
$k \times 10^7$	2·19	41·4	419	383	2070	13,200

Hence E = 36,600 cals./g.-mol.; log PZ = 18·58.

Tribromoacetic Acid.—A sample of this acid from Fraenkel and Landau was used without further purification. It was not possible to obtain perfectly clear solutions of the acid or its salts, presumably on account of the virtual impossibility of freeing them from slight traces of bromoform. Measurements were carried out at five temperatures, and at the three highest temperatures satisfactory first-order constants were obtained, the reaction proceeding to completion. At lower temperatures, however, the constants fell off in value markedly as the reaction proceeded. An explanation of this is afforded by the work of Eichloff (*Annalen*, **1905**, **342**, 123), who found that solutions of the free acid were quite stable to hydrolysis (though not to decarboxylation) in the absence of alkali, but that if the sodium salt were boiled with alkali, complete hydrolysis of the bromine atoms occurred in a very short time. In the present experiments, free alkali is formed during the course of the reaction. This is not sufficient to make the hydrolysis faster than the decarboxylation at the higher temperatures, but, as the hydrolysis presumably has a lower activation energy, the rates of the two reactions become comparable at the lower temperatures. Consequently, both tribromoacetate and bicarbonate ions are removed from the solution by the hydrolysis, so that the rate appears to decrease progressively. If this explanation is correct, the true rate constants can be found by calculating the velocity at zero time from the reaction–time curve. The initial rates so obtained fell upon the same Arrhenius line as the satisfactory constants from the upper temperatures. The following table shows the rates at the various temperatures.

Temp.	40·0°	47·2°	60·3°	64·9°	76·4°
$k \times 10^6$	22·2 *	46·4 *	229	472	1160

* Values from initial rates.

Hence $E = 24{,}100$; $\log PZ = 12{\cdot}25$.

Phenylpropiolic Acid.—Only at the highest temperature, 125°, did the reaction yield good first-order constants and proceed to completion. At the lower temperatures a steady decrease in the constants became more and more marked and very low end-points were obtained. Constants at the lower temperatures were calculated from the initial rates, and this procedure seemed to be justified by the fact that these values gave a good Arrhenius line, which passed through the value at 125°. The success of this treatment indicated that there was some secondary reaction, catalysed by the products of the decarboxylation, which removed phenylpropiolate and/or bicarbonate ions from the solution. No definite evidence of the nature of this reaction was obtained, but it seems probable that it might be the hydration of the triple bond, catalysed by bicarbonate ions. This reaction is known to occur extremely rapidly under very strongly acid conditions, and a very slow hydration indeed, under our conditions, would be sufficient to interfere with the slow decarboxylation. An alternative, and perhaps less probable, explanation might be in terms of some polymerisation of the acid. The results obtained for this acid were:

Temp.	76·2°	87·0°	100·5°	125·7°
$k \times 10^6$	1·61 *	4·73 *	27·8 *	367

* From initial rates.

Hence $E = 31{,}500$; $\log PZ = 13{\cdot}93$.

Malonic Acid.—Aqueous solutions of sodium malonate, when heated for 48 hours at 125°, showed no perceptible decomposition. Solutions of sodium hydrogen malonate were therefore used. The products of this decomposition are acetic acid and carbon dioxide. The rate was measured by taking samples which had been heated in sealed tubes for a given time, boiling for a few minutes to remove dissolved carbon dioxide, and titrating the second hydrogen ion of the malonic acid with sodium hydroxide, with cresol-red as indicator. (The reaction is so slow at 100° that boiling for a few minutes decomposes only a negligible amount of the remaining malonate.) First-order constants were obtained at all the temperatures as shown below, and the reaction accurately obeyed the Arrhenius equation.

Temp.	76·3°	100·0°	120·0°
$k \times 10^7$	3·38	50·0	305

Hence $E = 28{,}100$; $\log PZ = 11{\cdot}17$.

The results for all the acids are here collected together for comparison: the first column gives the rate at 76·0°, calculated from E and $\log PZ$.

Sodium salt.	$k_{76\cdot0} \times 10^7$.	E.	$\log PZ$.	Sodium salt.	$k_{7\cdot60} \times 10^7$.	E.	$\log PZ$.
Tribromoacetate	11,700	24,100	12·25	Phenylpropiolate ...	13·7	31,500	13·93
Trichloroacetate	388	36,600	18·58	Hydrogen malonate	3·26	28,100	11·17

Tri-iodoacetic Acid.—This was prepared from malonic acid (Angeli, *Ber.*, 1893, **26**, 595). Both the free acid and the sodium salt were exceptionally unstable, decomposing rapidly even at room temperature. The chief products of the decomposition were iodine, iodoform, and carbon dioxide, so the reaction is more complicated than a simple decarboxylation.

p-*Nitrophenyl- and* 2 : 4-*Dinitrophenyl-acetic Acids.*—The sodium salts of these acids decomposed readily at 100° in aqueous solution, the latter considerably more rapidly, the products being apparently sodium bicarbonate and the nitro- or dinitro-toluene. The presence of these compounds made the accurate estimation of the rate of the reaction a matter of great difficulty.

Dibromogallic Acid.—This was prepared by the bromination of gallic acid in chloroform, a reaction which was somewhat more vigorous than Biétrix's description (*Bull. Soc. chim.*, 1892, **7**, 412) would lead one to expect. The sodium salt and the free acid both decomposed very rapidly at 100°, but the presence of 4 : 6-dibromopyrogallol made quantitative measurements impracticable.

DISCUSSION OF RESULTS.

1. *The Monocarboxylic Acids.*—Although the decarboxylation is always kinetically of the first order, it might be supposed that the reaction was really a bimolecular one, involving the intervention of a molecule of water, the concentration of which may be regarded as constant throughout the reaction. The stoicheiometrical equation is $R{\cdot}CO_2Na + H_2O = R{\cdot}H + NaHCO_3$. Various considerations, however, make it more probable that the rate-determining step is the rupture of the carbon–carbon bond in the ion of the acid. This produces carbon dioxide and the negatively charged ion of the organic radical R, which then reacts instantly with water (cf. Dyson and Hammick, J., 1937, 1724). This scheme may be represented thus :

$$(1)\ R{\cdot}COO' = R' + CO_2 \qquad (2a)\ R' + H_2O = R{\cdot}H + OH'$$

$$(2b)\ CO_2 + H_2O \rightleftharpoons HCO_3' + H^{\cdot}$$

The evidence in favour of this mechanism may be summarised as follows.

(*a*) In any alternative scheme a molecule of water would be required to approach the ion of the acid in such a way that its oxygen atom could react with the carboxyl ion, as shown in Fig. 1. This is clearly a less probable point of attack for the oxygen atom than is the α-carbon atom, on account of the distribution of electrical charges in the ion of the acid. This may be expressed in another way by saying that if there were any direct action of water, we should expect it to be such that the oxygen atom of the water attacked the α-carbon atom (as in Fig. 2), removing the halogen or other groups by hydrolysis. It is well known that such hydrolysis actually does occur with the halogen-substituted acetic acids, and that it is strongly catalysed by bases (cf. tribromoacetic acid, p. 1187).

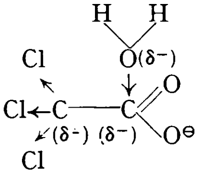

FIG. 1.

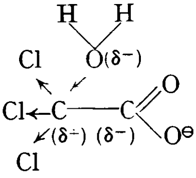

FIG. 2.

(*b*) If a direct attack of water were possible, as visualised in Fig. 1, it would be expected that the reaction would be catalysed by bases in a similar manner to the hydrolysis represented in Fig. 2. Actually, decarboxylations do not show such catalysis.

(*c*) Decarboxylation only occurs in those acids which have strongly electron-attracting groups attached to the α-carbon atom. These substituents can assist the reaction in two ways, if the genuine unimolecular scheme is correct. First, they weaken the carbon–carbon bond which is to be broken, and secondly, they tend to prepare the α-carbon atom for the receipt of a negative charge by withdrawing electrons from it. Moreover, the much lower activation energy required by tribromoacetic acid indicates that the weakening of this link is a most important step energetically, and in fact, that the activation energy is chiefly needed for the actual rupture of this bond.

(*d*) This view of the mechanism is also supported by the relationship between the values of E and $\log PZ$ for trichloro- and tribromo-acetic acids (see below).

It will be seen from the collected results that on passing from trichloro- to tribromoacetic acid the activation energy decreases by 12,500 cals., and PZ is decreased more than 10^6 times. This is the most striking example of a correlated change in E and $\log PZ$ which has hitherto been observed, and the magnitude of the ratio $d(\log PZ)/d(E^{-\frac{1}{2}})$ is of the same order as that previously found (Fairclough and Hinshelwood, J., 1937, 1575). If the mechanism suggested above is accepted, the correlation may be very simply explained on the lines of the tentative theory already put forward. The greater activation energy needed in the case of trichloroacetic acid is supposed to be due to the greater strength of the carbon–carbon bond in this acid. If it is assumed that there is a time-lag between activation and reaction, during which the vibrations of the ion of the acid must come into some suitable phase relationship, or during which the activation energy is transferred from its point of entry into the molecule to the seat of reaction, then the greater frequency of vibration of the C–C bond in trichloroacetic acid will enable such adjustment to take place more quickly. The time-lag will therefore be shorter in this acid, and the probability (*P*) that an activated molecule will decompose will be enhanced. In the light of the information gained by the study of this reaction, it seems more probable that the time-lag is required for transfer of the activation energy to the seat of reaction, since it is difficult to imagine any particular combination of vibrational phases which would be the most suitable for the rupture of a single link. There is no reason to believe that the energy is supplied directly to the reacting bond; indeed, the very high value of log *PZ* in the decomposition of trichloroacetic acid suggests that in these reactions activation occurs through several internal degrees of freedom, as in unimolecular decompositions in the gas phase.

The values of *E* and log *PZ* for phenylpropiolic acid lie between those of the halogenoacetic acids, although they do not fall on a line drawn between these when log *PZ* is plotted against $E^{-\frac{1}{2}}$. The different structural type of this acid, however, would be expected to modify both the modes of activation and the internal vibration frequencies to some extent. In so far as phenylpropiolic acid may be regarded as a substituted acetic acid, the agreement is as good as could be expected. This part of the discussion may be summarised by saying that the decarboxylations of these three acids are similar in mechanism, the initial step in the reaction being the breaking of the C–C bond in the acid ion, the negative organic ion produced reacting at once with water. The magnitude of the activation energy is supposed to depend on the strength of this C–C linkage, and the magnitude of log *PZ* to depend in part on the facility of energy transfer from the point at which it enters the molecule to the seat of reaction.

2. *Malonic Acid.*—The results for this acid are more difficult to interpret. Bernoulli and Wege (*Helv. Chim. Acta*, 1919, **2**, 511) found that a solution of malonic acid decomposes in aqueous solution with approximately the same activation energy but about five times as fast as the sodium hydrogen malonate used in the present work. It has already been stated that the neutral sodium salt does not decompose at all at these temperatures, or at least very much more slowly. These facts cannot be explained by assuming that it is the undissociated molecule which decomposes in both cases, since the degree of hydrolysis of the hydrogen malonate is so low that, if this were so, the difference would be much greater than that observed. It therefore seems that both the ion and the undissociated molecule can decompose, the latter more rapidly, so that it reacts preferentially when both species are present in solutions of the free acid. A similar state of affairs has recently been observed in the decomposition of oxalic acid by Dinglinger and Schröer (*Z. physikal. Chem.*, 1937, *A*, **179**, 401; 1938, **181**, 375), who conclude that the oxalate ion reacts less readily than the undissociated acid. Another analogous case may be the decarboxylation of acetoacetic acid (Pedersen, *J. Amer. Chem. Soc.*, 1929, **51**, 2098). The fact that both malonic acid and its singly charged ion undergo decarboxylation makes it appear improbable that the mechanism is the same as that proposed for the monobasic acids. Moreover, the activation energies required by these two species are approximately the same, and if the energy were simply needed to break a C–C bond, they might well be different, since ionisation might alter the strength of this bond. At present it is not possible to formulate a mechanism for the decarboxylation of dibasic acids, although it seems very probable that the mechanism is different from that followed by monobasic acids.

The author wishes to record his gratitude to Professor Hinshelwood for suggesting this work, and for criticism and advice, and to H.M. Department of Scientific and Industrial Research for a maintenance grant.

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[*Received, June 20th,* **1938.**]