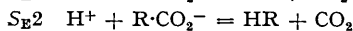
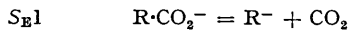


### 153. *The Mechanism of Decarboxylation. Part V. Kinetics of the Decarboxylation of Hydroxybenzoic Acids.*

By B. R. BROWN, D. LL. HAMMICK, and A. J. B. SCHOLEFIELD.

The rates of decarboxylation of salicylic, 2 : 4-dihydroxybenzoic, and 2 : 4 : 6-trihydroxybenzoic acids have been measured in resorcinol solution over a temperature range of 110—240°. The fall in activation energies (increase in rate) with increase in *o*- and *p*-substitution by hydroxyl groups supports the conclusion that with these acids the decarboxylation is an S<sub>E</sub>2 mechanism. The Hinshelwood-Fairclough relation  $\log_{10} PZ$  and  $1/E^\ddagger$  is obeyed.

RECENTLY Schenkel and Schenkel-Rudin (*Helv. Chim. Acta*, 1948, **31**, 514) suggested that decarboxylation may occur by two mechanisms, analogous to the S<sub>N</sub>1 and S<sub>N</sub>2 replacement reactions of Hughes and Ingold (*J.*, 1935, 244) :



Substantial evidence for the S<sub>E</sub>1 mechanism is available (*e.g.*, Pedersen, *J. Physical Chem.*, 1934, **38**, 559; Verhoek, *J. Amer. Chem. Soc.*, 1939, **61**, 186; Parts I, II, III, and IV of this series, Hammick *et al.*, *J.*, 1937, 1724; 1939, 809; 1949, 173 and 659). Examples of the S<sub>E</sub>2 mechanism are rapidly accumulating (Schubert, *J. Amer. Chem. Soc.*, 1949, **71**, 2639; Johnson and Heinz, *ibid.*, p. 2913).

The S<sub>E</sub>2 mechanism will be facilitated by a high electron density on the carbon atom next to the carboxyl group. Moreover, since the mechanism is essentially bimolecular and involves an acid molecule and a solvated proton, acids which are decarboxylated in this manner will be stable in alkaline but unstable in acid solution. Support for this view is found in the semi-quantitative results of Cazeneuve (*Bull. Soc. chim.*, 1896, **15**, 73) and of Hemelmeyr (*Sitz. Akad. Wiss. Wien*, 1912, **121**, 1359), who show that *o*- and *p*-hydroxybenzoic acids behave thus. The *m*-hydroxybenzoic acids, however, in which the hydroxyl groups cannot make any appreciable contribution to the electron density on the carbon atom next to the carboxyl group, are stable even in acid solution. The suggestion that the decarboxylation of *o*- and *p*-hydroxybenzoic acids may occur by a bimolecular mechanism involving attack of a proton on the negative  $\alpha$ -carbon atom has also been made by Fieser and Fieser ("Organic Chemistry," D. C. Heath and Co., Boston, 1944, p. 674).

The aim of the kinetic work here presented was to study the effect of the successive substitution of hydroxyl groups into the *o*- and *p*-positions of benzoic acid on the rate of decarboxylation in resorcinol, which was selected as solvent for reasons given in the Discussion below. The work of Hinshelwood, Laidler, and Timm (*J.*, 1938, 848) indicates that a comparison of activation energies with type and amount of substitution should provide evidence for or against an S<sub>E</sub>2 mechanism.

#### EXPERIMENTAL.

*Materials.*—Salicylic acid was crystallised twice from water and had m. p. 156°. 2 : 4-Dihydroxybenzoic acid ( $\beta$ -resorcylic acid) was crystallised three times from water and had m. p. 216°. 2 : 4 : 6-Trihydroxybenzoic acid was crystallised once from alcohol and twice from ether and had m. p. 189°.

The solvent, resorcinol, was distilled at atmospheric pressure, and had b. p. 276°, m. p. 110°.

*Apparatus.*—The method used to follow the reaction was by measurement of evolved carbon dioxide, at room temperature and pressure. The apparatus of Walton (*Z. physikal. Chem.*, 1904, **47**, 185) was modified for use at high temperatures (110—240°) and was very similar to the apparatus used by Schubert (*loc. cit.*). Temperature control was obtained by immersing the reaction vessel (containing about 0.3 g. of acid in 10 g. of resorcinol) in a lagged vapour-bath containing a suitable liquid boiling under reflux at the prevailing atmospheric pressure. Temperatures constant to  $\pm 0.1^\circ$  could be maintained for at least 4 hours. The bath liquids were distilled at atmospheric pressure, and fractions boiling over 0.2° were used to construct the Arrhenius plots. The hot solvent (resorcinol) was saturated with carbon dioxide before measurements were made.

The main source of error was likely to arise from variation of the temperature gradient between the evolved carbon dioxide (at the temperature of the reaction) and the measuring burette (at room temperature). This was minimised by using a standard procedure, and by protecting the connecting tubes from temperature changes.

*Results.*—Since the system had to be stabilised before readings were taken, it was impracticable to obtain an accurate value for the initial concentration of the acid. Moreover, it was inconvenient to prolong the decarboxylation in order to read the total volume of carbon dioxide evolved at the completion of the reaction. These difficulties were overcome by using the method of plotting devised by Guggenheim (*Phil. Mag.*, 1926, **2**, 538). Two series of values for the volume of carbon dioxide evolved,  $v$  and  $v'$ , separated by a time interval  $t$ , are obtained. A plot of  $\log_{10} (v' - v)$  against time yields a line of gradient  $-0.434k$ , where  $k$  is the velocity constant for the decarboxylation at the

temperature used. A typical series of results is shown in Table I. The observed values of  $\log_{10} (v' - v)$  are compared with those calculated from the equation to the line of gradient  $-0.434k$ .

TABLE I.

Decarboxylation of 2 : 4-dihydroxybenzoic acid in resorcinol (at 465.2° K.)

Time (sec.).	$v$ (ml.).	$v'$ (ml.).	$(v' - v)$ (ml.).	$\log_{10} (v' - v)$ (obs.).	$\log_{10} (v' - v)$ (calc.).
300	5.9	26.4	20.5	1.311	1.325
450	10.0	27.5	17.5	1.243	1.242
600	14.0	28.3	14.3	1.155	1.158
750	17.2	29.0	11.8	1.072	1.074
900	19.8	29.6	9.8	0.991	0.991
1050	21.9	30.1	8.2	0.914	0.908
1200	23.7	30.5	6.8	0.833	0.824

$t = 1200 \text{ sec.}$   $k = 12.8 \times 10^{-4} \text{ sec.}^{-1}$ .

Four determinations of  $k$  at this temperature yielded the values  $k = 11.0, 12.8, 14.0,$  and  $14.6 \times 10^{-4} \text{ sec.}^{-1}$ . Average  $k = 13.1 \times 10^{-4} \text{ sec.}^{-1}$ .

A plot of  $1/T$  and  $\log_{10} k$  (from Table II) gives the results collected in Table III.

TABLE II.

Effect of temperature.

<i>o</i> -Hydroxybenzoic acid.		2 : 4-Dihydroxybenzoic acid.		2 : 4 : 6-Trihydroxybenzoic acid.	
°K.	$10^4 k$ .	°K.	$10^4 k$ .	°K.	$10^4 k$ .
479.7	1.32	453.6	5.65	382.7	15.4
489.5	2.53	454.2	6.61	383.2	17.9
491.5	3.15	455.4	7.41	384.1	18.3
492.7	3.25	465.2	13.1	391.0	24.2
493.0	3.53	468.4	16.2	396.7	29.5
496.2	3.96	471.1	20.4	397.7	36.7
497.2	5.02	478.2	31.1		
508.2	8.95	480.3	36.7		
509.2	10.5				

TABLE III.

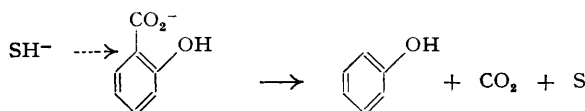
Acid.	$E$ (cals.).	$10^3/E\ddagger$ .	$\log_{10} PZ$ (from $k$ in $\text{sec.}^{-1}$ ).
Benzoic .....	$> 39,000$ *	—	—
<i>o</i> -Hydroxybenzoic .....	33,600	5.46	11.5
2 : 4-Dihydroxybenzoic .....	29,200	5.85	10.9
2 : 4 : 6-Trihydroxybenzoic .....	13,600	8.58	5.0

\* Estimated from the observation that benzoic acid is undecomposed at 250° in resorcinol.

### DISCUSSION.

The solvent resorcinol was chosen for these measurements for the following reasons : (1) the solvent had to be acidic in order that the bimolecular  $S_E2$  reaction would show pseudo-first-order kinetics, owing to the presence of a constant excess of acidic molecules, (2) the solvent had to be the same for each acid in order to give comparable results, hence a solvent liquid over a wide temperature range was required, and (3) it was desirable that the solvent should resemble the reaction products as closely as possible in order that they should cause the least possible change in medium.

The results in Table III indicate that the successive substitution of hydroxyl groups into the *o*- and *p*-positions of benzoic acid causes a progressive decrease in the energy of activation for decarboxylation. Since this substitution increases the electron density on the carbon atom next to the carboxyl group, it can be inferred that the substitution is reducing the repulsion between an attacking solvated proton and the acid molecule (cf. Hinshelwood, Laidler, and Timm, *loc. cit.*). The occurrence of this effect is consistent with the  $S_E2$  mechanism :

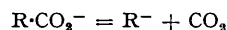


The remarkable drop in the  $PZ$  factor (of the equation  $k = PZ \cdot e^{-E/RT}$ ) on passing from 2:4-dihydroxy- to 2:4:6-trihydroxy-benzoic acid is perhaps to be associated with a steric effect of the second *o*-hydroxyl group in inhibiting the approach of the solvated proton.

The view that decarboxylation can take place by an  $S_E2$  mechanism involving the attack of a solvated proton on the  $\alpha$ -carbon atom is supported by kinetic studies on anthracene-9-carboxylic acid (Schenkel and Schenkel-Rudin, *loc. cit.*), certain cinnamic acids (Johnson and Heinz, *loc. cit.*), mesitoic acid (Schubert, *loc. cit.*), and on the *o*- and *p*-hydroxybenzoic acids. However, these authors put forward no evidence, nor have we been able to obtain any, as to the precise nature of the carboxylic entity which suffers reaction, *i.e.* to distinguish between (1) and (2):

- (1)  $\text{SH}^+ + \text{R}\cdot\text{CO}_2^- = \text{RH} + \text{S} + \text{CO}_2$
- (2)  $\text{SH}^+ + \text{R}\cdot\text{CO}_2\text{H} = \text{RH} + \text{S} + \text{CO}_2 + \text{H}^+$

On the other hand, studies of  $S_E1$  decarboxylations have always indicated that the carboxyl group is in the anionic form before decarboxylation:



In order to clarify the details of the  $S_E2$  mechanism further experiments are clearly required.

Hinshelwood and Fairclough (*J.*, 1937, 538, 1573) advance theoretical reasons for the expectation of a linear relationship between  $1/E^{\frac{1}{2}}$  and  $\log_{10} PZ$  in a series of closely related reactions. The accompanying

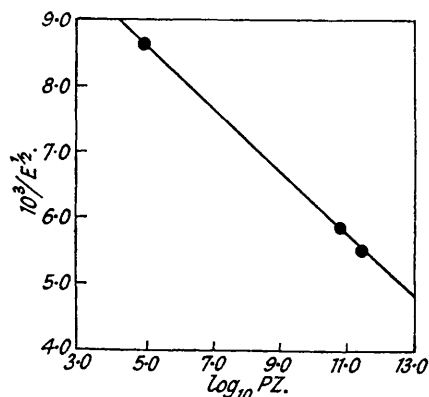


figure indicates that such a relationship holds for the decarboxylation of hydroxybenzoic acids. This result is interesting on account of the large range of  $E$  and  $PZ$  values covered by our data, and on account of the value  $-0.21 \times 10^4$  found for the slope of the line,  $d(\log_{10} PZ)/d(1/E^{\frac{1}{2}})$ , which is very close to that found by Hinshelwood and Fairclough (*loc. cit.*) for several reactions.

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