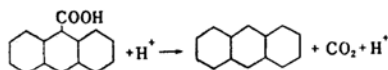


Thermal Decarboxylation of *p*-Chlorobenzoic Acid

By S. S. MUHAMMAD

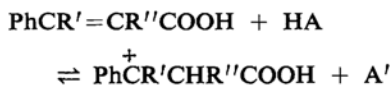
(Received February 13, 1960)

Though Fieser and Fieser^{1a)} had suggested in 1944 the probability of an electrophilic bimolecular (S_E2) mechanism for the decarboxylation of *o*- and *p*-hydroxybenzoic acids, no experimental evidence was available for this till 1948, when Schenkel and Schenkel-Rudin²⁾ recognized this as likely for the decomposition of anthracene-9-carboxylic acid:

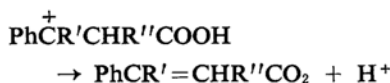


since Schenkel³⁾ had established the fact that this acid underwent decarboxylation more readily in acidic solvents such as sulfuric or dichloroacetic acid than in basic solvents such as 7:8 benzoquinoline. Schubert⁴⁾ tried to

establish a relation between the rate of decarboxylation and hydrogen ion concentration of the medium, by studying the decomposition of mesitoic acid in aqueous sulfuric acid of 80 to 100%. Johnson and Heinz⁵⁾ obtained evidence for the S_E2 mechanism by studying the rates of decarboxylation, under identical conditions, of different substituted cinnamic acids, $\text{PhCR}'=\text{CR}''\text{COOH}$. The order of rates found by them agreed with the electronic effects of the substituents R' and R'' on the basis of the following bimolecular mechanism:



followed by a comparatively fast step:



1) L. Fieser and M. Fieser, "Organic Chemistry", Heath & Co., Boston 1944; a p. 674, b 568.

2) H. Schenkel and M. Schenkel-Rudin, *Helv. Chim. Acta*, **31**, 514 (1948).

3) H. Schenkel, *ibid.*, **29**, 436 (1946).

4) W. M. Schubert, *J. Am. Chem. Soc.*, **71**, 2639 (1949).

5) W. S. Johnson and W. E. Heinz, *ibid.*, **71**, 2913 (1949).

Then Brown, Hammick and Scholefield⁶⁾ showed that the decarboxylation of salicylic, 2,4-dihydroxy- and 2,4,6-trihydroxybenzoic acids occurs by an S_E2 mechanism. These studies were extended by S. S. Muhammad and Mrs. Aziz Mirza on benzoic acid⁸⁾, *o*-chloro- and 2,4-dichlorobenzoic acids^{9,10)}. The technique employed was primarily to collect the carbon dioxide evolved in a gas burette. But in the present study a slightly different technique has been adopted. The results reported pertain to *p*-chlorobenzoic acid and these will be shortly extended to other acids.

Experimental and Results

Materials.—All the chemicals were of analar grade, and were used without further purification. The solvents, resorcinol, glycerol and aniline were of extra pure quality and when heated alone did not emit carbon dioxide.

Apparatus.—The heating device consisted of an oil bath heated electrically, the temperature control being achieved by means of a Sunvic energy regulator and a Sunvic relay. Temperatures were recorded with a 300°C thermometer having an accuracy of $\pm 0.5^\circ\text{C}$. The bath liquid was a local sweet oil which, on heating for 24 hr. at 300°C, emitted volatile vapours and then behaved as a nonvolatile liquid below this temperature.

The reaction vessel was a modified Walton's¹¹⁾ apparatus, the mouth of which was made of ground glass joint with stopper to which a glass tube was attached and this served as delivery tube for carbon dioxide liberated. The side tube had also a neck made of glass joint. The stopper for this had a spoon device where a weighed amount of the acid could be kept in a small test tube, which could be dropped by a slight turn of the stopper. Both the

stoppers were lubricated with the least quantity of Silicone grease.

The carbon dioxide was absorbed in baryta solution kept in an Erlenmeyer flask.

The oil thermostat with the modified Walton apparatus is shown in Fig. 1.

Procedure.—In order to find the order of reaction, different amounts of *p*-chlorobenzoic acid were taken with 20 g. of resorcinol in the Walton tube and heated for a definite interval. The liberated carbon dioxide was absorbed in baryta solution of approximately $N/10$ strength. Its exact titre value was determined by standardized $N/10$ oxalic acid before and after the absorption of carbon dioxide. The amount of acid decomposed, x , was calculated by the relation: $\Delta v \times 10^{-4}$ g. mol., where Δv is the difference in the titre values ' v_0 ' initially and ' v ' after absorption. Since the amount of acid initially taken, ' a ', is known, the amount of acid remaining at any interval, ' $a-x$ ', can be found.

In the first series of experiments, the initial amounts ' a ' were converted into relative concentrations, ' c ', and the corresponding amounts ' x ' decomposed in the same interval were converted into relative rates ' r ' (Table I).

The plot of $\log c$ against $\log r$ yields a slope of 1, indicating the order to be one.

In the second series of experiments, the same initial amount of the acid ' a ', was heated. The carbon dioxide evolved was absorbed in the same volume of the baryta solution of the same concentration. The latter solution was titrated by $N/10$ oxalic acid after a desired interval. The same operation being repeated for different desired intervals. Table II contains these data.

The plot of $\log (a-x)$ against time t gives straight line proving the first order character of the reaction.

The rate constants can be obtained by the equation $k = 2.303/t \cdot \log a/a-x$. Thus using the data of Expt. 4, we get $k = 2.303/12 \log 29.4/19.6 = 3.378 \times 10^{-2} \text{ min}^{-1} = 5.63 \times 10^{-4} \text{ sec}^{-1}$. Alternatively the rate constant can be derived by the relation

$$k' = \frac{x}{t} \times \frac{1}{\bar{a}}$$

where x is the amount decomposed in the interval t and \bar{a} is the average concentration during this interval i. e. $\{a + (a-x)\}/2$. Thus the data of Expt. 4, give

$$\begin{aligned} k' &= \frac{9.8 \times 10^{-4}}{12} \times \frac{1}{(29.4 + 19.6) \times 10^{-4}/2} \\ &= \frac{9.8 \times 10^{-4}}{12 \times 24.5 \times 10^{-4}} = 3.33 \times 10^{-2} \text{ min}^{-1} \\ &= 5.56 \times 10^{-4} \text{ sec}^{-1} \end{aligned}$$

In subsequent experiments, the latter method of deriving the rate constant has been used.

In the third series of experiments, different initial amounts of the acid, ' a ', were heated at constant temperature, T , and the amounts ' x ', decomposed in 12 minutes were determined in each case. The rate constants were calculated as above. At each temperature, 5 observations were made and the mean of these was taken as the rate constant at that temperature. These results are presented in Table III.

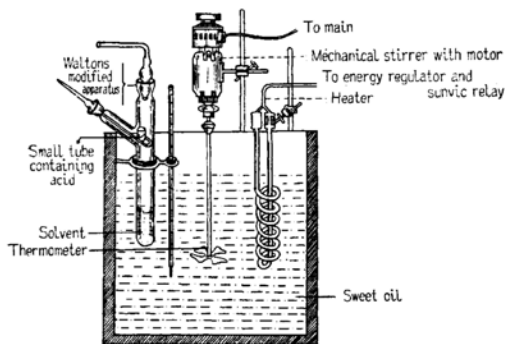


Fig. 1.

6) B. R. Brown, D. L. Hammick and A. J. B. Scholefield, *J. Chem. Soc.*, 1950, 778.

7) B. R. Brown, W. W. Elliott and D. L. Hammick, *ibid.*, 1951, 1384.

8) S. S. Muhammad and Aziz Siddiqui, *J. Indian Chem. Soc.*, 31, 726 (1954).

9) S. S. Muhammad and Aziz Siddiqui, *ibid.*, 33, 570 (1956).

10) Aziz Mirza, Ph. D. thesis approved by the Osmania University, 1957 pp. 100–106.

11) J. H. Walton, *Physik. Chem.*, 47, 185 (1904).

TABLE I. SOLVENT RESORCINOL, $T=235^{\circ}\text{C}$

Weight of acid, g.	Weight, g., decomposed per sec.	Relative concentration c	Relative rate r	$\log c$	$\log r$
0.12	5.83×10^{-5}	1	1	0	0
0.16	8.00	1.33	1.37	0.1239	0.1367
0.20	10.00	1.67	1.72	0.2227	0.2355
0.25	12.17	2.08	2.09	0.3181	0.3201
0.35	17.5	2.92	3.00	0.4654	0.4771
0.40	20.33	3.33	3.49	0.5224	0.5428
0.50	25.67	4.17	4.40	0.6201	0.6435
0.60	29.67	5.00	5.09	0.6990	0.7067

TABLE II.

A 0.460 g. portion of acid was taken in each experiment (i. e. $a=29.4 \times 10^{-4}$ g. mol.). The carbon dioxide formed was absorbed in 40 cc. of baryta solution which was titrated with N/10 oxalic acid.

Expt. No.	Time, t min.	Titre value of N/10 Oxalic acid, T	Amount of acid decomposed, x ($x=T \times 10^4$ g. mol.)	$(a-x) \times 10^4$	$\log(a-x)$
1	0	33.4	—	29.4	1.4683
2	4	29.8	3.6	25.8	1.4116
3	8	26.4	7.0	22.4	1.3502
4	12	23.6	9.8	19.6	1.2923
5	15	21.4	12.0	17.4	1.2405
6	20	19.0	14.4	15.0	1.1761
7	26	16.5	16.9	12.5	1.0969
8	32	15.0	18.4	11.0	1.0414

In order to examine the above results, it was desirable to derive the activation energy E , frequency factor A , free energy of activation ΔF° and entropy of activation ΔS° .

The plot of $\log k$ vs. $1/T$ (Fig. 2) gave the activation energy E .

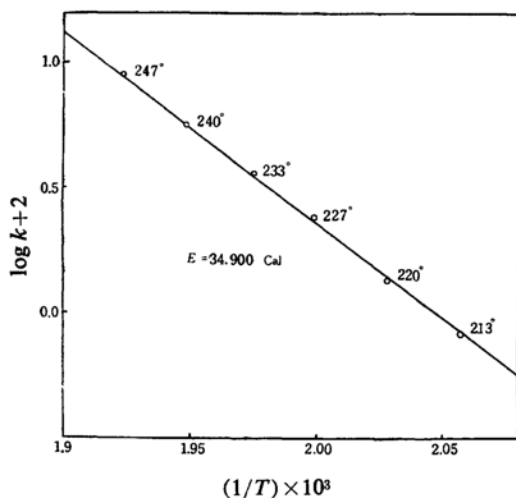


Fig. 2.

The Arrhenius equation $k=Ae^{-E/RT}$ was used to calculate the frequency factor A and the Eyring

equations¹²⁾

$$\Delta F^{\circ} = 2.303 RT \log (RT/Nh k)$$

$$\Delta S^{\circ} = (\Delta H^{\circ} - \Delta F^{\circ})/T$$

yielded the free energy and entropy of activation. The term ΔH° is the enthalpy of activation, taken equal to $E - RT$, where E is the observed activation energy and T the temperature at which entropy and free energy are being calculated. The values of the constants used are¹³⁾: $R=1.987$ cal. and 8.31439×10^7 erg, $N=6.02308 \times 10^{23}$, $h=6.6252 \times 10^{-27}$ erg, $T^{\circ} = ^{\circ}\text{C} + 273.15$. The results of these calculations are shown in Table IV.

Effect of Other Solvents.—The solvent glycerol is also effective in bringing about decarboxylation of *p*-chlorobenzoic acid, but the rate of decarboxylation is less in glycerol than in resorcinol. Thus, while at 233°C in resorcinol 2.5% of the acid decomposed per minute, in glycerol under identical conditions the rate of decarboxylation is 1.9% per minute. Besides, the rate constants for decarboxylation in glycerol calculated from the first and the second order rate equations show large trends.

Addition of a small quantity of aniline to glycerol solution retards the rate of decarboxylation and when enough of aniline is added, the reaction completely stops. When the acid was dissolved in pure aniline, it did not decompose at 247°C , which was the highest temperature employed in the present investigation.

12) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw Hill Book Co., (1941).

13) G. W. C. Kaye and T. H. Laby, "Tables of Physical and Chemical Constants", Longmans (1956).

TABLE III.

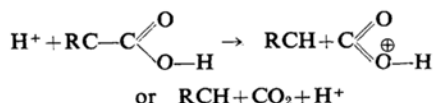
Expt. No.	$a \times 10^4$ g. mol.	$x \times 10^4$ g. mol.	$a \times 10^4$ g. mol.	$k = \left(\frac{x}{a} \times \frac{1}{12} \right) \text{min}^{-1}$
(a) $T = 213^\circ\text{C}$				
1	58.8	5.6	56.0	0.83×10^{-2}
2	44.1	4.3	41.95	0.85
3	39.2	3.6	37.4	0.80
4	35.3	3.4	33.6	0.84
5	29.4	2.9	27.95	0.86
				Mean..... <u>0.84</u>
(b) $T = 220^\circ\text{C}$				
1	58.8	8.6	54.5	1.32
2	44.1	6.6	40.8	1.35
3	39.2	6.0	36.2	1.38
4	35.3	5.2	32.7	1.33
5	29.4	4.6	27.1	1.42
				Mean..... <u>1.36</u>
(c) $T = 227^\circ\text{C}$				
1	73.5	18.2	64.4	2.36
2	58.8	14.3	51.4	2.40
3	44.1	11.2	38.5	2.42
4	35.3	8.6	31.0	2.31
5	23.5	6.0	20.5	2.44
				Mean..... <u>2.39</u>
(d) $T = 233^\circ\text{C}$				
1	73.5	25.6	60.7	3.51
2	58.8	20.8	48.4	3.58
3	44.1	16.0	36.1	3.69
4	35.3	12.2	29.2	3.48
5	23.5	8.4	19.3	3.63
				Mean..... <u>3.58</u>
(e) $T = 240^\circ\text{C}$				
1	88.2	43.8	66.3	5.51
2	70.6	35.0	53.1	5.49
3	58.8	29.4	44.1	5.55
4	44.1	22.1	33.05	5.57
5	29.4	14.8	22.0	5.61
				Mean..... <u>5.55</u>
(f) $T = 247^\circ\text{C}$				
1	88.2	61.6	57.4	8.94
2	70.6	49.4	45.9	8.97
3	58.8	42.0	37.8	9.26
4	44.1	30.8	29.0	8.68
5	29.4	20.4	19.2	8.86
				Mean..... <u>8.94</u>

TABLE IV.

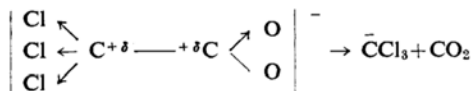
Property	k , 220°C	E	$\log A$	ΔH 220°C	ΔF°	ΔS° 220°C
Value	$2.25 \times 10^{-4} \text{sec}^{-1}$	34900 cal.	11.81	33900 cal.	37600 cal.	-7.5 cal. deg^{-1}

Discussion

The data presented above show that *p*-chlorobenzoic acid is stable in basic solvents and is unstable in acidic solvents. In this respect, it is analogous with salicylic acid⁶⁾ and orthochlorobenzoic acid⁹⁾ which undergo decomposition through an electrophilic bimolecular (S_E2) mechanism, involving the replacement of the carboxyl:

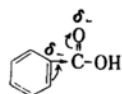


In *p*-chlorobenzoic acid, the inductive effect of chlorine in the para position is likely to cause electron deficiency on the α -carbon. The result of this would be that decarboxylation would not occur in acid medium and would be facilitated in neutral and basic media. This would be in harmony with the view of Fairclough¹⁴⁾, according to whom in trichloroacetic and tribromoacetic acids the α -carbon is attached to strongly electron attracting chloro and bromo groups which weakens the carbon-carboxy bond and facilitates its unimolecular rupture:



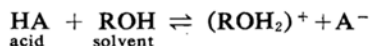
According to Fieser and Fieser¹⁶⁾, the inductive effect estimated from dipole moments accounts well for the activating or deactivating influence of different groups, but does not explain the orientation and it is seen that although the majority of electron attracting groups orient an entering group to the meta position, halogen substituents, like the electron repelling amino and hydroxyl groups are ortho, para directing. This is due to the resonance effect. Thus in chlorobenzene resonance leads to development of electron density at the ortho and para positions (with reference to chlorine atom). In *p*-chlorobenzoic acid, structures in which carboxyl also partakes of the resonance are possible. But according to Schubert⁴⁾, in the presence of substituents, the resonance interaction of the carboxyl with the benzene nucleus is inhibited. This leads to the weakening of the bond between the carboxyl and α -carbon and to its easy rupture. Another interesting explanation is that of Royals¹⁵⁾, according to whom the presence of meta orienting groups like carboxyl produces an electromeric effect indicated in the accompanying structure, due

to which nucleophilic reactivity is developed at the α -carbon atom adjacent to meta orienting group. Hence an electrophilic reagent attacks this position and displaces the meta orienting group:

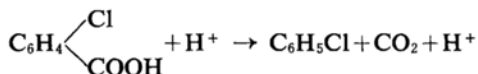


This also accounts satisfactorily the decarboxylation of benzoic acid⁸⁾ in the solvent resorcinol.

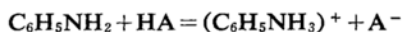
The bimolecular electrophilic substitution (S_E2) mechanism also accounts for the behavior of *p*-chlorobenzoic acid in the solvent glycerol which has been recently used by Clark¹⁶⁾ in decarboxylations. Glycerol being a polyhydric compound may act as a protophilic solvent and facilitate the ionization of *p*-chlorobenzoic acid to a limited extent.



where $(ROH_2)^+$ is solvated hydrogen ion. The "hydrogen ions" so formed will facilitate the decarboxylation:



The trends in the rate constants during decarboxylation in glycerol may be due to the fact that along with decarboxylation, the ester formation between glycerol and the acid takes place and the ester so formed decomposes decarboxylatively introducing complications in the interpretation of rate data. The retarding effect of aniline on decarboxylation in glycerol is also consistent with the S_E2 mechanism proposed, since aniline removes the hydrogen ions present and thus causes retardation in their attack on the carboxylic acid. On the contrary if decarboxylation were to occur via the first order decomposition of the carboxylate anion by the S_E1 mechanism, the rate should have increased due to the carboxylate anions being formed in abundance:



Summary

The decarboxylation of *p*-chlorobenzoic acid has been studied in the solvent resorcinol. The activation energy, frequency factor and free energy and entropy of activation have been calculated. It is shown that the reaction follows the S_E2 mechanism.

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14) R. A. Fairclough, *J. Chem. Soc.*, 1938, 1186.

15) E. Royals, "Advanced Organic Chemistry" Constable & Co., p. 450.

16) L. W. Clark, *J. Am. Chem. Soc.*, 77, 3130 (1955).