mentally. Since the entropy change for the reaction which was calculated to be +43 cal./deg. mole at 700°K. is much larger than the experimental entropy of activation given above (neglecting the small difference in temperature), the activated complex appears to have a structure much closer to cyclobutane than to the products.

Since it is possible that a short-lived tetramethylene biradical may be an intermediate in the reaction, it was of interest to estimate the difference in the entropy between a cyclobutane molecule and the fully formed biradical in order to compare this entropy difference with the entropy of activation. Although the uncertainty in the calculated entropy value for the biradical is appreciably greater than that for cyclobutane on account of the less exact information concerning its structure, estimates made by the use of Pitzer's method,[17] as well as other methods, indicate that the entropy change for the formation of the biradical is at least +15 cal./deg. mole. Since this is larger than the observed entropy of activation, it appears that the structure of the activated complex does not correspond to that of the fully formed biradical (not coiled). However, the activated complex may subsequently undergo a transformation into the biradical.

Bawn and Milsted[18] have discussed the stability of hydrocarbon biradicals and have estimated the energy of activation to be about 15 kcal./mole for the process

$$—CH_2CH_2CH_2CH_2— = CH_2{=}CH_2 + CH_2{=}CH_2$$

If the frequency factor associated with this activation energy of decomposition is in the region 10^{10}–10^{13} sec.$^{-1}$ and if the tetramethylene biradical does not react with molecules more readily than the methyl radical does,[19] it can be calculated that for the conditions used in the experiments in the present work almost all of the tetramethylene radicals would decompose before they could react either with added hydrogen or with another molecule of cyclobutane.[20] Although no indication of the presence of a biradical as an intermediate has been obtained, one cannot conclude from the available data that a tetramethylene biradical is not formed momentarily during the decomposition.[21] However, there is no evidence to show that the presence of a biradical would mean that the rate measured would not correspond to that of a simple unimolecular process.

Acknowledgment.—The authors wish to thank Dr. Frank Buff and Dr. C. E. H. Bawn for helpful discussion and Dr. G. W. Rathjens, Jr., for information and comments concerning the entropy of cyclobutane at 286°K.

NOTE ADDED IN PROOF:—The observed activation energy for the cyclobutane decomposition would not be in disagreement with the values of 58 and 60 kcal./mole for *D* (C–C) which have been calculated by F. H. Seubold, Jr., *J. Chem. Phys.*, **21**, 1616 (1953), and by H. O. Pritchard, R. G. Sowden and A. F. Trotman-Dickenson, *Proc. Roy. Soc.* (*London*), **218A**, 416 (1953), respectively. The latter article also presents data on the effect on inert gases on the decomposition.

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[17] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

[18] C. E. H. Bawn and J. Milsted, *Trans. Faraday Soc.*, **35**, 889 (1939).

[19] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); T. G. Majury and E. W. R. Steacie, *Disc. Faraday Soc.*, No. 14, 45 (1953).

[20] The possibility that a trimethylene biradical may react with a molecule of cyclopropane in the thermal decomposition of cyclopropane has been suggested by E. S. Corner and R. N. Pease, THIS JOURNAL, **67**, 2067 (1945).

[21] In the pyrolysis of cyclobutene the initial step appears to involve the rupture of only one bond since preliminary experiments by F. Kern and W. Cooper in this Laboratory indicate that an important reaction is the isomerization to butadiene.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Kinetics of the Decarboxylation of Phenylmalonic Acid in Aqueous Solution[1]

BY EDWARD GELLES

RECEIVED JULY 13, 1953

The rate of decarboxylation of phenylmalonic acid has been measured in aqueous solution at 45° over a range of concentration and *p*H. The singly charged anion decomposes more rapidly than the un-ionized acid while the doubly charged anion appears to be stable. The acid ionization constants of phenylmalonic acid at 25° are 2.65×10^{-3} and 9.4×10^{-6}.

Recent studies of carbon isotope effects on rates of decarboxylation reactions[2] indicate that the change in rate on substitution of C^{14} is more than double that on substitution of C^{13}. In connection with attempts to elucidate the cause of this anomaly some measurements were made of the rate of decarboxylation of phenylmalonic acid in aqueous solution. These are reported in the present paper.

The mechanism of decarboxylation reactions in general has been shown in recent years to exhibit a plurality of character.[3] In the case of malonic acids decarboxylation in aqueous solution is considered to involve the unimolecular decomposition of the un-ionized acid and its anions. The kinetics of decarboxylation of many substituted malonic acids have been studied, for example, by Bernoulli[4] and co-workers, who obtained apparent first-order rate constants without, however, analyzing the contributions to the rate due to the acid and anions. The only quantitative study of the relative rates

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[1] This work was assisted by the American Petroleum Institute through Research Project 50.

[2] For example, P. E. Yankwich and E. C. Stivers, *J. Chem. Phys.*, **21**, 61 (1953).

[3] For a recent review see B. R. Brown, *Quart. Rev. Chem. Soc.*, **5** [2], 141 (1951).

[4] A. L. Bernoulli and H. Jakubowitz, *Helv. Chim. Acta*, **4**, 1018 (1921).

TABLE I

$d(CO_2)/dt = 11.2 \times 10^{-3}(H_2A) + 35 \times 10^{-3}(HA^-)$

Decarbxln., %	$10^3(H_2A)$	$10^3(HA^-)$	$10^3(A^=)$	$10^3(HAc)$	$10^3(Ac^-)$	$10^5(H^+)$	Titer		$\frac{d(CO_2)}{dt} \times 10^3$	Time, hr.
							Calcd.	Obs.		
0	0.31	22.0	5.7	0.0	0.0	3.63	0.74		0.773	
10	.19	18.4	6.6	1.0	1.8	2.62	.65	0.65	.646	4.0
20	.11	14.9	7.2	1.6	4.0	2.00	.55	.55	.523	8.8
30	.07	12.05	7.45	2.0	6.4	1.52	.465	.47	.423	14.7
40	.04	9.3	7.5	2.1	9.1	1.16	.375	.37	.326	22.2
50	.02	6.45	7.5	2.0	12.0	0.81	.28	.28	.226	32.3

of decarboxylation of these several species is for malonic acid itself,[5] where it has been shown that the dibasic acid decarboxylates considerably faster than the acid anion. Work on dibromomalonic acid indicates that in this case the singly charged anion is more reactive than the acid, while the doubly charged anion is stable.[6]

In the present paper the dependence of the rate of decarboxylation of phenylmalonic acid on concentration and *p*H is examined.

Experimental

Diethyl phenylmalonate was prepared according to "Organic Syntheses."[7] Portions of the ester were hydrolyzed prior to kinetic experiments by shaking the ester dissolved in ether with aqueous alkali at room temperature, following the procedure of Basterfield and Hamilton.[8] The phenylmalonic acid was recrystallized from ether–ligroin, melting at about 152° with decomposition.

Fresh aqueous solutions of the acid prepared by weight gave an alkali titer corresponding to over 95% dibasic acid. All solutions were made up at 25°, and concentrations quoted refer to this temperature. *p*H measurements were made at 25° with a Beckman glass electrode *p*H meter. Kinetic experiments were conducted in a water thermostat at 45.00 ± 0.02°. Five-cc. aliquots were withdrawn from the reaction mixtures at intervals and diluted. CO_2 was expelled and the solutions were titrated against 0.153 *N* sodium hydroxide using phenolphthalein as indicator. The sodium hydroxide was standardized against constant boiling hydrochloric acid. The initial *p*H of reaction mixtures was adjusted by addition of standard sodium hydroxide or hydrochloric acid.

Results

The ionization constants of phenylmalonic acid were measured at 25° by titration with standard alkali using a Beckman glass electrode *p*H meter. The ionization constants are found to be $K_1 = 2.65 \times 10^{-3}$ and $K_2 = 9.4 \times 10^{-6}$. The value of the first ionization constant may be compared with one of 2.7×10^{-3} previously obtained by conductivity measurements.[9]

Preliminary kinetic experiments showed that the rate of decarboxylation increased with *p*H, indicating that the acid anion of phenylmalonic acid was more reactive than the un-ionized dibasic acid.

Experiments in the *p*H range 0.7–1.0 were initially interpreted in terms of the decarboxylation of the dibasic acid only, according to the reaction scheme

$$C_6H_5CH(COOH)_2 \longrightarrow C_6H_5CH_2COOH + CO_2 \quad (1)$$

Extrapolation to higher hydrogen ion concentrations around *p*H 0 indicated that the first-order rate constant for the decarboxylation of the un-ionized acid, *k*, was about 1×10^{-2} hour^{-1}.

The general rate equation for the decarboxylation may be written as

$$d(CO_2)/dt = k(H_2A) + k'(HA^-) + k''(A^=) \quad (2)$$

where H_2A, HA^- and $A^=$ represent the un-ionized phenylmalonic acid and its two anions, and *k*, *k′* and *k″* are the respective first-order rate coefficients.

In the *p*H range 4–6 the contribution of the un-ionized acid to the rate of decarboxylation is negligible and the decomposition of the anions can be studied independently. In this *p*H range it was found that with a variation of two powers of 10 in the concentration of the doubly charged anion there appeared to be no contribution to the rate from this species. Experiments could be interpreted in terms of the rate equation

$$d(CO_2)/dt = k'(HA^-) = 35 \times 10^{-3}(HA^-) \quad (3)$$

An experiment in this *p*H range is shown in Table I. This table illustrates the general method of calculation. The initial hydrogen ion concentration from the measured *p*H and the initial alkali titer were used to calculate the concentrations, in moles/liter, of all the participating species at the start of the reaction and at 10% stages of decarboxylation. The equilibria between the various species present in the reaction mixtures include the ionization equilibria of phenylmalonic acid H_2A and its anions HA^- and $A^=$, and of the phenylacetic acid HAc and its anion Ac^-. The ionization constant of phenylacetic acid is 4.88×10^{-5} at 25°.[10]

The alkali titers (cc. 0.153 *N* NaOH) corresponding to the various stages of reaction as calculated from the listed concentrations are given in Table I. Instantaneous rate values were calculated from rate equation 3 and from these the times of reaction at 10% stages of decarboxylation were derived. The observed alkali titers corresponding to these times as read off from the experimental alkali titer–time curves were compared with the calculated titers. The excellent agreement in the high *p*H range showed that the doubly charged anion is stable.

With the value thus obtained for the rate constant of the unimolecular decarboxylation of HA^-, $k' = 35 \times 10^{-3}$ hr.$^{-1}$, experiments at a lower *p*H were interpreted. The concentrations of H_2A, HA^- and H^+ at 10% stages of reaction were calculated from the initial alkali titers and the concentration of any added hydrochloric acid. Taking the value for *k′* obtained independently at higher

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[5] G. A. Hall, THIS JOURNAL, **71**, 2691 (1949).

[6] J. Muus, *J. Phys. Chem.*, **39**, 343 (1935).

[7] "Organic Syntheses," Col. Vol. II, J. Wiley and Sons, Inc., New York, N. Y., p. 288.

[8] S. Basterfield and L. A. Hamilton, *Trans. Roy. Soc., Canada*, III, **27**, 125 (1933).

[9] S. Basterfield and J. W. Tomecko, *Can. J. Research*, **8**, 447 (1933).

[10] J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).

*p*H, the value of *k*, the rate constant for the un-ionized acid, was adjusted by trial and error in each experiment until agreement between observed and calculated titers was obtained. Table II shows some typical experiments with the initial concentrations of the various species involved and the best values of *k*. With those values almost perfect agreement between observed and calculated titers was maintained to 70% decarboxylation in each experiment. It may be seen that the decarboxylation of phenylmalonic acid over the *p*H range studied can be expressed in terms of the rate equation

TABLE II

$10^4(H_2A)$	$10^4(HA^-)$	$10^4(A^=)$	$10^4(H^+)$	10^3k	$10^3k'$
0.20	90	141	0.060	..	35
3.1	220	57	0.36	..	35
30.6	230	6.2	3.47	11.2	35
200	73	0.1	73	11.2	35
240	30	...	214	11.2	35
245	12.5	...	517	10.8	35
269	3.5	...	2000	10.0	35

$$d(CO_2)/dt = 11.2 \times 10^{-3}(H_2A) + 35 \times 10^{-3}(HA^-) \quad (4)$$

In the experiments at higher hydrogen ion concentrations the neglect of activity coefficients may account for the observed variation in the value of *k*.

An examination of the concentrations of H_2A and H^+ involved in those experiments shows that the hydrogen ion-catalyzed reaction of the un-ionized acid cannot be significant. It may be added that the contribution of the unimolecular decomposition of the un-ionized acid to the rate of decarboxylation can be expressed in an entirely equivalent manner in terms of the hydrogen ion-catalyzed reaction of the singly charged anion from which it is kinetically indistinguishable.

Discussion

The present study of the decarboxylation of phenylmalonic acid in aqueous solution at 45° has shown that the un-ionized acid and the singly charged anion undergo unimolecular decarboxylation while the doubly charged anion is stable. The singly charged anion decomposes about three times more rapidly than the un-ionized acid.

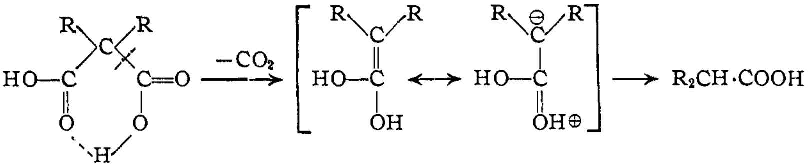
These results must be considered in relation to the available data on malonic acid[5] and dibromomalonic acid.[6] With both these acids the doubly charged anion appears to be stable toward decarboxylation. The first-order rate constants of decarboxylation at 45° for the three malonic acids and their acid anions are listed in Table III in $\log_e$, hour^{-1} units. The values for malonic acid and dibromomalonic acid were calculated from the available data at 80–90° and 25–35°, respectively.

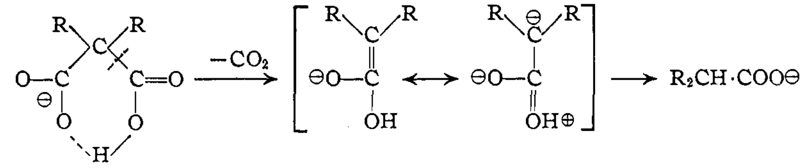
TABLE III

Acid	10^4k	$10^4k'$
Dibromomalonic acid	$\ll 85000$	85000
Phenylmalonic acid	112	350
Malonic acid	1.4	0.2

The introduction of electron attracting substituents is reflected in a greatly increased ease of fission of the carbon–carbon bond in both acid and singly charged anion as shown in Table III. The same general inductive effect leads to the easier proton transfer to a water molecule: the first ionization constants of malonic, phenylmalonic and dibromomalonic acids are 1.4×10^{-3}, 2.6×10^{-3} and unity, and the second ionization constants are 2.1×10^{-6}, 9.4×10^{-6} and about 10^{-2}, respectively, at 25°.

The decarboxylation of the acid and the singly charged anion may be represented as


(5)


(6)

The stability of the doubly charged anion is to be attributed to the high electron density in the carbon–carbon bonds and the difficulty of accommodating the negative charge in the fission process giving rise to CO_2.

There will also be a greater electron-density in the carbon–carbon bond undergoing fission in the singly charged anion than in the acid. Inductive effects thus lead to a greater reactivity of the un-ionized acid, as is observed for the unsubstituted malonic acid. The introduction of an electron attracting group adjacent to the carbon–carbon bond to be broken will lead to a resonance stabilization of the negative charge on the adjacent carbon atom in the fission process. This effect will lead to an increase in the relative reactivity of the anion as compared with the acid. The transfer of the proton from one carboxyl group to the other, may also be energetically significant. This transfer is more facile in the anion than in the acid, and the relative facility of the process may be increased by the introduction of substituent groups. Further kinetic data on the decarboxylation of substituted malonic acids are to be desired.

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