trum should be reinvestigated with greater resolution in the hope of finding more details of the vibrational structure.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Temperature Coefficient of the Intermolecular Carbon Isotope Effect in the Decarboxylation of Normal Malonic Acid

BY PETER E. YANKWICH, R. L. BELFORD AND GIDEON FRAENKEL

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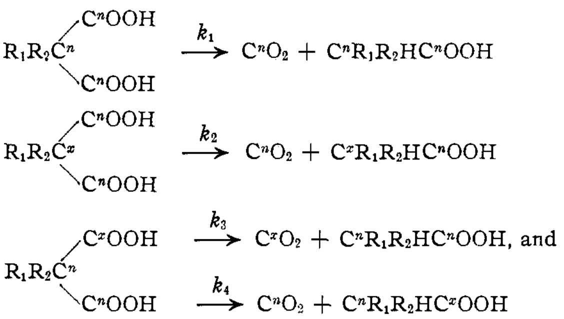
The intermolecular carbon isotope effect in the decarboxylation of isotopically normal malonic acid has been measured in 80% aqueous sulfuric acid in the range 56 to 129°. The magnitudes of the results are in accord with predictions based on the simplified model of Bigeleisen, but their mode of temperature dependence is not. The temperature coefficients of the possible corresponding oxygen isotope effects (O^{17} and O^{18}) have been found to be negligible. It is concluded that the mechanism of decarboxylation in 80% sulfuric acid is similar to that in dilute hydrochloric acid solution, as reported by Hall.

Introduction

Isotope effects in the thermal decarboxylation of malonic acids have been the subject of a number of studies.[1-7] In the notation introduced by Bigeleisen and Friedman,[2] (where *n* and *x* denote different isotopes or concentrations of isotopes of carbon), the deviation from unity of the ratio k_4/k_3 is a measure of the *intra*molecular isotope effect, while that of $k_1/2k_3$ is one measure of the *inter*molecular effect. The former can be determined from analysis of the carbon dioxide obtained by complete decarboxylation to acetic acid, while the latter is gotten from analysis of the first carbon dioxide evolved.



Bigeleisen and Friedman,[2] and Lindsay, Bourns and Thode[3] have determined the intermolecular isotope effect at the melting point of solid malonic acid. Material from several sources was employed. Lindsay, Bourns and Thode[5] have reported measurements of this effect at several temperatures above the melting point. Bigeleisen,[8] in a revision of previous calculations,[9] has shown that theoretical predictions of the magnitudes of the effects observed are in accord with these experiments, except that the latter do not show the predicted temperature coefficient. The predictions and experimental results are summarized in Table I.

TABLE I

INTERMOLECULAR ISOTOPE EFFECT IN DECARBOXYLATION OF NORMAL MALONIC ACID (C^{13} EFFECT)

	$100[(k_1/2k_3) - 1]$		
T, °C.	Calcd.	Obsd.	Ref.
137.5	3.5	3.7 ± 0.2	2, 10
138	3.5	4.6	3, 10
137	3.5	3.4	5, 11
149	3.4	4.1	
173	3.3	3.4	
196	3.1	3.6	

In all of these experiments the carbon isotope ratio was determined on the first 1% or so of carbon dioxide evolved after the initiation of decarboxylation by submersion of the reaction vessel in a high temperature bath. The interpretation which has been made of results so obtained is subject to challenge because the rates of melting and of decarboxylation of malonic acid are not very different. For example, in order that the isotopic constitution of the first 1% of carbon dioxide evolved reflect the influence of temperature it is necessary that much less than 1% decarboxylation occur before the solid malonic acid has melted. Actually there is considerably more than 1% decarboxylation (at bath temperatures of 140 or 200°) before melting is complete, and this effect introduces another complication into the interpretation of results from these experiments because under such conditions the intermolecular isotope effect cannot be measured directly.[12]

Fry and Calvin[6] have measured the intramolecular C^{14}-isotope effects in decarboxylations of phenyl- and α-naphthylmalonic acids at the melting points and at several lower temperatures in dioxane–aqueous hydrochloric acid solution. While the effect of temperature on results obtained from solution decarboxylation is masked by their stated errors in radioactivity measurement, the difference between results from solution runs at low temperatures and pure solid runs at about 100° higher is so

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(1) P. E. Yankwich and M. Calvin, *J. Chem. Phys.*, **17**, 109 (1949).

(2) J. Bigeleisen and L. Friedman, *ibid.*, **17**, 998 (1949).

(3) J. G. Lindsay, A. N. Bourns and H. G. Thode, *Can. J. Chem.*, **29**, 192 (1951).

(4) A. Roe and M. Hellman, *J. Chem. Phys.*, **19**, 660 (1951).

(5) J. G. Lindsay, A. N. Bourns and H. G. Thode, *Can. J. Chem.*, **30**, 163 (1952).

(6) A. Fry and M. Calvin, *J. Phys. Chem.*, **56**, 901 (1952).

(7) P. E. Yankwich and E. C. Stivers, *J. Chem. Phys.*, **20**, Dec. (1952).

(8) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

(9) J. Bigeleisen, *J. Chem. Phys.*, **17**, 425 (1949).

(10) Eastman Kodak Co. malonic acid.

(11) British Drug Houses malonic acid.

(12) If decarboxylation were rapid compared with melting, only an intramolecular isotope effect could be observed.

much larger than that which would correspond to the predicted very small temperature coefficient[9] as to suggest a possible solvent effect.

The purpose of the work reported here has been to determine the intermolecular isotope effect and its temperature coefficient under conditions of completely homogeneous decomposition, and to ascertain the existence or absence of a large solvent effect. The system employed consisted of normal malonic acid dissolved in 80% aqueous sulfuric acid solution.

Experimental

Materials.—The malonic acid used was Eastman Kodak Co. white label grade. Preliminary tests showed that the purity of the material (99.9 ± 0.1% by acidimetric titration; m.p. 135°) was not increased significantly by recrystallization and it was used without further purification. Lindsay, Bourns and Thode[8] have demonstrated that the carboxyl and methylene carbon atoms of this material have the same isotopic constitution.

Sulfuric acid solution was made by dilution with distilled water of Grasselli 96% C.P. reagent sulfuric acid. The concentration, 80.0 ± 0.5%, was checked by titration with standard alkali.

Apparatus and Procedure.—The apparatus consisted of a combination reaction vessel and sweep gas heater, a reaction vessel of about 200-cc. volume, and a more or less conventional high vacuum apparatus for drying, collection, purification and quantity determination of the effluent carbon dioxide. Carbon dioxide-free helium was used as a sweep gas; the temperature of the decarboxylation was determined by the boiling point of the particular working fluid employed in the combination heater.

About 4 g. of dry malonic acid was weighed into a small sample tube which was suspended on a long rod above the 150 ml. of aqueous sulfuric acid in the reaction vessel. As the temperature of this vessel was brought to the desired level, a slow sweep of helium through the whole apparatus was maintained. During the various runs the rate of helium flow was varied between 25 and 300 cc./min. The effluent carbon dioxide was dried before collection by passage through either Anhydrone or 96% sulfuric acid.

When thermal equilibrium had been established in the heater and reactor, the first collection trap was cooled in liquid nitrogen. Decarboxylation was started by breaking the sample tube against the bottom of the reaction vessel; the sample dissolved in a few seconds. After a predetermined period the second collection trap was cooled, the flow of gases shifted to it and the collection of the next sample (B) begun. In a similar fashion, the third (C) sometimes a fourth sample (D) of effluent carbon dioxide were collected.

After collection of all samples, the reactor was detached from the apparatus and the gas handling section, including the first collection trap, evacuated. This trap was then warmed in Dry Ice–alcohol mixture and the first sample (A) distilled into a calibrated manometer, where its size was determined; the sample was then distilled into a previously evacuated mass spectrometer sample bulb. The other samples were measured and transferred in similar fashion.

Isotope Analyses.—There are carbon and possibly oxygen isotope effects in the decarboxylation of malonic acid. In the determination of the carbon isotope effect it is necessary to apply a correction to the observed isotope ratio of the effluent carbon dioxide to account for the fact that $C^{13}O_2^{16}$ and $C^{12}O^{16}O^{17}$ are measured together in the mass spectrometer. That this correction was essentially independent of decarboxylation temperature was ascertained by observation of the ratio of ion currents $(m/e\ 46)/(m/e\ 44+45) = R_O$, and the value -0.00080 was applied to the observed ratio of ion currents $(m/e\ 45)/(m/e\ 44)$ after the latter was corrected for incomplete resolution.

The several ratios of the various samples were obtained from measurements with a Consolidated-Nier Isotope-Ratio Mass Spectrometer; additional electronic stabilization was used with the low voltage power supply as a precautionary measure. The ratios of each sample were determined once on each of at least three introductions of carbon dioxide into the manifold of the spectrometer. A large sample of tank carbon dioxide was employed as a working standard and all other measured ion current ratios were expressed in terms of those found for it. This procedure eliminated the effect of small daily variations in the response of the instrument. Frequent cross checks were made among effluent gas samples, tank carbon dioxide and carbon dioxide obtained from combustion of malonic acid. The mass spectrum of each gas sample was determined in the range m/e 27 to m/e 48. The sample was rejected if this spectrum deviated appreciably from that of tank carbon dioxide which had been subjected to the same high vacuum manipulations. Typical mass spectra are shown in Table II.

TABLE II

MASS SPECTRA OF TYPICAL EXPERIMENTAL SAMPLES

Sample	Output ,volts			
m/e	II-18 Tank	13 Comb.	26A Decarbox.	26B
48	0.000	0.000	0.000	0.007
47	.001	.001	.002	.001
46	.081	.083	.083	.084
45	.230	.236	.248	.230
44	19.1	19.5	19.5	19.5
43	0.009	0.006	0.096	0.016
42	.003	.003	.003	.004
41	.004	.004	.014	.007
40	.001	.002	.000	.001
39	.002	.003	.011	.004
38	.001	.001	.004	.001
37	.000	.000	.002	.000
36	.000	.000	.000	.000
32	.007	.008	.011	.010
31	.000	.001	.050	.001
30	.004	.007	.005	.005
29	.021	.024	.051	.023
28	1.63	1.70	1.70	1.65
27	0.005	0.020	0.020	0.008
R (45/44)	0.011809	0.011913	0.012990	0.011429

Calculations.—In these experiments the corrected isotope ratio of the effluent carbon dioxide (R_C) (at per cent. decarboxylation → 0) is compared with that (R_D) of carbon dioxide obtained from a total combustion of malonic acid. Three samples of malonic acid were burned completely in three different combustion trains with copper oxide wire–lead chromate–lead peroxide packings; in each case the resultant carbon dioxide was collected in an efficient spiral trap immersed in liquid nitrogen. The average corrected ratio of the three combustion samples was taken as R_D. In terms of the two carbon isotope ratios measured, $(k_1/2k_3) = (R_D/R_C)$.[13] The corrected ratios for each sample of acceptable purity are collected in Table III, along with the values of $k_1/2k_3$ calculated therefrom; the appended errors are average deviations.

Results

It will be noted that no data for A samples are tabulated; no A sample met the criterion of purity described above. It is likely that trace impurities in the malonic acid itself were responsible for this fact.

The data for R_O do not permit one to rule out the existence of a detectable temperature coefficient for the oxygen isotope effect, but do permit the conclusion that the temperature coefficient is so small that its neglect will not influence appreciably the accuracy of the calculation of the carbon isotope effect.

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(13) For the sake of rigor the data should be corrected to zero decomposition. The simple equation given was used throughout the calculations because correction of typical results to zero decomposition gave values of $(k_1/2k_3)$ insignificantly larger than the averages shown in Table III.

TABLE III

CORRECTED ISOTOPE RATIOS OF EXPERIMENTAL SAMPLES; CALCULATED INTERMOLECULAR ISOTOPE EFFECTS

Run temp., °C.	Sample	Decarbox., %	$Ro \times 10^6$	$Rc \times 10^6$	$(k_1/2k_3)$	Average $(k_1/2k_3)$
			A. Samples from decarboxylations			
56	26B	0.10–0.39	4095 ± 1	10423 ± 2	1.0439	
	26C	.39– .89	4086 ± 1	10406 ± 1	1.0456	
	27B	.06– .34	4095 ± 3	10398 ± 1	1.0464	
	27C	.34– .78	4086 ± 3	10408 ± 1	1.0454	
	27D	0.78–1.05	4086 ± 2	10410 ± 5	1.0452	1.0453 ± 0.0006
79	14B	0.21–0.48	4094 ± 2	10505 ± 4	1.0358	
	14C	.48– .99	4096 ± 1	10500 ± 1	1.0363	
	15B	.22– .56	4095 ± 2	10486 ± 3	1.0377	
	15C	0.56–1.00	4096 ± 1	10488 ± 2	1.0375	
	15D	1.00–1.19	4096 ± 1	10493 ± 0	1.0370	
	16B	0.16–0.31	4089 ± 2	10472 ± 2	1.0390	
	16C	.31– .47	4105 ± 0	10482 ± 0	1.0381	
	16D	.47– .69	4105 ± 1	10472 ± 0	1.0390	1.0376 ± 0.0009
100	8B	0.22–0.92	4099 ± 3	10521 ± 1	1.0342	
	8C	0.92–1.94	4104 ± 1	10510 ± 4	1.0353	
	9B	0.06–0.36	4104 ± 1	10515 ± 3	1.0348	
	9C	.36– .59	4100 ± 2	10511 ± 4	1.0352	
	9D	.59– .87	4098 ± 1	10514 ± 1	1.0349	
	10B	.03– .44	4100 ± 2	10521 ± 3	1.0342	1.0348 ± 0.0004
129	17B	0.08–0.48	4090 ± 0	10523 ± 2	1.0340	
	17C	0.48–4.78	4094 ± 1	10531 ± 1	1.0332	
	18B	0.04–1.03	4087 ± 0	10524 ± 1	1.0339	
	18C	1.03–5.13	4090 ± 0	10536 ± 1	1.0327	1.0336 ± 0.0007

B. Samples from combustion of malonic acid

	$Ro \times 10^6$	$R_D \times 10^6$
11	......	10880 ± 2
12	4143 ± 1	10883 ± 2
13	4148 ± 1	10879 ± 2

C. Tank carbon dioxide, working standard

Sample	$Ro \times 10^6$	$R\text{std.} \times 10^6$
II-18	4139 ± 0	10783 ± 1

The average values of $100[(k_1/2k_3) - 1]$ calculated from the figures in the last column of Table III are plotted *versus* $1000/T$ in Fig. 1. The vertical rectangles encompass the calculated average deviations, while the short horizontal bars represent the maximum and minimum isotope effects observed at each temperature. The dashed line is calculated from Bigeleisen's revised model[8]; the solid line is self-explanatory.

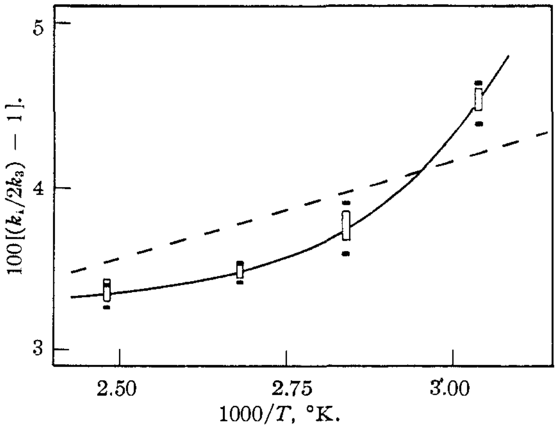

Fig. 1.—Influence of temperature on intermolecular isotope effect: ------, Bigeleisen's model; ———, this research.

Discussion

It has been mentioned in the introduction that the relation between the rates of melting and decarboxylation of malonic acid makes it unlikely that the results reported by Lindsay, Bourns and Thode[5] for the temperature coefficient of the intermolecular isotope effect are other than repeat determinations of the same quantity at the melting point of malonic acid, *ca.* 135°.[14] Apart from this, their stated experimental error is such that the expected effect of temperature variation would have been masked.

It is apparent from examination of Fig. 1 that the magnitudes of the effects reported here are in accord with the predictions of Bigeleisen's simplified model. While one may always invoke additional complication of such a model to explain the results of experiment, it is difficult to envisage just what these complications might be in this case to yield a strongly curved plot of $100[(k_1/2k_3) - 1]$ *versus* $1/T$ rather than an essentially linear one. If the results from runs at 56° are considered to be out of line, the most likely cause would be diffusion error in the collection of the several samples. The possibility that such error might be important was tested in the first two runs made, 8 and 9. In run 8 the helium sweep rate was 25 cc./min., while in run 9 it was 200 cc./min. Since the rate of sweep

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[14] Five-gram samples of malonic acid in a test-tube-like reactor were immersed in a thermostated oil-bath until melting was essentially complete, as evidenced by an increase in the temperature of the melt above 135°. The reactor was then plunged into ice-water. Malonic acid remaining was determined by titration. Minimum decarboxylation at a bath temperature of 140° was 8.9%, at 200°, 8.1%.

would have determined the magnitude of any diffusion error the small differences between results calculated for these runs is taken as proof that such error is insignificant. Considerable care was exercised to exclude from the various parts of the apparatus any material which could absorb or exchange with carbon dioxide.

There is the possibility that the medium employed here, 80% sulfuric acid, has caused important changes in the solution decarboxylation mechanism as found by Hall.[15] Average first-order rate constants obtained from kinetic analysis of the sample collection data for pairs of runs at two temperatures are compared in Table IV with those calculated from Hall's results. Our constants must be regarded as approximate because sweep collection of gas samples is a rather poor technique if really precise kinetic information is sought. We believe, however, that the data shown in Table IV indicate strongly that the rate and heat of activation of the decarboxylation in 80% sulfuric acid are the same as in 0.381 *M* hydrochloric acid,[15] and that it is likely that the mechanism is the same, *i.e.*, decomposition of the undissociated diacid.[16]

TABLE IV

RATE CONSTANTS FOR DECARBOXYLATION

T, °C.	Runs	$k \times 10^6$, sec.$^{-1}$ Calcd.	$k \times 10^6$, sec.$^{-1}$ Obsd.
56	26, 27	0.82	0.95
79	14, 15	2.0	1.8

We are now investigating the isotope effects and kinetics of this reaction in other solvent media.[17]

Acknowledgments.—This research was supported by the A.E.C. We are indebted to Mrs. R. W. Hill, who performed the mass spectrometer analyses.

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

[16] Preliminary experiments in this Laboratory have shown that the rate of the decarboxylation in 96% sulfuric acid is nearly the same as in the 80% solution, while that in 100% sulfuric acid is larger by a factor *ca.* 20.

[17] Tentative results for quinoline solutions indicate that the rate of decarboxylation in that solvent is very nearly the same as that in 100% sulfuric acid. At 79°, $(k_1/2k_2)$ = 1.0468 ± 0.0003, in quinoline.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Reactions of Lithium Aluminum Hydride with Representative Elements of the Main Groups of the Periodic System[1]

BY THOMAS WARTIK AND H. I. SCHLESINGER

RECEIVED JULY 14, 1952

Whereas treatment of alkyl derivatives of the alkali metals and of the metals of the main and sub-groups II with lithium aluminum hydride leads almost exclusively to the formation of the corresponding metal hydrides, the trialkyls of boron, aluminum and gallium react as represented by the equation: $LiAlH_4 + R_3M \rightarrow LiMH_3R + R_2AlH$. The unexpected character of the reaction is pointed out and briefly discussed. As judged by the behavior of a limited number of examples, alkyls of main groups IV, V and VI do not react with lithium aluminum hydride. The behavior of the alkyls is contrasted with the behavior of the corresponding halides. Vapor tensions of dimethylaluminum hydride at several temperatures have been determined, as have its apparent molecular weights. In the gas phase at temperatures between 83 and 167° it appears to be a mixture of trimer and dimer in varying proportions; in isopentane solutions it seems to be largely trimeric at 20°.

In an earlier paper[2] dealing with the reactions between lithium aluminum hydride and metal alkyls, it was shown that alkyl derivatives of the first main group of the periodic system (as illustrated by methyl lithium) and those of the second group (as illustrated by beryllium, magnesium, zinc and cadmium alkyls) are transformed to the hydrides of these elements. Only when dimethylaluminum hydride was used as the hydrogenating agent in place of lithium aluminum hydride, was definite evidence obtained of the formation of mixed hydride alkyls (*i.e.*, of compounds of the type $CH_3M^{II}H$ in which M^{II} is a metal of the second group). In contrast to this behavior, the methyl derivatives of the third group elements, boron, aluminum and gallium, produce dimethylaluminum hydride and the compounds $LiM^{III}CH_3H_3$, in which M^{III} represents any one of the elements in question.

So far as our present information goes, lithium aluminum hydride does not react with alkyls of the fourth, fifth and sixth main groups. This statement is based on the behavior of the reagent toward alkyl silanes, alkyl germanes, alkyl stannanes, tetramethyllead, trimethylamine, and toward ethers or diethyl sulfide.

Thus it appears that the more electropositive the element with which the alkyl groups are associated, the more readily are the latter replaced by hydrogen in these reactions. The reverse of this statement applies to the hydrogenation of halides. Thus the chlorides of elements of the first main group do not react with lithium aluminum hydride, and the chlorides of second group elements either do not react or react incompletely, giving mixtures from which pure compounds could not be isolated. The halides of the third,[3a] of the fourth,[3b] and of the fifth main groups[4] readily give the corresponding

[1] Taken from Final Reports submitted to the Navy on Contracts N173-10421, NRL-C-3147, N6ori-20 for the years 1945-1948, and from a thesis submitted by Thomas Wartik to the Department of Chemistry of the University of Chicago in part fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **73**, 4585 (1951).

[3] (a) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947). (b) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2692 (1947).

[4] H. I. Schlesinger, *et al.*, Final Report on Contract N173s-10421, for the year 1945-1946, p. 8, in which it was shown that arsenic trichloride and antimony pentachloride in ether solution react with lithium aluminum hydride to produce arsine and stibine, respectively. Halides of sixth group elements have not been studied.