

erocyclic amines it favors the left-hand side of this equation. That dinitrogen tetroxide may act as a bifunctional Lewis acid is seen from its compounds with the ethers, e.g.,  $N_2O_4 \cdot 2Et_2O$ .<sup>2</sup> It should be noted, however, that the compound  $N_2O_4 \cdot 2Et_2O$  is almost certainly highly, if not completely, dissociated even at  $-35^\circ$ , and that solvolytic reactions of the sort  $N_2O_4 \cdot 2B + 2Et_2O \rightleftharpoons N_2O_4 \cdot 2Et_2O + 2B$  are unimportant.

### Experimental

**Preparation of Materials.**—Dinitrogen tetroxide for use in these studies was prepared and purified by methods previously described.<sup>2</sup>

Eastman Kodak Co. reagent grade diethyl ether was fractionated, dried over sodium and redistilled before use.

Pyridine,  $\gamma$ -picoline, isoquinoline, 2-methylquinoline and 2,6-lutidine were obtained from the Reilly Tar and Chemical Corporation. Quinoline,  $\alpha$ -picoline,  $\beta$ -picoline and triethylamine were obtained from the Eastman Kodak Company. All these amines were dried for two weeks over barium oxide, carefully fractionated, retaining only a small middle fraction, and stored over barium oxide. They were all distilled afresh from barium oxide just before use. (The distillations in the case of quinoline and isoquinoline were under reduced pressure.) The purities of the amines were checked by comparison of boiling points with literature values and by titrating weighed samples of each amine against standard acid using a pH meter. These tests showed the amines to be quite pure.

Acridine obtained from the Eastman Kodak Company was recrystallized from aqueous alcohol. The recrystallized sample melted at  $111^\circ$  (lit.  $110$ – $111^\circ$ ).

**Procedure.**—The following technique was adopted. A cooled ( $-75^\circ$ ) ethereal solution of the amine was dropped

from a jacketed dropping funnel into a cooled solution of dinitrogen tetroxide in ether, magnetically stirred, and maintained at  $-75^\circ$ . The precipitated addition compounds were usually filtered and sometimes washed with fresh, cold ether if the amine were in excess. The solvent and excess reactant were pumped off under vacuum at a temperature of  $-10^\circ$  or below. Since none of the resulting addition compounds is completely stable at room temperature, the weight of reaction product formed was found by allowing a known weight of water to be drawn (by vacuum) into the reaction flask, thus hydrolyzing the product. From the weight of the flask plus solution, the known weight of the empty flask plus the weight of the water, the weight of the product was calculated. Since this method involves taking a small difference between two large weights, it is of limited accuracy.

**Analysis.**—The aqueous solutions obtained by the above procedure were analyzed for amine by making the solution alkaline and by distilling the amine into an excess of standard acid followed by back titration using a pH meter. After removing the amine from a particular aliquot, Devarda's alloy was added to reduce the remaining nitrogen to ammonia, which was distilled into boric acid solution and titrated with standard acid using brom cresol green as indicator. Even if the weight of product is not known, or is known only approximately, this analysis will accurately indicate the formula if it is assumed that the product consists entirely of amine and dinitrogen tetroxide.

**Acknowledgment.**—The fact that this research has been supported in part from funds granted by The Ohio State University Research Foundation to the University for aid in fundamental research is gratefully acknowledged.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Intermolecular Carbon Isotope Effect in the Decarboxylation of Normal Malonic Acid in Quinoline Solution<sup>1</sup>

BY PETER E. YANKWICH AND R. LINN BELFORD

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The intermolecular carbon isotope effect in the decarboxylation of isotopically normal malonic acid has been measured in quinoline solution in the range  $34$  to  $118^\circ$ . The complexity of the decomposition is such that neither the magnitudes nor the mode of temperature dependence of the results are in accord with predictions based on the simplified model suggested by Bigeleisen. It is concluded that the mechanism of the decarboxylation in quinoline involves at least one rapid, reversible equilibrium antecedent to the rate-determining step. The low entropy of activation for the reaction seems to require that the rate-determining step be a bimolecular process involving a molecule of solvent.

In a recent paper<sup>2</sup> we presented the results of experiments designed to yield the temperature coefficient of the intermolecular carbon isotope effect in the decarboxylation of malonic acid of normal isotopic constitution under conditions of homogeneous decomposition. The solvent chosen for those studies was 80% aqueous sulfuric acid. A plot of the isotope effect data obtained vs.  $1/T$  was strongly curvilinear (*vide infra*) over the temperature range explored ( $56$ – $129^\circ$ ), whereas a linear plot is predicted by calculations based on the corrected<sup>3</sup> simple model of Bigeleisen.<sup>4</sup> We did not offer an explanation of this apparent dis-

crepancy, and further work to test the relation between theory and experiment seemed desirable.

In the present paper we present isotope effect results for malonic acid decarboxylation in quinoline. This solvent was chosen because studies of malonic acid decarboxylation in a variety of media<sup>5,6</sup> indicated that in quinoline the solute was highly solvated, and inappreciably ionized, resulting in a similar simplification of treatment of results as if the solute were not solvated at all.<sup>7</sup>

### Experimental

**Materials.**—The malonic acid was the Eastman Kodak Co. white label grade. Preliminary tests showed that the purity of the material ( $99.9 \pm 0.1\%$  by acidimetric titration; m.p.  $135^\circ$ ) was not increased significantly by recryst-

(1) Presented before the Division of Physical and Inorganic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

(2) P. E. Yankwich, R. L. Belford and G. Fraenkel, *THIS JOURNAL*, **75**, 832 (1953).

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

(4) (a) J. Bigeleisen, *J. Chem. Phys.*, **17**, 425 (1949); (b) J. Bigeleisen and L. Friedman, *ibid.*, **17**, 998 (1949).

(5) G. Fraenkel, R. L. Belford and P. E. Yankwich, in preparation.

(6) Y. Ogata and R. Oda, *Bull. Inst. Phys. Chem. Research (Tokyo)*, *Chem. Ed.*, **23**, 217 (1944), made a related study.

(7) A study of these isotope effects for decomposition in a non-catalytic solvent is in progress in this Laboratory.

tallization, and it was used without further purification. Lindsay, Bourns and Thode<sup>8</sup> have demonstrated that the carboxyl and methylene carbon atoms of this material have essentially the same isotopic constitution.

The quinoline employed was Eastman Kodak Co. white label grade (synthetic); it was found to have been dried thoroughly and was used as received.

**Apparatus and Procedure.**—The apparatus and general procedure have been described previously.<sup>2</sup> Two modifications only were instituted for the present experiments: the entire gas handling system and the reactor were reconstructed so as to make their volume as small as was compatible with good experimental technique; a combination trap consisting of an Anhydrone-filled tube followed by a spiral immersed in Dry Ice-alcohol mixture was inserted between the reactor and the sampling system.

About 3 g. of dried malonic acid and 50 cc. of quinoline were combined after being brought to the decarboxylation temperature. The sweep rate of preheated, carbon dioxide-free helium was approximately 250 cc. per min.

**Isotope Analyses.**—The several isotope ratios of the various samples were obtained from measurements with a Consolidated-Nier Isotope-Ratio Mass Spectrometer. The carbon and oxygen ratios of each sample, except as noted, were determined once on each of at least three introductions of sample carbon dioxide into the manifold of the spectrometer. Two working standards, one consisting of tank carbon dioxide, the other of carbon dioxide obtained from total combustion of malonic acid, were employed during the work; frequent cross checks were made among the effluent-gas samples and the working standards. To eliminate the effects of small daily variations in the response of the mass spectrometer, all measured ion current ratios were expressed in terms of those of the tank carbon dioxide standard. The mass spectrum of each gas sample was determined in the range  $m/q$  27 to 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. The runs at 34° required exception to this procedure and are discussed separately below.

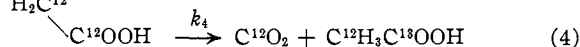
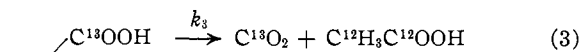
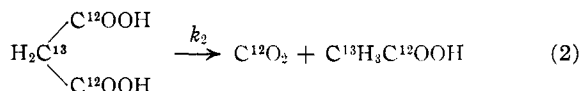
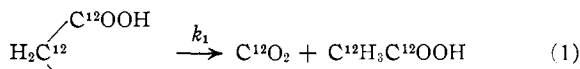
The observed carbon isotope ratio of the effluent carbon dioxide must be corrected for the contribution to the ion current at  $m/q$  45 of the species  $C^{12}O^{16}O^{17}$ . That this correction was virtually temperature independent was concluded from the values of the ratio of ion currents ( $m/q$  46)/( $m/q$  44 + 45) =  $R_D$ , in which  $C^{12}O^{16}O^{18}$  is measured, and the value -0.00080 was applied to the measured ratio of ion currents ( $m/q$  45)/( $m/q$  44) after the latter was corrected for incomplete resolution.<sup>9</sup>

**Runs at 34°.**—When a decarboxylation temperature of 34° was employed the effect of impurities with  $m/q$  near 44 became quite noticeable; contaminants with  $m/q$  41 or below appeared to have no effect, but those with  $m/q$  42 or 43 caused pronounced changes in the conditions in the ion-source, thus affecting the ratios measured. Most of the impurity at  $m/q$  42 could be removed by distillation of the sample between Dry Ice and liquid nitrogen temperatures, but the same treatment never resulted in complete removal of the substances responsible for the ion current at  $m/q$  43. However, it was observed that the non-separable impurities at  $m/q$  43 did not affect the operation of the ion-source, and correction for its presence (maximum peak *ca.* 60 millivolts, compared with 20,000 millivolts at  $m/q$  44) could be made.

As a test of the conclusion that the non-separable impurities at  $m/q$  43 would not affect the results, a different sample

handling procedure was employed in run 57. The effluent carbon dioxide was collected in a bubbler filled with 0.2 *M* sodium hydroxide solution three-fourths saturated with barium chloride. The barium carbonate precipitate was washed thoroughly with water and dried in air; it was then converted to carbon dioxide gas with concentrated sulfuric acid. The corrected carbon isotope ratio compares well with those from other runs at this temperature. The low oxygen ratio found is due to exchange with water or sulfuric acid.

**Calculations.**—Bigeleisen and Friedman<sup>4b</sup> introduced the notation commonly employed to describe malonic acid carbon isotope effects: the deviation



from unity of the ratio  $k_1/2k_3$  is a measure of an intermolecular isotope effect, and it is with this entity that the present research is concerned. The deviation from unity of  $k_4/k_3$  measures the intramolecular isotope effect; other intermolecular isotope effects are related to the ratios  $k_1/2k_4$  and  $k_2/k_1$ .<sup>10</sup>

In these experiments the corrected isotope ratio of the effluent carbon dioxide,  $R_C$ , is compared with that,  $R_D$ , of carbon dioxide obtained from total combustion of malonic acid (taken here as the average result of three burnings). Where the per cent. decarboxylation is 2 or 3 the relation  $(k_1/2k_3) = (R_D/R_C)$  is quite accurate. In cases of more extensive decomposition  $R_C$  as observed must be corrected to zero reaction. The derivation of the general relation proceeds easily from the kinetic equation for the value of the ratio ( $C^{13}O_2/C^{12}O_2$ ) at any fraction of decarboxylation,  $f$ , and yields

$$\frac{k_1}{2k_3} = \frac{(1 + \frac{k_4}{k_3}) \log(1 - f)}{2 \log \left[ 1 + \frac{R_C(1 + \frac{k_4}{k_3})}{2R_D(\frac{k_4}{k_3}R_C - 1)} \left\{ (1 - 2R_D)f + R_D \left( 1 - [1 - f]^{k_2/k_1} \right) \right\} \right]} \quad (5)$$

In order to apply equation (5) it is necessary to know  $k_4/k_3$  and  $k_2/k_1$  at the temperature of the reaction, in this study 118°. The value chosen for  $k_4/k_3$ , 1.033, was obtained by interpolation on results of the related investigation of the temperature coefficient of the intramolecular isotope effect<sup>11</sup>; a value of 0.96 was taken for  $k_2/k_1$  in accordance with the findings of Ropp and Raaen.<sup>12</sup> It should be noted that a value of  $k_1/2k_3$  calculated by equation (5) is about 50 times more sensitive to the chosen  $k_4/k_3$  than to  $k_2/k_1$ , and that a variation in  $k_4/k_3$  is reduced by a factor of 10 in its effect on  $k_1/2k_3$ .

(10) The isotope effect terminology used here was introduced by Lindsay, Bourns and Thode.<sup>8</sup>

(11) P. E. Yankwich and R. L. Belford, in preparation.

(12) G. A. Ropp and V. F. Raaen, *THIS JOURNAL*, **74**, 4992 (1952).

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

(9) In the previous paper in this series<sup>2</sup> it was stated that the temperature coefficients of the possible  $O^{17}$  and  $O^{18}$  isotope effects in the decarboxylation of malonic acid in aqueous sulfuric acid solution had been found to be negligible. That this statement is in error was kindly pointed out to us by a referee, but the correction to the manuscript was overlooked. The exchange of oxygen between the malonic acid and the water and sulfuric acid in the solvent is likely sufficiently rapid that the  $R_D$  data tabulated in the previous paper are merely repeat determinations of the consequences of a complicated set of related possible fractionations.

TABLE I  
CORRECTED ISOTOPE RATIOS OF EXPERIMENTAL SAMPLES; CALCULATED INTERMOLECULAR ISOTOPE EFFECTS

Run Temp., °C.	Sample	Decarbox., %	A. Samples from decarboxylations			Av. ( $k_1/2k_3$ )
			$R_0 \times 10^4$	$R_c \times 10^4$	( $k_1/2k_3$ )	
34	52A	0.00-0.10	4156 ± 0	10299 ± 2	1.0565	1.0567 ± 0.0011
	52B	.10-0.20	4151 ± 0	10285 ± 0	1.0579	
	52C <sup>13</sup>	.20-0.25	4136	10289	1.0575	
	53B	.40-0.60	4143 ± 1	10316 ± 1	1.0548	
	55B <sup>13</sup>	.02-0.10	4163	10300	1.0564	
	55C <sup>13</sup>	.10-0.15	4148	10281	1.0583	
	57	.00-0.50	4090 ± 2	10311 ± 5	1.0553	
59	40B	0.04-0.12	4131 ± 3	10381 ± 2	1.0482	1.0494 ± 0.0011
	40C	.12-0.19	4121 ± 1	10385 ± 2	1.0478	
	41A	.00-0.15	4139 ± 1	10364 ± 0	1.0499	
	41B	.15-0.29	4143 ± 2	10360 ± 5	1.0503	
	41C	.29-0.52	4148 ± 0	10380 ± 1	1.0483	
	47B	.49-1.00	4154 ± 0	10355 ± 0	1.0508	
	47C	1.00-1.50	4156 ± 1	10359 ± 1	1.0504	
79	48A	0.00-0.22	4152 ± 1	10427 ± 1	1.0438	1.0438 ± 0.0002
	48B	.22-0.73	4155 ± 1	10417 ± 1	1.0445	
	48C	.73-1.46	4157 ± 1	10425 ± 1	1.0438	
	49A	.00-0.25	4150 ± 1	10427 ± 1	1.0437	
	49B	.25-0.66	4156 ± 1	10426 ± 1	1.0436	
	49C	.66-1.41	4153 ± 1	10426 ± 2	1.0436	
99	45B	0.15-1.06	4129 ± 2	10464 ± 0	1.0399	1.0409 ± 0.0008
	45C	1.06-2.76	4134 ± 1	10460 ± 1	1.0403	
	46B	0.09-0.26	4143 ± 1	10446 ± 1	1.0416	
	46C	0.26-0.47	4144 ± 1	10445 ± 1	1.0417	
118	43A	0.0-13.2	4137 ± 2	10499 ± 3	1.0372	1.0379 ± 0.0009
	43B	13.2-20.3	4141 ± 1	10491 ± 1	1.0393	
	43C	20.3-28.1	4143 ± 1	10543 ± 1	1.0391	
	44A	0.0-30.0	4153 ± 1	10524 ± 1	1.0373	
	44B	30.0-45.1	4164 ± 1	10574 ± 1	1.0385	
	44C	45.1-55.0	4152 ± 1	10621 ± 2	1.0385	

B. Samples from combustion of malonic acid

	$R_0 \times 10^4$	$R_D \times 10^4$
11-13	4146 ± 1	10881 ± 2

C. Tank carbon dioxide; working standard

	$R_0 \times 10^4$	$R_{\text{standard}} \times 10^4$
II-18	4139 ± 0	10783 ± 1

The corrected carbon and oxygen isotope ratios for each sample are collected in Table I, along with the values of  $k_1/2k_3$  to which they correspond; the appended errors are average deviations.

### Results

The A samples are missing for certain runs; in these cases the sample either was too small for isotope analysis or could not be purified easily. The low value for  $R_0$  of sample 57 is due to exchange with water or sulfuric acid (*vide supra*).

The values of  $\ln(k_1/2k_3)$  calculated from the last column of Table I are plotted *versus*  $1/T$  in Fig. 1. The vertical rectangles encompass the calculated average deviations, while the short horizontal bars represent the maximum and minimum result at each temperature. The dashed curve is a similar plot of the data obtained for decarboxyla-

tion in 80% aqueous sulfuric acid<sup>2</sup>; the heavy straight line is calculated from Bigeleisen's revised model.<sup>3</sup>

### Discussion

The theory of absolute reaction rates permits, in principle, the calculation of the ratio of rate constants for isotopic molecules; methods of calculation have been developed by Bigeleisen.<sup>14</sup> If the transmission coefficients for reactions (1) and (3) are assumed equal

$$(k_1/2k_3) = (m_3^*/m_1^*)^{1/2} \left[ 1 + \sum_i^{3n-6} G(u_i) \Delta u_i - \sum_i^{3n'-6} G(u_i^\ddagger) \Delta u_i^\ddagger \right] \quad (6)$$

where  $G(u)$  is the free energy function of Bigeleisen and Mayer,<sup>15</sup>  $u = hc\omega/kT$ ,  $\ddagger$  refers to vibrations in the activated complex, and  $\Delta u_i$  is the change in  $u$  upon passing from the heavy molecule to the

(14) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(15) J. Bigeleisen and M. G. Mayer, *ibid.*, **15**, 261 (1947).

(13) Only a single introduction made to mass spectrometer. With samples of carbon isotope constitution near that of natural carbon, a single-introduction ratio is the same as that calculated from three or more introductions,  $\pm 2$  in the last digit.

light molecule. The terms  $m^*$  are the effective masses of the molecules in the transition state along the coordinate of decomposition. These are taken, after Slater,<sup>16</sup> as the reduced masses of the imaginary diatomic molecules formed by the atoms between which bond rupture is occurring. In order to apply equation (6) to actual isotopic reactions it is necessary either to know or to make assumptions about the vibrational modes of the normal and activated molecules.

Bigeleisen's model<sup>3</sup> assumes that the only vibrations affected significantly by the process of activation are those between the  $C^{12}-C^{12}$  and  $C^{12}-C^{13}$  atom pairs in the isotopic malonic acid molecules described by equations (1) and (3); these vibrations disappear in the activated complex. This model is admittedly oversimplified, but Bigeleisen has used it to explain successfully the isotope effects in a number of reactions.<sup>3</sup> The lower straight line in Fig. 1 is a plot of  $\ln(k_1/2k_3)$  vs.  $1/T$  as predicted by this model, with  $\omega_{C-C}$  taken as  $900\text{ cm}^{-1}$ . It is seen that while the isotope effect for decompositions in aqueous sulfuric acid at temperatures above  $60-70^\circ$  may conform to the behavior predicted by this model, neither the lower temperature results for this medium nor the results obtained at any temperature with quinoline solutions so conform.

An alternate calculation by Pitzer<sup>17</sup> involves an assumption similar to the above as regards the skeletal C-C vibrations but attempts to approximate the activated complex in terms of the models *plane*  $XYZ_2$  for the  $\text{HOOCCH}_2$ -fragment and *linear*  $XYZ$  for  $-\text{COOH}$ . The actual values of  $(k_1/2k_3)$  obtained on this basis are much larger than those observed in experiments with  $C^{13}$  (at  $99^\circ$  the value 1.075 is predicted, while 1.041 is observed with quinoline medium, 1.035 with sulfuric acid).

In view of earlier successes of the Bigeleisen model it is reasonable to expect that it will explain those of the results reported here and in the previous paper<sup>2</sup> obtained under conditions of *thermal*, *i.e.*, uncatalyzed, reaction. The data for decompositions at the higher temperatures in the case of the sulfuric acid experiments are in good agreement with the predictions of this model, and the kinetics data lend support to the conclusion that malonic acid decarboxylation is a unimolecular, *thermal* process under these conditions.<sup>18,19</sup>

The lower temperature results with sulfuric acid media and the entire series of experiments in quinoline can be explained if there are presumed to operate one or more rapid reversible equilibria prior to the rate determining step in the decarboxylation. The possible effect of a single equilibrium of this nature has been calculated by Fry and Calvin<sup>20</sup> in conjunction with their work on isotope fractionation in the decompositions of oxalic and substituted malonic acids, and by Bigeleisen<sup>3</sup> in discussion of the alkaline hydrolysis

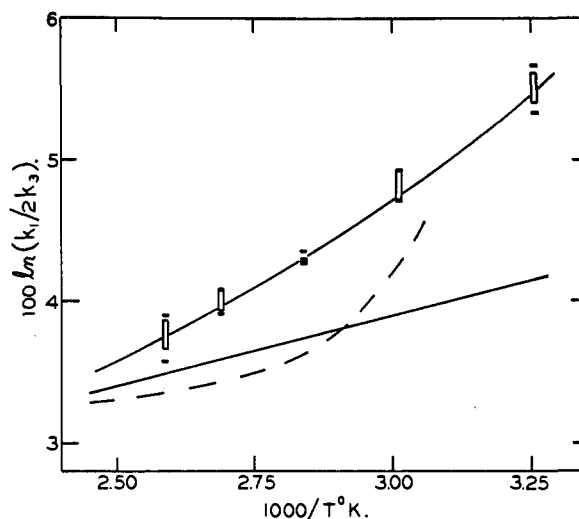
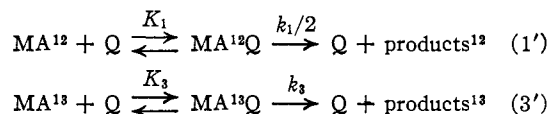


Fig. 1.—Influence of temperature on the intermolecular carbon isotope effect; — (upper), quinoline medium; — (lower), Bigeleisen's model; ----, 80% aqueous sulfuric acid medium.

of ethyl benzoate,<sup>21,22</sup> the Cannizzaro reaction, benzoin condensation, and benzoic acid rearrangement.<sup>23</sup> An *isotopic pair* of these preactivation equilibria may be represented in the present situation by the scheme



the  $K$ 's are equilibrium constants and  $\text{Q}$  represents a catalyst. The result of the equilibrium step is to multiply the *thermal* rate constant ratio by that of the  $K$ 's, whence  $(k_1/2k_3)_{\text{observed}} = (K_1/K_3) \times (k_1/2k_3)$ . In form, the ratio  $K_1/K_3$  is the equilibrium constant of an acid-base type isotopic exchange reaction. One can calculate approximate values of such ratios, given suitable information concerning the effects of isotopic substitution on the vibrations of the substances involved, by the methods of Urey<sup>24</sup> and Bigeleisen and Mayer.<sup>15</sup>

In the absence of reliable information concerning the malonic acid vibrational frequencies in quinoline, one must guess on the basis of other evidence whether the ratio  $K_1/K_3$  will be greater or less than unity, *i.e.*, whether it will result in enhancement or reduction of the *thermal* isotope effect. Quinoline does not form a salt with malonic acid, and the carbonyl absorption band is only slowly shifted toward shorter wave lengths in the transition from pure dioxane to pure quinoline solvent.<sup>5</sup> These facts lead one to suppose that  $K_1$  and  $K_3$  are small, and that  $C^{13}$  will tend to concentrate in malonic acid rather than in the malonic acid-quinoline complex. Thus,  $K_1/K_3$  will be greater than unity, as required by the results.

(16) N. B. Slater, *Proc. Roy. Soc. (London)*, **194**, 113 (1948).

(17) K. S. Pitzer, *J. Chem. Phys.*, **17**, 1341 (1949).

(18) At  $90^\circ$  the specific rate constant for the reaction is  $7.1 \times 10^{-6}$  sec.<sup>-1</sup> in dilute aqueous hydrochloric acid<sup>19</sup> and approximately  $6.5 \times 10^{-6}$  sec.<sup>-1</sup> in 80% sulfuric acid.<sup>5</sup>

(19) G. A. Hall, Jr., *This Journal*, **71**, 2691 (1949).

(20) A. Fry and M. Calvin, *J. Phys. Chem.*, **56**, 897, 901 (1952).

(21) W. H. Stevens and R. W. Attree, *Can. J. Research*, **27B**, 807 (1949).

(22) There is an error in Bigeleisen's calculation, the C-O stretching frequency having been taken as  $1700\text{ cm}^{-1}$ .

(23) W. H. Stevens and R. W. Attree, *J. Chem. Phys.*, **18**, 574 (1950).

(24) H. C. Urey, *J. Chem. Soc.*, 562 (1947).

If we postulate that equilibria of the type just mentioned are responsible for the observed deviations from the predictions of Bigeleisen's model, such equilibria are impressed upon the *thermal* decarboxylation mechanism in a manner which is very temperature sensitive in the sulfuric acid experiments, while the results obtained with quinoline medium indicate that one mechanism predominates over the temperature range investigated. The heat and entropy of activation figures shown in Table II indicate the possibility that the catalyzed reaction predominates in sulfuric acid solution at low temperatures but may be overwhelmed by the *thermal* reaction as the temperature is increased. In addition the *thermal* reaction will be favored at higher temperatures by decrease in *pro-catalytic* solvation. In this regard it is interesting to make comparison with the results obtained for the decarboxylation of mesitoic acid in 86% sulfuric acid.<sup>26,27</sup> The isotope effect in that decomposition was measured at temperatures near 60 and 90°. The ratios of the isotope effects at 60 and 90° found for mesitoic acid in sulfuric acid, malonic acid in sulfuric acid and calculated for Bigeleisen's model are:  $1.19 \pm 0.09$ ,  $1.21 \pm 0.04$  and 1.07, respectively.

TABLE II  
HEAT AND ENTROPY OF ACTIVATION AT 90° FOR MALONIC ACID DECARBOXYLATION

Medium	$\Delta H \ddagger$ , kcal./mole	$\Delta S \ddagger$ , e. u.
Melt <sup>26</sup>	33.0	4.5
Dil. HCl <sup>19</sup>	30.1	0
Quinoline <sup>5</sup>	17.8	-27

While the antecedent equilibrium picture just described is adequate to explain the isotope effect results, there remains yet to be examined for the case of decarboxylation in quinoline the effect, on the calculation, of the apparent bimolecularity of the rate-determining step as indicated by the

(25) From data of C. N. Hinshelwood, *J. Chem. Soc.*, **117**, 156 (1920).

(26) A. A. Bothner-By and J. Bigeleisen, *J. Chem. Phys.*, **19**, 755 (1951).

(27) W. H. Stevens, J. M. Pepper and M. Lounsbury, *ibid.*, **20**, 192 (1952).

large negative entropy of activation. The carboxyl carbon and hydrogen atoms are the two most likely sites for attack by a quinoline molecule. In the hyperbolic sine calculation of the rate constant ratios, a ratio of terms for a pair of isotopic asymmetric stretching frequencies would be involved. Since we have employed here Bigeleisen's modification of the Eyring method, it is necessary to calculate the equivalent of the Slater reduced mass term in equation (6). For this purpose the extension by Benson<sup>28</sup> of the Slater treatment indicates that the ratios of the asymmetric stretching frequencies of isotopic C-C-N and O-H-N molecules must be computed. The straightforward calculation is carried out by methods indicated by Kohlrausch.<sup>29</sup> The results rule out the likelihood of attack on the carboxyl hydrogen atom, since the calculated reduced mass factor is very close to unity. The factor calculated for attack on the carboxyl carbon depends somewhat on the angle of attack which is assumed; in the vicinity of a C-C-N angle of 90°, the reduced mass factor is near 1.022, which is to be compared with 1.0198 calculated for isolated C-C bond rupture.

The conclusion which one can reach on the basis of this computation is that the isotope effect results alone, at least for the experiments in quinoline solution, do not permit one to distinguish between two likely mechanisms: a solvation equilibrium followed by *thermal*, uncatalyzed decomposition of the complex; a solvation equilibrium followed by a bimolecular decomposition of the complex, possibly by rearrangement involving a quinoline molecule originally hydrogen bonded to the malonic acid. The kinetics data, however, require the assumption of the bimolecular process. No similar conclusions can now be reached for the results obtained with sulfuric acid solutions because of the lack of kinetics data below 80°.

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