51%. It is evident, therefore, that the yields of N-disubstituted hydrazines, based upon the amount of hypochlorite used, rise markedly as the ammonia/hypochlorite ratio required to produce chloramine is increased beyond stoichiometric quantities to a 3/1 reaction mixture.

Preparation of Some N-Dialkylhydrazines.—For the preparation of larger quantities of unsymmetrically disubstituted hydrazines the following procedure was employed. An ice-cold solution of chloramine, prepared by adding 250 ml. (0.25 mole) of a cold 1 *M* sodium hypochlorite solution to 750 ml. of aqueous ammonia (0.75 mole), was allowed to react with one mole of the appropriate amine (mole ratio, amine to hypochlorite = 4:1). All reaction mixtures were permitted to rise to room temperature over a period of four hours before aliquots were analyzed iodometrically for the dialkyl hydrazine content and then further treated to effect isolation of the desired hydrazine. The water soluble amines, dimethylamine and diethylamine, react quickly with chloramine in the cold. With water-insoluble amines it was found desirable to agitate the reaction mixture vigorously for a period of 30 minutes after the solutions had reached room temperature. The water-soluble hydrazines were recovered by fractional distillation (method A). The less soluble dialkyl hydrazines were extracted from the reaction mixtures with petroleum ether (method B). The various dialkyl hydrazines were converted into the hydrogen oxalates for characterization and analysis. Given yields for typical experiments represent grams of the purified hydrogen oxalates actually recovered.

N-Dimethylhydrazine hydrogen oxalate, $(CH_3)_2NNH_2 \cdot H_2C_2O_4$: method A, 20 g. (53.2%), m.p. 142° (lit. 142°[7]).

N-Diethylhydrazine hydrogen oxalate, $(C_2H_5)_2NNH_2 \cdot H_2C_2O_4$: method A, 18.2 g. (40.8%), m.p. 138°.

Anal. Calcd. for $C_6H_{14}N_2O_4$: C, 40.49; H, 7.91; N, 15.72. Found: C, 40.85; H, 8.03; N, 15.50.

N-Di-*n*-propylhydrazine hydrogen oxalate $(C_3H_7)_2NNH_2 \cdot H_2C_2O_4$: method B, 11.8 g. (40%), m.p. 168°.

Anal. Calcd. for $C_8H_{18}N_2O_4$: C, 46.44; H, 8.79; N, 13.56. Found: C, 46.31; H, 8.86; N, 13.11.

N-Di-*n*-butylhydrazine hydrogen oxalate, $(C_4H_9)_2NNH_2 \cdot H_2C_2O_4$: method B, 15.0 g. (41.7%), m.p. 170°.

Anal. Calcd. for $C_{10}H_{22}N_2O_4$: C, 51.25; H, 9.49; N, 11.96. Found: C, 51.50; H, 9.09; N, 12.08.

Acknowledgment.—This investigation was carried out under the sponsorship of the Office of Ordnance Research as one phase of a fundamental study of the synthesis of hydrazine, Contract No. DA-11-022-ORD-828.

[7] C. Harries and T. Haga, *Ber.*, **31**, 56 (1898).

URBANA, ILLINOIS

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

Intramolecular Carbon Isotope Effect in the Decarboxylation of the Mono-anion of Malonic Acid in Quinoline Solution

BY PETER E. YANKWICH AND H. S. WEBER

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The intramolecular carbon isotope effect in the decarboxylation of the mono-anion of malonic acid in quinoline solution has been investigated over the temperature range 79–138°; temperature dependence of the oxygen isotope constitution of product carbon dioxide suggests that the C–O linkages are involved directly in the process of activation. The carbon isotope effect results are compared with those previously obtained for the intermolecular case in terms of the simple bond-rupture model suggested by Bigeleisen. This comparison yields reasonable values for the equilibrium constant for isotope discrimination in anion formation and the ratio of the isotopic constants for complex formation involving the solvent.

Introduction

In a recent paper[1] we presented the results of experiments designed to measure over the temperature range 67.5 to 119° the intermolecular isotope effect in the decarboxylation of the mono-anion of malonic acid in quinoline solution. From the temperature dependence of that isotope effect, and the influences of solvent and added 1-butylpiperidine on the rate of decarboxylation and the position of the carbonyl absorption band, it was inferred that there were, impressed upon that due to bond rupture, isotope effects originating in equilibria between solvent and solute and/or in non-random distribution of C^{13} among the various anionic species.

In the investigation to be reported here, work with the malonic acid–quinoline–butylpiperidine system was extended to the determination of the intramolecular isotope effect over the temperature range 79–138°; the results are compared with the intermolecular isotope effect in the common temperature interval.

Experimental

No basic change was made in the materials, apparatus, general procedure, isotope analyses or calculation methods employed in previous studies[1–3]; the minor modifications required in the present work are described below.

Procedure.—In a typical experiment 45 ml. of quinoline and 0.4 ml. (2.3 mmoles) of 1-butylpiperidine were mixed and brought to the desired temperature, as was 104 mg. (1 mmole) of malonic acid. The acid was then combined with the mixed solvent and effluent gas collection started; the reaction time ranged from 2.5 hours at 138° to 77 hours at 79°. Because of these very long collection times, even when the sweep rate of preheated carbon dioxide-free helium was reduced to 10–20 cc./min. it was necessary to make even more thorough the purification of the product carbon dioxide. To this end, the samples of product gas were subjected to three distillations: the first from a Dry Ice–alcohol bath at −78° to a trap cooled in liquid nitrogen; the second and third from that trap held between −155 and −145° to one cooled in liquid nitrogen. Quantitative transfers of carbon dioxide were assured by continuous monitoring of the ambient pressure in the distillation apparatus; occasional checks were made by means of accurate quantity determinations before and after purification.

Calculations.—Since we do not *know* from which end of the anion the carbon dioxide product comes, it will be convenient to adopt a variant of the notation employed in the previous paper[1]; having reference only to the carbon skeletons of the molecules, we write

$$C^{12}—C^{12}—C^{12} \xrightarrow{k_1} C^{12} + C^{12}—C^{12} \quad (1)$$

$$C^{12}—C^{13}—C^{12} \xrightarrow{k_2} C^{12} + C^{13}—C^{12} \quad (2)$$

$$C^{13}—C^{12}—C^{12} \xrightarrow{k_3} C^{13} + C^{12}—C^{12} \quad (3)$$

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[1] P. E. Yankwich and H. S. Weber, THIS JOURNAL, **77**, 4513 (1955).

[2] P. E. Yankwich and R. L. Belford, *ibid.*, **76**, 3067 (1954).

[3] P. E. Yankwich and R. L. Belford, *ibid.*, **75**, 4178 (1953).

$$C^{12}—C^{12}—C^{13} \xrightarrow{k_4} C^{12} + C^{12}—C^{13} \qquad (4)$$

Since the notation employed exerts no influence on the results calculated, $(k_4/k_3)_{\rm obsd} = 2(X_D/X_C) - 1$ in the present situation where the malonic acid carbons are homogeneous in the carbon isotopes; X_D is the mole fraction of C^{13} in the carbon dioxide obtained from combustion of malonic acid, and X_C is that in the effluent carbon dioxide.

Results

The observed oxygen isotope ratios, $(m/q\ 46)/(m/q\ 44)$, and corrected carbon isotope ratios for each experimental sample are collected in Table I along with the values of $(k_4/k_3)_{\rm obsd}$ computed from the latter. The uncertainty in any R is ±2 in the last digit, or less; the appended errors are average deviations.

TABLE I

OXYGEN AND CARBON ISOTOPE RATIOS OF EXPERIMENTAL SAMPLES; CALCULATED INTRAMOLECULAR ISOTOPE EFFECTS

A. Samples from decarboxylations

Run temp., °C.	Sample	$R_O \times 10^6$	$R_C \times 10^6$	$(k_4/k_3)_{\rm obsd.}$	Av. $(k_4/k_3)_{\rm obsd.}$
79	12	4215	10713	1.0351	
	13	4210	10710	1.0356	1.0354 ± 0.0003
89.5	5	4202	10709	1.0358	
	6	4199	10699	1.0377	
	7	4210	10704	1.0368	
	8	4207	10704	1.0368	1.0368 ± 0.0005
102.5	14	4199	10720	1.0337	
	15	4193	10708	1.0360	
	16	4195	10708	1.0360	
	17	4198	10713	1.0351	1.0352 ± 0.0008
115.5	1	4198	10720	1.0337	
	2	4200	10725	1.0328	
	3	4197	10724	1.0330	
	4	4204	10726	1.0326	
	27	4210	10726	1.0337	1.0332 ± 0.0004
138	19	4199	10732	1.0315	
	20	4208	10732	1.0315	
	21	4204	10723	1.0332	
	23	4198	10718	1.0341	
	26	4184	10724	1.0330	
	28	4193	10722	1.0334	1.0328 ± 0.0008

B. Samples from combustion of malonic acid

Sample	$R_C \times 10^6$
Cb-3	10901
Cb-4	10907
Cb-5	10901

C. Reference standard

Sample	$R_O \times 10^6$	$R_C \times 10^6$
1328	4160	10883

To facilitate calculations to be described below, we define the operator L so that $L(x) = 100 \ln(x)$. The values of $L(k_4/k_3)_{\rm obsd}$ obtained from the last column of Table I are plotted *versus* $1000/T$ in Fig. 1; the vertical rectangles encompass the average deviations, while the short horizontal bars represent the maximum and minimum result at each temperature. A least-squares fitted line runs through the rectangles. The upper band is plotted from the earlier results for the intermolecular isotope effect in this system; the shading represents the smoothed average deviations of the experimental points.

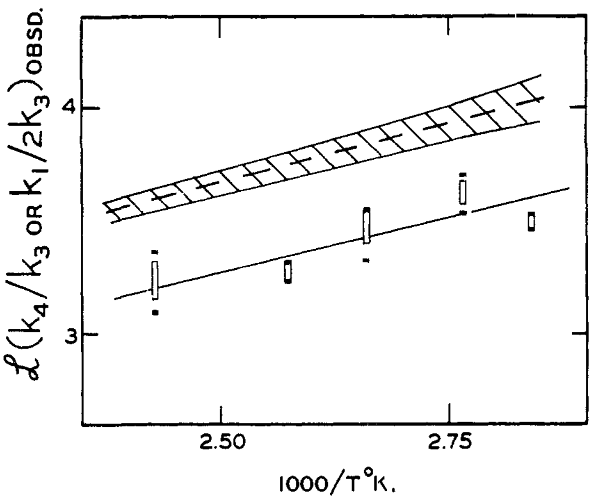

Fig. 1.—Influence of temperature on the carbon isotope effects: ——, intramolecular, this research; - - -, intermolecular[1] (shading represents smoothed average deviations of the experimental results).

In Fig. 2 the difference between the two lines, which is $L(k_1/2k_4)_{\rm obsd}$, is compared with the similar quantity for decarboxylation of the free acid in quinoline.

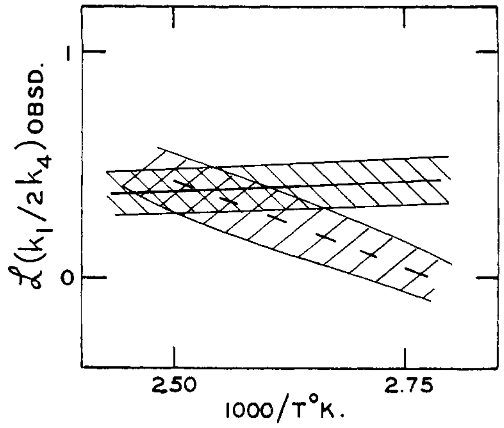

Fig. 2.—Temperature dependence of $L(k_1/2k_4)_{\rm obsd}$: ——, mono-anion in quinoline; - - -, free acid in quinoline.[2]

Discussion

The experimental data for the intermolecular and intramolecular isotope effects may be compared in the range $1000/T = 2.5$ to 2.75, or about 90 to 127°. This is not a very wide span of temperature and conclusions based upon the temperature dependences of the several isotope effects are subject to rather large error. Examination of Fig. 2, for example, suggests strongly that the difference in mechanism for decarboxylation of free acid and mono-anion which is indicated by kinetics studies[4] is reflected in the distribution of energy upon activation over isotopic bonds. The plot of $L(k_1/2k_4)_{\rm obsd}$ for the mono-anion presents what one would term a normal aspect; *i.e.*, the small positive isotope effect increases slowly as the tempera-

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[4] G. Fraenkel, R. L. Belford and P. E. Yankwich, THIS JOURNAL, **76**, 15 (1954). The decomposition of the free acid is first-order in quinoline, that of the anion independent.

ture falls. The corresponding plot derived from the experiments on the free acid decarboxylation exhibits a temperature dependence in the reverse sense. One cannot find an easy solution to the problem thus presented by having recourse to the assumption of strikingly different solvent–solvate complexing situations in the two cases, or the like, since Urey[5] has set forth the conditions necessary for the value of an isotopic exchange reaction equilibrium constant to cross unity (this would be required in the present case), and calculation leads to the finding that where such crossing is found the temperature dependence of the constant is quite small, much smaller than that exhibited by the plot of $L(k_1/2k_4)_{\text{obsd}}$ for the free acid in Fig. 2.

While we must yet speculate as to the state of affairs in the free acid system, the results obtained with the mono-anion are susceptible to manipulation in terms of assumed simple models for the decomposition.

As before[1] we define equilibrium constants for the formation of hydrogen-bonded structures of the type O-H · · · N as

$$\text{—C}^{12}\text{OOH} + \text{Q} \overset{K_1}{\rightleftharpoons} \text{—C}^{12}\text{OOHQ} \qquad (5)$$

$$\text{—C}^{13}\text{OOH} + \text{Q} \overset{K_3}{\rightleftharpoons} \text{—C}^{13}\text{OOHQ} \qquad (6)$$

where Q represents a molecule of quinoline solvent. Further, there is the possibility for isotope discrimination in the formation of the anionic species with C^{13} in a terminal position in the carbon skeleton; we define the equilibrium constant, K_x, for this process as

$$\underset{(2-Z)}{\text{HOOC}^{12}\text{C}^{12}\text{H}_2\text{C}^{13}\text{OO}^-} \rightleftharpoons \underset{(Z)}{{}^-\text{OOC}^{12}\text{C}^{12}\text{H}_2\text{C}^{13}\text{OOH}} \qquad (7)$$

where $(2 - Z)$ and (Z) are the relative concentrations of the two species, respectively, and $K_x = (Z)/(2 - Z)$. We ignore for the present any effect of negative charge on the frequencies of the carbon skeleton.

The form of the ratio (K_1/K_3) is that of the equilibrium constant of an acid–base type isotope exchange reaction,[6] and if the symbol f represents a partition function from which common factors have been removed we get the approximations

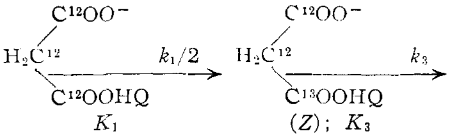
$$\frac{K_1}{K_3} = \frac{(f_{\text{C}^{13}\text{OOH}})/(f_{\text{C}^{12}\text{OOH}})}{(f_{\text{C}^{18}\text{OOHQ}})/(f_{\text{C}^{12}\text{OOHQ}})} \qquad (8)$$

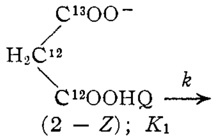
and

$$K_x = \frac{(f_{\text{C}^{13}\text{OOH}})/(f_{\text{C}^{12}\text{OOH}})}{(f_{\text{C}^{13}\text{OO}^-})/(f_{\text{C}^{12}\text{OO}^-})} \qquad (9)$$

Comparing these, we estimate that the deviations from unity of K_x and (K_1/K_3) will have the same sign and that that of K_x will be the larger.

The manner in which the equilibria defined above influence the isotope effect observed depends upon whether the carbon dioxide evolved originates in the carboxyl group or in the carboxylate group. For example: *if COOH is the source of CO_2*, then





(10)

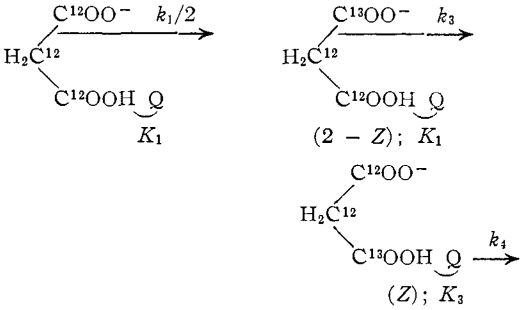
and

$$(k_1/2k_3)_{\text{obsd}} = (k_1/2k_3)(K_1/K_3)\ [(1)/(Z)] \qquad (11)$$

$$(k_4/k_3)_{\text{obsd}} = (k_4/k_3)(K_1/K_3)[(2) - (Z)/(Z)] \qquad (12)$$

$$(k_1/2k_4)_{\text{obsd}} = (k_1/2k_4)(K_1/K_1)[(1)/(\ 2 - .Z)] \qquad (13)$$

but *if CO_2^- is the source of CO_2, then*



(14)

and

$$(k_1/2k_3)_{\text{obsd}} = (k_1/2k_3)(K_1/K_1)\ [(1)/(2 - Z)] \qquad (15)$$

$$(k_4/k_3)_{\text{obsd}} = (k_4/k_3)(K_3/K_1)[(Z)/(2 - Z)] \qquad (16)$$

$$(k_1/2k_4)_{\text{obsd}} = (k_1/2k_4)(K_1/K_3)[(1)/(Z)] \qquad (17)$$

Since the k ratios are the products of temperature-dependent and temperature-independent parts,[7] equations like 11–13 and 15–17 apply equally well to situations where either or both type of part is included in a formulation. As a matter of convenience we shall deal with the temperature-dependent parts of the several isotope effects.

In principle one can calculate observed k ratios from the known or assumed properties of the reagent molecules and the activated complexes by application of techniques developed by Bigeleisen and Mayer,[8] Bigeleisen[7] and Urey.[5] In practice, at least in the case of a system which is as complicated as that discussed here, little is known and much must be guessed at concerning vibrational frequencies of molecules and activated complexes, etc.

Over the temperature range $1000/T = 2.50 - 2.75$, the data in Fig. 1 are represented well by the equations

$$L(k_1/2k_3)_{\text{obsd}} = 1.12(1000/T) + (0.85 \pm 0.08) \qquad (18)$$

and

$$L(k_4/k_3)_{\text{obsd}} = 0.98(1000/T) + (0.81 \pm 0.06) \qquad (19)$$

The temperature dependence of an isotope effect is related directly to the magnitude of the effect[6,9]; specifically, where the vibration frequencies involved are of the magnitudes found for carboxylic acids, the change in a calculated isotope effect over the range $1000/T = 2.50 - 2.75$ averages $16 \pm 2\%$ of the mean value in that range of the temperature-dependent part. Use of this figure permits one to calculate the mean value of the temperature-dependent part, and from it and the observed mean, a value for the temperature-independent part. By this technique we calculate the following effective

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

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

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

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

(9) H. Eyring and F. W. Cagle, *J. Phys. Chem.*, **56**, 889 (1952).

mass factors: for $(k_1/2k_3)$, 1.021 ± 0.007; for (k_4/k_3), 1.020 ± 0.005.

The error inherent in these calculated effective mass factors is sufficiently large to preclude accurate speculation in terms of the three-center model for which a calculation method has been derived by Bigeleisen and Wolfsberg.[10] We assume for both effective mass factors the value (1.0198) predicted by the simple bond-rupture model suggested by Bigeleisen[6] for the decarboxylation of the free acid; the frequency lost upon activation is also taken to be 900 cm.$^{-1}$.[11] These assumptions permit the calculation of $(k_1/2k_3)_{\text{model}}$ and $(k_4/k_3)_{\text{model}}$ and through them (K_1/K_3) and K_x.

Since K_x is not very different from unity, we take $L(Z) = -L(2 - Z) = {}^1/_2L(K_x)$. Then from the corresponding unprimed equations above, we obtain

$$
\begin{aligned}
L(k_1/2k_3)_{\text{obsd}} - L(k_1/2k_3)_{\text{model}} &= A \\
&= L(K_1/K_3) - {}^1/_2L(K_x) \qquad (11') \\
&= {}^1/_2L(K_x) \qquad (15') \\
L(k_4/k_3)_{\text{obsd}} - L(k_4/k_3)_{\text{model}} &= B \\
&= L(K_1/K_3) - L(K_x) \qquad (12') \\
&= -L(K_1/K_3) + L(K_x) \qquad (16')
\end{aligned}
$$

In Table II are collected the values calculated for A and B at two temperatures; the appended errors were obtained from equations 18 and 19. Shown in Table III are the estimates, resulting from combination of A and B in the appropriate fashion in each case, of $L(K_x)$ and $L(K_1/K_3)$ for the two sources of carbon dioxide product.

TABLE II

VALUES OF A AND B (BASED UPON RESULTS OF THIS RESEARCH COMBINED WITH THE BOND-RUPTURE MODEL OF BIGELEISEN)

$1000/T$	2.50	2.75
A	0.25 ± 0.08	0.27 ± 0.08
B	− .13 ± .06	− .15 ± .06

TABLE III

CALCULATED VALUES FOR $L(K_x)$ AND $L(K_1/K_3)$

$1000/T$	2.50		2.75	
	$L(K_x)$	$L(K_1/K_3)$	$L(K_x)$	$L(K_1/K_3)$
COOH source	0.76 ± 0.20	0.63 ± 0.13	0.84 ± 0.20	0.69 ± 0.13
CO_2^- source	.50 ± .16	.63 ± .17	.54 ± .16	.69 ± .17

It was argued above that in absolute value $L(K_x)$ should exceed $L(K_1/K_3)$ and that the quantities themselves should be similarly related to unity. The median values shown in Table III for the COOH group as source of product carbon dioxide meet this condition, but the effective experimental errors given for the collection of calculated values are such as to preclude a decision as to whether CO_2^- can be excluded from consideration for the same role. Of course, the figures in Tables II and III depend upon the choice of model made above, and it is possible that a more reasonable or more detailed construct would yield a definite conclusion on this point.[12] However, one can say that the simple model does not exclude any significant feature of the picture we have developed of the decomposition of the anion in quinoline solution.

Acknowledgments.—We are indebted to Mrs. Beverly Thomas for the mass spectrometric analyses, and to Mr. Evaldas Veleckis for carrying out preliminary experiments. This research was supported by the A. E. C.

URBANA, ILLINOIS

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(10) J. Bigeleisen and M. Wolfsberg, *J. Chem. Phys.*, **21**, 1972 (1953); **22**, 1264 (1954).

(11) For consistency, Bigeleisen takes the ratio of the isotopic frequencies $\omega C^{12}\text{-}C^{12}/\omega C^{12}\text{-}C^{13}$ to be the same as the effective mass factor for the C–C bond ruptured. If a more complicated model is employed, this simplification cannot be used[10] and recourse must be had to direct calculation of the frequencies of the isotopic molecules. It is important to note, however, that the nature of the calculation method[6] is such that the simple bond-rupture model may yield results practically identical to those obtained with a very complicated model. This is of especial interest since the temperature variation of the oxygen isotope constitution of carbon dioxide product is such as to indicate that the decomposition does not proceed by simple bond-rupture.

(12) In a previous paper[1] we obtained the value $L(K_x) = 0.6 \pm 0.2$ for the carboxylate model and remarked that this seemed more likely to us than the estimate of a referee that $L(K_x) = 1.0$; the values for this quantity recorded in Table III are from 0.5 to 0.8 (±0.2) over the common temperature range of the two sets of experiments, and appear to make that comment unnecessary.