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

Intermolecular Carbon Isotope Effect in the Decarboxylation of Malonic Acid in Dioxane Solution

BY PETER E. YANKWICH AND RICHARD M. IKEDA

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The intermolecular carbon isotope effect in the decarboxylation of malonic acid in dioxane solution was studied over the temperature range 40 to 99°. In quinoline solutions the principal reactants are mono- and bi-complexes of the solvent with the solute; it is concluded that dioxane is ineffective as a complexing agent in the same sense. The complexing in quinoline contributes an additional 1% isotope effect, to that originating in the kinetic process, through isotope fractionation in the equilibria. The effect of the complexing on the reaction coördinate motion apparently is quite small, if there is such an effect at all. A detailed treatment is given of the possible models for the effects of complex formation on the total isotope fractionation.

Introduction

Previous studies of carbon isotope fractionation in the decarboxylation of malonic acid and its mono-anion in quinoline solvent[1-4] have made interpretive use of the complexing by quinoline of the reacting molecules. In the case of the free acid decomposition there is the additional complication that the reaction is possibly first order with respect to the quinoline.[5] Dioxane is apparently kinetically neutral in both the free acid and mono-anion decompositions, and neither reactant is appreciably complexed in this medium. In order to establish more firmly the magnitude of complexing isotope effects and to shed light upon the effects of kinetic participation by added organic base in the decarboxylation of the free acid, we have initiated a group of studies in which dioxane is employed as the solvent.

In this paper we report the results of an investigation of the intermolecular carbon isotope effect in the decarboxylation of malonic acid in dioxane solution at temperatures between 40 and 99°.

Experimental

Materials.—The malonic acid was Eastman Kodak Company yellow label grade; it was purified by multiple sublimation *in vacuo*. The pure acid was subjected to isotope analysis by the method described in an earlier publication[3] and was found to be homogeneous throughout in the carbon isotopes.

The *p*-dioxane was Eastman Kodak Company white label grade. It was purified by refluxing over metallic sodium under a nitrogen atmosphere for 36 hr. and then distilling through an efficient column. Boiling point and refractive index values agreed with those reported in the literature; the purity as assessed by vapor phase chromatographic methods was better than 99.98%. (No impurities of kinetic significance were suspected, but traces of organic bases in some solvents have been found in similar studies to yield contaminants which were only difficultly removable and which had drastic effects on the reproducibility of the mass spectrometric measurements on effluent carbon dioxide.)

Apparatus and Procedure.—In a typical experiment approximately 300 mg. (3 mmoles) of malonic acid was weighed into a thin-walled capsule, which was then evacuated and sealed. The capsule and some pieces of broken glass were placed in a tubular reaction vessel to which had been added 25 ml. (approx. 300 mmoles) of dioxane. The solvent was frozen, the reaction vessel (which was fitted with two breakoff seals) evacuated and sealed. The vessel was placed in an oil-bath thermostated to ±0.05°, and ten minutes allowed for thermal equilibrium to be established. Reaction was initiated by breaking the capsule containing the malonic acid (through vigorous shaking of the reaction vessel). The decomposition was arrested by quenching the tubes in ice-water.

Carbon dioxide product was swept out of the reactor (through the breakoff sealed tubulations) with a stream of dry CO_2-free helium. The gas stream passed first through a trap cooled in Dry Ice–alcohol mixture (for dioxane removal), then through a trap immersed in liquid nitrogen. The product carbon dioxide was purified by distillation, the "boiler" temperature being kept in the range −175 to −140° by cold Michie Sludge Test Solvent (Phillips Petroleum Company, Special Products Division). The volume of carbon dioxide was measured manometrically after the purification.

Isotope Analyses.—The basic procedures employed have been described in detail in previous publications[1,2] from this Laboratory.

Calculations.—Having reference only to the carbon skeletons of the molecules, we write, in the now standard notation of Bigeleisen and Friedman[6]

$$C^{12}-C^{12}-C^{12} \xrightarrow{k_1/2} C^{12} + C^{12}-C^{12} \qquad (1)$$

$$C^{13}-C^{12}-C^{12} \xrightarrow{k_3} C^{13} + C^{12}-C^{12} \qquad (2)$$

In the present situation, where the methylene and carboxyl carbons have the same isotopic constitution, $(k_1/2k_3)_{obsd} = (X_D/X_C)$; X_D is the mole fraction of C^{13} in the carbon dioxide obtained from the combustion of malonic acid starting material, and X_C is that of the effluent carbon dioxide. The derivation of this relation assumes an infinitesimal degree of reaction; however, the error in its use is smaller than the effect of scatter in the primary data provided the actual extent of reaction is less than 4–5%.

Nuclear Magnetic Resonance Measurements.—Proton magnetic resonance measurements, for chemical shift determination, were made at room temperature with Varian equipment on solutions of the same compositions as those employed in the isotope fractionation studies.

Results

The corrected carbon isotope ratios, R, for each experimental sample are collected in Table I along with the values of $(k_1/2k_3)_{obsd}$ to which they correspond. The uncertainty in any R is ±2 in the last digit, or less; the appended errors are average deviations. Let the operator L be defined so that $L(x) = 100 \ln(x)$. The values of $L(k_1/2k_3)_{obsd}$ 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 equation of this line is

$$L(k_1/2k_3)_{obsd.} = (2.18 \pm 0.08)(1000/T) - (2.66 \pm 0.25) \qquad (3)$$

(1) P. E. Yankwich and R. L. Belford, THIS JOURNAL, **75**, 4178 (1953).

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

(3) P. E. Yankwich and H. S. Weber, *ibid.*, **77**, 4513 (1955).

(4) P. E. Yankwich and H. S. Weber, *ibid.*, **78**, 564 (1956).

(5) G. Fraenkel, R. L. Belford and P. E. Yankwich, *ibid.*, **76**, 15 (1954).

(6) J. Bigeleisen and L. Friedman, *J. Chem. Phys.*, **17**, 998 (1949).

(The errors appended here are standard errors. The standard deviation of experimental points from the computed line is ±0.07.) The upper band is plotted from the earlier determinations of the intermolecular isotope effect in quinoline solvent[1]; the shading represents the smoothed average deviations of the experimental points. The quinoline data are represented well by the equation

$$L(k_1/2k_3)_{obsd} = (2.53 \pm 0.08)(1000/T) - (2.83 \pm 0.24) \quad (4)$$

the standard deviation of the experimental points from the computed line is ±0.11.

TABLE I

CORRECTED ISOTOPE RATIOS OF EXPERIMENTAL SAMPLES; CALCULATED INTERMOLECULAR ISOTOPE EFFECTS

Run temp., °C.	Expt. no.	Decarbox., %	Rc × 10⁵	$(k_1/2k_3)$ obsd.	Av. $(k_1/2k_3)_{obsd}$
	A. Samples from decarboxylations				
40.3	4	0.6	10363	1.0432	
	5	.6	10362	1.0432	
	6	.5	10361	1.0434	1.0433 ± 0.0001
50.3	11	.8	10386	1.0408	
	12	.8	10374	1.0421	1.0415 ± .0007
60.2	13	1.0	10397	1.0398	
	21	1.2	10392	1.0403	
	22	1.1	10403	1.0392	1.0398 ± .0004
71.3	7	1.4	10420	1.0375	
	8	1.3	10413	1.0382	
	9	1.3	10410	1.0385	
	10	1.3	10410	1.0385	1.0382 ± .0004
80.4	14	1.9	10427	1.0368	
	15	1.9	10438	1.0357	
	16	2.0	10447	1.0348	1.0358 ± .0007
88.8	1	0.7	10459	1.0337	
	2	1.8	10454	1.0342	
	3	3.0	10461	1.0335	1.0338 ± .0003
99.1	17	2.7	10478	1.0318	
	18	3.1	10477	1.0319	
	19	3.7	10475	1.0321	
	20	2.8	10473	1.0323	1.0320 ± .0002

B. Samples from combustion of malonic acid

	R_D × 10⁵
C1	10812
C2	10820
C3	10809
C4	10812
C5	10820

In Table II are collected values for the proton chemical shifts observed for the malonic acid hydrogens in dioxane solutions. The sign and magnitude conventions are those of Gutowsky.[7]

TABLE II

CHEMICAL SHIFTS OF MALONIC ACID HYDROGENS[7]

Hydrogen position	Solvent: Quinoline	Dioxane
Methylene	−0.12	....
Carboxyl	+0.96	+0.56

Discussion

In the previous studies in which quinoline was employed as a solvent,[1-4] we found it necessary, in order to explain the observed carbon isotope fractionation and to account for certain rate data,[5] to postulate the occurrence of complex formation antecedent to the rate-determining step in the decomposition. It was assumed that the complexed acid was the actual reagent,[1] that only a single solvent molecule was involved in the formation of the complex[2] and that the source of carbon dioxide product was the complexed carboxyl group. Similar arguments were advanced in interpretation of other data by Fry and Calvin[8] and by Bigeleisen.[9] These various assumptions have received little test beyond their apparent importance in explanation of certain isotope fractionation results; some of them can be tested in no other way.

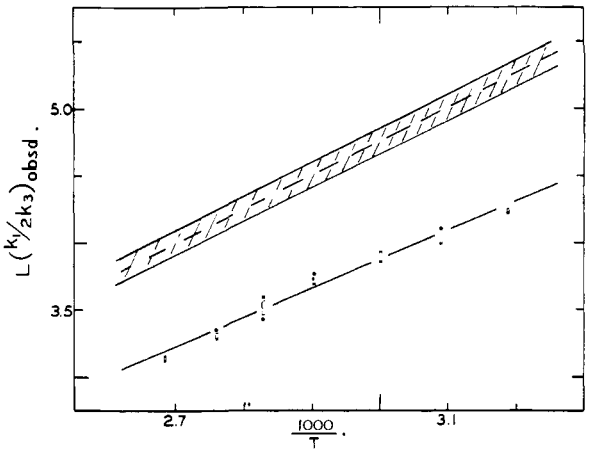

Fig. 1.—Influence of temperature on the intermolecular carbon isotope effect: ———, dioxane solvent, this research; – – – –, quinoline solvent[1] (the shading represents the smoothed average deviations in the original data.

It now seems possible to give these hypotheses more careful consideration than before in the light of experimental results, though for the sake of completeness it is necessary to introduce certain complexities into the models for the decomposition. The approach is based upon that employed in our earlier work, the direction of extension being suggested by the recent review of Bigeleisen and Wolfsberg.[10]

State of Malonic Acid in Quinoline and Dioxane Solutions.—When quinoline is added to dioxane solutions of malonic acid, there is a gradual shift of the carbonyl absorption band to lower frequencies; quinoline does not form a salt with malonic acid.[11] The rate of decarboxylation of malonic acid depends upon the solvent.[12,13] For example, at approximately 100°, the apparent first-order specific rate constants in units of 10^{-6} sec.$^{-1}$ in a number of solvents are: dioxane,[5] 6.6; water,[14] 20, the melt (extrapolated),[15,16] 2.5, glacial acetic acid,[17] 13,

(7) H. S. Gutowsky, *Ann. N. Y. Acad. Sci.*, **70**, 786 (1959).

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

(9) J. Bigeleisen, *ibid.*, **56**, 823 (1952).

(10) J. Bigeleisen and M. Wolfsberg, *Adv. Chem. Phys.*, 1, 15 (1958).

(11) E. J. Corey, THIS JOURNAL, **75**, 1172 (1953).

(12) L. W. Clark, *J. Phys. Chem.*, **60**, 825, 1150, 1340, 1583 (1956); **61**, 1009 (1957); **62**, 79, 368, 1468 (1958), has studied the decarboxylation of malonic acid in 20-odd organic solvents of widely different catalytic power.

(13) L. W. Clark, *ibid.*, **62**, 500 (1958).

(14) G. A. Hall, THIS JOURNAL, **71**, 2691 (1949).

(15) J. Laskin, *Trans. Siberian Acad. Agr. Forestry*, **6**, No. 1 (1926).

(16) C. N. Hinshelwood, *J. Chem. Soc.*, 1561 (1920).

(17) J. Lindner, *Monatsh.*, **28**, 1041 (1907).

anisole,[12] 2.7, quinoline,[5,13] 470. It is not surprising, therefore, that the apparent rate constant for the decomposition in dioxane solutions containing added quinoline is an almost linear function of the quinoline concentration. Clark[13] has shown that the entropy of activation in quinoline solution is only a few entropy units and the influence of quinoline on the decarboxylation seems to be through complex formation. Since the addition of quinoline accelerates the decomposition, the actual reagent is presumably a solvent-containing complex.

Additional evidence of complex formation and for the site of solvent attachment is found in the results of the proton magnetic resonance experiments. The methylene hydrogen chemical shift observed in quinoline is in good agreement with the value expected for methylene hydrogen in a hydrocarbon, about -0.15.[7] Although the corresponding measurement could not be made in dioxane due to hydrogens of the solvent, it was evident from the n.m.r. spectra that the value could not have been far different. The chemical shift expected for a carboxyl hydrogen is about $+0.50$, so the shift observed with dioxane solvent confirms the absence[5] of complexing of the malonic acid at that position. The large value of the chemical shift observed for the carboxyl hydrogen in the case of quinoline solvent would correspond, qualitatively, to a loosely shielded proton possibly undergoing some equilibrium process; this description seems to fit quite well our hypothesis of complexing through hydrogen-bonding at the carboxyl position in the case of quinoline solvent.

In the absence of information concerning the quinoline concentration dependence of the chemical shift observed for carboxyl hydrogen, we cannot tell whether one or both of the carboxyl groups are involved, nor the extent to which they are involved; *i.e.*, we cannot tell from the shift observed whether the equilibrium constant for complex formation is small or large. The implication of the slow shift in carbonyl absorption frequency is that the equilibrium constant is small, else the shift would have been saturated, except for smaller medium effects, at an added quinoline concentration equivalent to the malonic acid present. Clark's results, and others indicated above, show that general medium effects on the decarboxylation rate are small, the very large rate increases observed in certain cases correlating well structurally with the catalytic power of the solvent molecules. The dependence of the observed rate constant for the decomposition upon concentration of quinoline in dioxane solutions of malonic acid furnishes a possible route to the estimation of the equilibrium constant for complex formation, since deviations from linearity occur at very high concentrations of quinoline. To carry out this estimation it is necessary to consider first the various models for the process.

Complexing Models; Notation for Equilibria and Kinetic Processes.—In considering the decarboxylation under complexing conditions one must allow for the occurrence of no, single and double complexing; the actual reagent may be a solvated but uncomplexed species, the single complex or the double complex; and, in the case of the single complex, carbon dioxide may originate from either the complexed or the free carboxyl group. Species identifications are given and equilibrium and rate constants defined in Table III. It is important to note that the rate constants are defined in terms of the isotopic constitution of the products formed and do not carry the identification of the actual reagent; thus, k_4 might measure the specific decarboxylation rate of A_3, B_3, B_4 or D_3, depending upon the complexing situation assumed. In all the expressions, S indicates a molecule of solvent functioning as complexing agent.

This paper is concerned primarily with the intermolecular isotope effect. The experimental data are related to quantities defined in Table III as

$$(k_1/2k_3)_{obsd} = (X_D/X_C) = (k_1/k_3) \times P = (k_1/k_3) \times M \times N \quad (5)$$

P, a multiplier which depends upon the complexing model and solvent concentration, is the product of two functions: M, which is independent of solvent concentration, and N, which is dependent upon solvent concentration. In similar fashion, the intramolecular isotope effect may be expressed as

$$(k_4/k_3)_{obsd} = (2X_D/X_C') - 1 = (k_4/k_3) \times P' \quad (6)$$

where X_C' is the mole fraction of C^{13} in the whole carbon dioxide effluent at complete reaction. The quantities P and P' for various models of the decomposition are given in Table IV, along with the functions M and N.[18]

TABLE III

NOTATION

A. Species in solution

A_1: $HOOC^{12}C^{12}H_2C^{12}OOH$ D_1: $SHOOC^{12}C^{12}H_2C^{12}OOHS$
A_2: $HOOC^{12}C^{13}H_2C^{12}OOH$ D_2: $SHOOC^{12}C^{13}H_2C^{12}OOHS$
A_3: $HOOC^{12}C^{12}H_2C^{13}OOH$ D_3: $SHOOC^{12}C^{12}H_2C^{13}OOHS$

B_1: $HOOC^{12}C^{12}H_2C^{12}OOHS$
B_2: $HOOC^{12}C^{13}H_2C^{12}OOHS$
B_3: $HOOC^{12}C^{12}H_2C^{13}OOHS$
B_4: $SHOOC^{12}C^{12}H_2C^{13}OOH$

B. Equilibrium constants

$$K_1 = \frac{(B_1)}{(A_1)(S)} \qquad K_2 = \frac{(B_2)}{(A_2)(S)}$$

$$K_3 = \frac{(B_3)}{(A_3)(S)} \qquad K_4 = \frac{(B_4)}{(A_3)(S)}$$

$$K_i = \frac{(D_1)}{(B_1)(S)} \qquad K_{ii} = \frac{(D_2)}{(B_2)(S)}$$

$$K_{iii} = \frac{(D_3)}{(B_4)(S)} \qquad K_{iv} = \frac{(D_3)}{(B_3)(S)}$$

$$K' = K_3K_{iv} = K_4K_{iii} = \frac{(D_3)}{(A_3)(S)^2}$$

C. Specific rate constants

$$\xrightarrow{k_1} C^{12}H_3C^{12}OOH + C^{12}O_2$$

$$\xrightarrow{k_2} C^{13}H_3C^{12}OOH + C^{12}O_2$$

$$\xrightarrow{k_3} C^{12}H_3C^{12}OOH + C^{13}O_2$$

$$\xrightarrow{k_4} C^{12}H_3C^{13}OOH + C^{12}O_2$$

(18) Depending upon the situation, k_1 as defined in (1) and used in the first member of (5) may be different from k_1 as defined in Table III and used in the third and fourth members of (5). The constant as defined in (1) will be employed only in the quantity $(k_1/2k_3)$obsd; in all other use, the constant has the significance required by the decarboxylation model as given in Table III.

TABLE IV

MODELS FOR THE DECARBOXYLATION OF MALONIC ACID IN THE PRESENCE OF A COMPLEXING AGENT

Model no.	Carboxyls complexed	Reactant species	Origin of CO_2	P	P'
I	Neither	A	COOH	M_0	1
II	One	B	COOHS	M_3N_1	(K_4/K_3)
III	One	B	COOH	M_4N_1	(K_3/K_4)
IV	One	A	COOH	M_0N_1	1
V	Both	B	COOHS	M_3N_2	(K_4/K_3)
VI	Both	B	COOH	M_4N_2	(K_3/K_4)
VII	Both	D	COOHS	M_1N_2	1
VIII	Both	A	COOH	M_0N_2	1

$$M_0 = \frac{1}{2} \qquad M_1 = \frac{K_1K_i}{K'} \qquad M_3 = \frac{K_1}{K_3} \qquad M_4 = \frac{K_1}{K_4}$$

$$N_1 = \frac{(1 + SK_3 + SK_4)}{2(1 + SK_1)} \qquad N_2 = \frac{(1 + SK_3 + SK_4 + S^2K')}{2(1 + SK_1 + S^2K_1K_i)}$$

Estimation of Equilibrium Constants.—The non-linearity in the dependence of the specific rate constant for the decarboxylation of malonic acid upon quinoline concentration in dioxane–quinoline solutions[5] offers a possibility for estimation of the maximum values of the equilibrium constants affecting the concentrations of A_1, B_1 and D_1, *i.e.*, K_{1Q} and K_{iQ}. The calculation is straightforward for the case of one carboxyl group complexed, and at 99.6° (the temperature for which the kinetics data are available) the apparent maximum value of $K_{1Q} = 0.0653$,[19] corresponding to 36% of malonic acid in pure quinoline solution being in the form of the mono-complex.

Similar equilibrium constant estimates for the case of both carboxyl groups complexed depend slightly upon the relation between K_1 and K_i which originates in their sequential character; there is a symmetry number effect in addition. From the work of Irving and Williams on ethylenediamine complexing of metal ions,[20] we estimate that, at the level of K_{1Q} observed, the sequence effect is a factor of the order of $^1/_2$; combining the symmetry and sequence factors, we obtain $K_{1Q} = 4K_{iQ}$. At 99.6° the kinetics data yield: $K_{1Q} = 0.0384$, $K_{iQ} = 0.0096$,[21] corresponding to 24% of the malonic acid in pure quinoline solution being in the form of the mono-complex and 2% in the form of bi-complex.

The equilibrium constant data above, which are maximum values, the near linearity of the rate constant as a function of quinoline concentration at low to moderate concentrations, the large difference in rate constants in pure dioxane and pure quinoline and the proton chemical shift data lead us to the following conclusions: (1) in quinoline solution there is complexing of malonic acid at the carboxyl groups; (2) some bi-complex may be formed; (3) the most important reactant species in quinoline solution is the mono-complex[22]; (4) though solvation occurs in both solvents, complexing as defined above does not occur in dioxane solution to an extent sufficient to affect powerfully the rate of the decarboxylation and will be assumed zero for the purpose of interpreting the isotope fractionation results; (5) the kinetics data are consonant with the following models for the decarboxylation: dioxane solution—I; quinoline solution—II, III, V, and VI.

Effect of Complexing on Reaction Coördinate Motion.—An experimental isotopic rate constant ratio is the product of two factors, one temperature independent (TIF) and one temperature dependent (TDF). The reaction coördinate motion determines TIF; TDF has components arising in: the internal motions of the normal molecules, the internal coördinates of the activated complexes orthogonal to the reaction coördinate [these constitute the temperature dependent part of (k_1/k_3) in (5)], and fractionation factors arising in various equilibria, P in (5). Values of TIF for the quinoline and dioxane solvent systems have been calculated in terms of two models (3-particle carbon skeleton, CH_2-single particle = 9-particle model) for the malonic acid molecule by the methods described in an earlier paper[23]; the results are collected in Table V.

TABLE V

INTERMOLECULAR ISOTOPE EFFECTS: CALCULATED VALUES OF TIF[24]

Solvent	3-Particle model	9-Particle model
Quinoline	1.0003 ± 0.0033	0.9935 ± 0.0041
Dioxane	0.9971 ± 0.0031	0.9921 ± 0.0041
Difference	0.0032 ± 0.0045	0.0014 ± 0.0058

As expected, these two models yield characteristic values for the temperature independent factor, and the data at hand are insufficient to evaluate the relative worth of these two representations of the malonic acid molecule. However, (as expected from the large temperature dependences observed) these "experimental" TIF values are very low; it is disturbing that some are less than unity, this possibility having been rejected earlier on apparently good grounds.[25] While we cannot place much confidence in the actual TIF values, a good deal of confidence can be placed in the difference values, since the closeness of the experimental slopes for the two solvent system results reduces drastically, in the difference between a pair of TIF values, the effects of extrapolation and scatter in the plots employed in the calculation.[23]

In comparing the difference values we see that for both models the effect of solvent change on the reaction coördinate motion is small and within experimental error. The internal coördinates orthogonal to the reaction coördinate may be slightly

(19) This value of K_{1Q} fits the kinetics data to better than 10% on the average. It is sufficiently precise for estimating the strength of quinoline as a complexing agent.

(20) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

(21) These values permit a fit of the kinetics data to better than 5% on the average. The data available are not of sufficient accuracy to permit a selection between monocomplexing and mono- and bi-complexing models on this basis alone.

(22) There is no reason to believe that the bi-complex is a *protected* species; the specific rate constant for its decomposition must be quite similar to that for the mono-complex. Its relative concentration is sufficiently small, however, that the influence of its decomposition on the observed isotope fractionation can be neglected.

(23) P. E. Yankwich and R. M. Ikeda, THIS JOURNAL, **81**, 1532 (1959).

(24) The error figures appended to the TIF and difference values are estimated from the compound error in the slopes of the plots in Fig. 1 (these being among the input data for the calculations). They probably are too large.

(25) J. Bigeleisen, *Can. J. Chem.*, **30**, 443 (1952).

different in the quinoline-complexed and dioxane-dissolved malonic acid molecules, so one cannot say that the near identity of the TIF's in the isotopic rate constant ratios implies a similar equality of those parts of the temperature dependent factors which originate in the rate-determining step of the reaction, though they would not be expected to be greatly dissimilar. It seems very likely[10] that these *structural* effects of complex formation are much smaller than the *equilibrium* effects. We believe that the approximately 0.8 difference in $L(k_1/2k_3)_{obsd}$ for the two solvent systems is due primarily to the equilibrium effects of complexing, *i.e.*, that it is $L(P_Q) - L(P_D)$. This conclusion requires that $L(k_1/k_3)_Q = L(k_1/k_3)_D$.

Components of P_Q.—The P functions shown in Table IV depend upon the equilibrium constants defined in Table III. In estimating the maximum values of K_{1Q} and K_{iQ} account was taken of sequence and symmetry number effects. *In the absence of isotopic effects*, we have the relations

$$K_1 = 2K_3 = 2K_4 = 4K_i = 2K_{iii} = 2K_{iv} \quad (7)$$

These make possible the expression of all P functions in terms of two ratios of isotopic equilibrium constants, $(K_1/2K_3)$ and (K_4/K_3).[26] In view of the separation of the carboxyl groups in malonic acid, we shall assume the equalities

$$K_{1Q} = 2K_{4Q} = 4K_{iQ} = 2K_{ivQ} \quad (8)$$

which yield $(K_1/2K_3)_Q = (K_4/K_3)_Q$.[27] These isotopic equilibrium constant ratios have the form of equilibrium constants for isotopic exchange reactions. At the temperatures involved in these studies, they do not differ from unity by more than 1 or 2%, and insignificant error is introduced into the model evaluation below by assuming their equality.

Evaluation of Models. Calculation of $(K_1/2K_3)_Q$.—Comparison of the several models permitted by the kinetics of the decarboxylation in quinoline is based upon the equation

$$L(k_1/2k_3)_{obsd\ Q} - L(k_1/2k_3)_{obsd\ D} = L(P_Q) \quad (9)$$

$L(P_Q)$ is a function of K_{1Q}, the concentration of quinoline $- S_Q$, and $(K_1/2K_3)_Q$. As a matter of convenience, the isotope effects observed at $1000/T = 2.75$ will be employed; there is but small dependence of $L(P_Q)$ on temperature. At this temperature $P_Q = 1.0080 \pm 0.0013$.

Model II.—For the value of K_{1Q} estimated to be the maximum, 0.0653, $(K_1/2K_3)_Q = 1.0097 \pm 0.0016$; this is well within the expected limit of 2% deviation from unity. The two quantities are related: if the occurrence of complexing were overestimated and the actual value of K_{1Q} were essentially zero, then $(K_1/2K_3)_Q = P_Q$; an upper limit would be computed for $K_{1Q} = \infty$, but since $(K_1/2K_3)_Q = 1.016 \pm 0.003$ in this situation, the 2% limit on the value of the equilibrium isotope effect does not impose a limit on the extent of complexing. This model is satisfactory.

(26) Implicit here is the assumption that the actual sequence effects are sufficiently similar to those estimated that one can write: $(K_1/2K_3) = (2K_i/K_{iii})$ and $(K_4/K_3) = (K_{iv}/K_{iii})$. In view of the apparently small value of K_{1Q}, these should be accurate approximations.

(27) Our conclusions above concerning the non-complexing role of dioxane toward malonic acid require that $(K_1/2K_3)_D = (K_4/K_3)_D = 1$.

Model III.—At the level of K_{1Q} estimated, $(K_1/2K_3)_Q = 0.9572 \pm 0.0070$. While we have maintained in earlier papers that the sense of this isotopic equilibrium constant ratio with respect to unity should be such as to enhance the observed isotope effect in a weak complexing situation, there is little experience with calculation and only a few experimental data on very different systems upon which to base such an assumption. It is highly unlikely, however, that there could be a 4.3% isotope effect associated with these equilibria; on this basis alone the model can be rejected as unsatisfactory. The deviation from unity of $(K_1/2K_3)_Q$ for this model decreases with increasing strength of complexing, but K_{1Q} would have to be larger than 0.47 to reduce the apparent equilibrium isotope effect to 2%. The maximum value of 0.0653 for this constant may be in error, but not that much.

Model V.—With $K_{1Q} = 0.0384$ and $K_{iQ} = 0.25K_{1Q} = 0.0096$, it is found that $(K_1/2K_3)_Q = 1.0093 \pm 0.0015$; the lower limit is again P_Q, while the upper limit of 1.0200 requires that $K_{1Q} = 0.35$. Thus, the limit imposed upon the extent of complexing by the limit on the value of the equilibrium isotope effect lies far outside the apparent experimental range of K_{1Q} values. Thus model V is a satisfactory representation of the complexing and decarboxylation of malonic acid in quinoline. Since there is no reason to believe that formation of the bi-complex would not occur, model V is preferable to model II on this ground.

Model VI.—At the levels of K_{1Q} and K_{iQ} estimated, it is found that $(K_1/2K_3)_Q = 0.9461 \pm 0.0088$. K_{1Q} must be larger than 0.19 for the equilibrium isotope effect to deviate from unity by 2% or less. At the observed level of K_{1Q}, a calculated 5.4% equilibrium isotope effect makes this model unsatisfactory; the lower limit imposed upon K_{1Q} by the requirement that the isotope effect be reduced to 2% is well outside the apparent experimental range.

Comparison of the applicable models confirms the conclusions stated above with regard to the complexing of malonic acid in these solvents. Further, it is now established directly that the sense of $(K_1/2K_3)$ with respect to unity is such as to increase the observed isotope fraction above that due to the kinetic process. It is interesting to note in this regard that a much more approximate treatment of the complexing in quinoline and dioxane of the mono-anion of malonic acid yielded at $1000/T = 2.75$ an isotopic equilibrium constant ratio of 1.0069 ± 0.0013. While the best value obtained above is somewhat higher, 1.0093 ± 0.0015, the correspondence between these results is a strong indication of the validity of our argument above that the contribution to (k_1/k_3) of a structural component of the complexing equilibria is small; certainly, ionization of one carboxyl group is a more significant structural change than hydrogen-bonding to the solvent at the same site. It seems probable that most of the difference in the numbers just compared can be ascribed to a net charge effect.

Validity of the Assumption that $(K_1/2K_3)_D = (K_4/K_3)_D = 1$.—This assumption is a consequence

of our conclusion that dioxane is not an effective complexing agent for malonic acid in the sense defined above. To test this assumption suppose that K_{1D} is so much smaller than K_{1Q} as to be effectively zero, and that although $(K_1/2K_3)_D = (K_4/K_3)_D$, they are different from unity. Then, using model II for computation (the test is most stringent with this model), we have

$$L(k_1/2k_3)_{\text{obsd Q}} - L(k_1/2k_3)_{\text{obsd D}} = L(P_Q) - L(P_D) = 0.80 \pm 0.13$$

Substitution of the value of K_{1Q} into the ratio P_Q/P_D yields $(K_1/2K_3)_D = 0.81525\,(K_1/2K_3)_Q + 0.17684$. Consider three values for $(K_1/2K_3)_Q$ related to the discussion above: 1.0200, 1.0097 and 0.9800; the corresponding values of $(K_1/2K_3)_D$ are 1.0084, 1.0000 and 0.9758. The largest possible value for $(K_1/2K_3)_D$ is 1.0084, when the corresponding quantity for quinoline is at the assumed 2% effect upper limit; the minimum value, 0.98, corresponds to $(K_1/2K_3)_Q = 0.9852$, *the larger relative equilibrium isotope effect being associated with the weaker complexing agent.* In view of the great disparity between K_{1Q} and K_{1D} this situation is unreasonable. The value estimated for K_{1Q} is a maximum, so 1.0097 represents a probable maximum for $(K_1/2K_3)_Q$; since, if they both differ from unity, the sense with respect to unity of $(K_1/2K_3)_Q$ and $(K_1/2K_3)_D$ should be the same, the assumption that the latter is indistinguishably different from unity is warranted. A more definite test of this point could be made if values of P_Q'/P_D' were available.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

Some Reactions of the Allyl Radical

BY ALVIN S. GORDON, S. RUVEN SMITH AND JAMES R. MCNESBY[1]

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In a previous publication[2] it was shown that allyl radicals disappear *via* radical–radical reactions until about 450°. At this temperature allyl radicals abstract hydrogen sufficiently well so that propylene appears in the products early in the reaction. With increasing temperature, hydrogen is abstracted more readily until, at temperatures over 500°, it is a more important reaction than disappearance *via* radical–radical processes. In the present paper it is shown that the energy of activation for abstraction of hydrogen from cyclopentane by allyl radicals is 31.8 ± 3.6 kcal. (std. deviation). The corresponding value for abstraction by methyl radicals is 9.3 kcal. In addition, the allyl radical and the methyl radical are shown to discriminate between H and D abstraction in about the same way.

Introduction

There are no reported data in the literature for abstraction of H atoms by allyl radicals over a temperature range. Szwarc[3] and his colleagues have estimated a value of 14–17 kcal. for abstraction of H from toluene by the allyl radical.

The value of the activation energy for the abstraction of H from the cyclopentane is of interest because of the large resonance energy in the allyl radical. It is also of interest to establish the energy of activation difference for abstraction of H and D atoms compared to the same difference for the methyl radical.

Experimental

Apparatus and Materials.—A cylindrical quartz reaction flask with flat parallel windows was placed in an aluminum block furnace. It was irradiated by an SC-100 medium pressure mercury lamp.[4] The lamp was housed in a parabolic mirror housing, set co-axially with the axis of the reaction vessel.

Approximately equimolar mixtures of cyclopentane and acetone-d_6[5] (Ad_6) were used. A chromatogram of the mix showed it to be free of impurities. They were photolyzed with the full beam of the SC-100 lamp and the products toepleted into a flask with two break seals. The reaction was allowed to proceed less than 2% toward completion. The small side arm through which the gases were admitted was sealed off from the system by black Apiezon wax to avoid pyrolyzing any constituents. Finally the side tube was sealed off above the Apiezon wax. The sample flask was attached to a gas chromatography unit and the seals broken after the volume above the break seal was thoroughly evacuated. The contents of the flask were swept onto the column by helium. We used a technique previously described[6] of reproducibly increasing the temperature of the column during the run. A 6-ft. 1.5 wt. % squalane on Pelletex[7] column was used with a starting temperature of −190°. The methane and propylene fractions were trapped and analyzed on the mass spectrometer. The areas of the methane, propylene and butene-1 fractions were measured by an electronic integrator.

Results and Discussion

Methane, propylene and butene-1 formations are controlled by the reactions

$$CD_3COCD_3 \xrightarrow{h\nu} 2CD_3 + CO \qquad (1)$$

$$CD_3 + \square \longrightarrow CD_3H + \square\cdot \qquad (2)$$

$$CD_3 + Ad_6 \longrightarrow CD_4 + CD_3COCD_3 \qquad (2a)$$

$$\square\cdot \longrightarrow C_2H_4 + CH_2{=}CH{=}CH_2 \qquad (3)$$

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(5) Manufactured by Merck Ltd., Montreal, Canada.

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(7) Special carbon black manufactured by G. Cabot.