scopically; a fraction condensing at $-196°$ (0.015 g.) shown spectroscopically to contain fluoroform, perfluorocyclopropane, tetrafluoroethylene and a trace of silicon tetrafluoride; and a fraction condensing at $-132°$ (0.272 g.) shown by spectroscopic examination and molecular weight measurement to be nearly pure perfluorocyclopropane (mol. wt. found 148, calcd. 150). The infrared spectrum of this fraction showed strong bands at 1275 and 864 cm.$^{-1}$. These have been identified as the characteristic bands of perfluorocyclopropane. The amount produced represented a yield of over 95% based on trimethyltrifluoromethyltin destroyed.

The white crystalline solid produced (1.04 g.) decomposed at 250° without melting. It was insoluble in water but dissolved in 50% sulfuric acid; distillation of the resulting solution followed by precipitation of the fluoride as lead chlorofluoride in the usual way identified the solid as trimethyltin fluoride.

This represents a yield of 98% based on the trimethyltrifluoromethyltin destroyed.

Anal. Calcd. for C_3H_9SnF: F, 10.4. Found: F, 10.5, 10.8.

Pyrolysis of Trimethyltrifluoromethyltin with Tetrafluoroethylene.—Trimethyltrifluoromethyltin (1.40 g.) and tetrafluoroethylene (2.00 g.) in an evacuated Pyrex tube (100 ml.) were heated to 150° for 15 hours. At the end of this time a white solid had appeared in the tube, and fractionation of the volatile products gave unchanged tetrafluoroethylene (1.27 g.; mol. wt. found 100, calcd. 100) unchanged trimethyltrifluoromethyltin (0.05 g., 4%) and perfluorocyclopropane (0.92 g.; mol wt. found 153, calcd. 150) shown spectroscopically to contain a small amount of perfluorocyclobutane.

Hydrolysis of Trimethyltrifluoromethyltin.—Trimethyltrifluoromethyltin (0.1880 g., 0.808 mmole) and 10% aqueous sodium hydroxide (5 ml.) were heated to 75° for 15 hours in a Pyrex tube (20 ml.) Fractionation of the products gave fluoroform (0.0568 g., 0.811 mmole; mol. wt. found 70, calcd. 70) identified spectroscopically. When trimethyltrifluoromethyltin (0.232 g.) was added to water (0.177 g.) at

20° in a Pyrex tube (10 ml.) the two liquids were immiscible and no reaction was immediately apparent, but after heating to 100° for 15 hours the tin compound had decomposed and fluoroform (0.065 g., 93%), was found. A similar tube containing trimethyltrifluoromethyltin (0.273 g.) and water (0.932 g.) was kept at 20° for 6 days with intermittent shaking, when fluoroform (0.077 g., 95%) was found.

Reaction of Trimethyltrifluoromethyltin with Chlorine.—Trimethyltrifluoromethyltin (7.27 g., 31.2 mmole) and chlorine (2.21 g., 31.2 mmoles) in an evacuated Pyrex tube (50 ml.) were allowed to warm up from -196 to $-46°$ and placed in a slush-bath at this temperature; the bath was then allowed to warm up slowly and kept at 20° for 24 hours, when the yellow color of the chlorine had gone. Fractionation of the volatile products gave a fraction condensing at $-196°$ (0.18 g.) shown spectroscopically to contain fluoroform (4% yield) and chlorotrifluoromethane, (3% yield) a fraction condensing at $-132°$ (1.59 g.; mol. wt. found 52, calcd. 50.5) identified spectroscopically as methyl chloride and a fraction condensing at $-78°$ which consisted of unchanged trimethyltrifluoromethyltin (0.58 g., 8%). The solid remaining in the reaction tube was purified by vacuum sublimation and identified as dimethyltrifluoromethyltin chloride, m.p. 46–47°.

Anal. Calcd. for $C_2H_6(CF_3)SnCl$: CF_3, 27.3; Sn, 46.9; Cl, 14.0: equiv. wt., 253. Found: CF_3, 25.3; Cl, 13.9; Sn, 46.6; equiv. wt., 247.

In view of the slightly low result for the CF_3 analysis by alkaline hydrolysis, which was reproducible and unchanged by resublimation of the sample, the solution was tested for fluoride ion after hydrolysis, but none was found. The equivalent was determined by titration with 0.1 N sodium hydroxide solution, using bromthymol blue as indicator. The infrared spectrum of dimethyltrifluoromethyltin chloride showed the absorption bands (Nujol mull): 2910(m), 2850(m), 1616(w), 1212(w), 1149(vs), 1070(vs), 790(s), 724(m). An attempt was made to estimate the boiling point of the chloride by vapor pressure measurements, but extensive decomposition occurred at 70–80°.

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

By Peter E. Yankwich and Richard M. Ikeda

The intramolecular carbon isotope effect in the decarboxylation of malonic acid in dioxane solution was studied between 89 and 129°. Through comparison of the results with those obtained earlier for the intermolecular isotope effect in the same solvent and those obtained from studies of both isotope effects in quinoline solutions, values have been obtained for the various complexing equilibrium contributions to the over-all isotope fractionation which agree well with values reported previously and with predictions of absolute and relative magnitude made by Bigeleisen and Wolfsberg. The very high temperature dependence of the isotope effect is indicative of a temperature-independent factor in the isotopic rate constant ratio which is certainly not much greater than unity, and which appears to be somewhat less than unity on the basis of calculations with two very different models. There seems to be no obvious explanation for this deviation from theoretical expectation.

Introduction

Recently[1] we reported measurements over the temperature range 40 to 99° of the intermolecular carbon isotope effect in the decarboxylation of malonic acid in dioxane solution. Comparison with earlier results obtained on quinoline solutions indicated that the structural effect, if any, of solvent complexing was small compared with the equilibrium effect; further, good correspondence was found between values for this equilibrium effect calculated on two bases: 1, comparison of the intermolecular isotope effects in quinoline[2] and

dioxane solutions of the free acid; and 2, comparison in terms of simpler models of the intermolecular[3] and intramolecular[4] isotope effects in the decarboxylation in quinoline solutions of the monoanion of malonic acid.

In the investigation to be reported here, the intramolecular carbon isotope effect in the decarboxylation of malonic acid in dioxane solutions was studied over the temperature interval 89–129°. Since the effect of the reaction coördinate motion is expected to be somewhat different on the observed intramolecular isotope effect than on the

(1) P. E. Yankwich and R. M. Ikeda, This Journal, **81**, 5054 (1959).

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

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

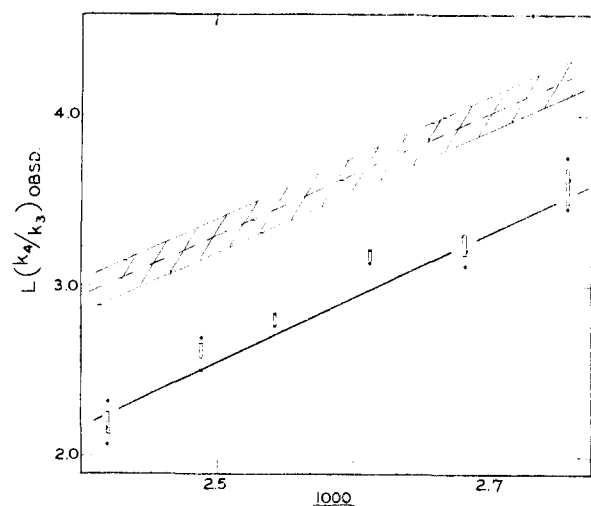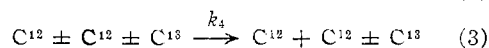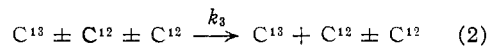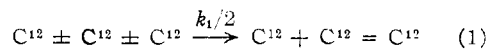(4) P. E. Yankwich and H. S. Weber, *ibid.*, **78**, 564 (1956).

Fig. 1.—Influence of temperature on the intramolecular carbon isotope effects: ————, dioxane solvent, this research; — — — —, quinoline solvent[8] (the shading represents the smoothed average deviations in the original data).

intermolecular effect, it was anticipated that this study would shed additional light on the influence of complex formation on observed isotope effects.

Experimental

No basic change was made in the materials, apparatus, general procedure, isotope analysis technique or calculation methods employed in the previous study.[1] Reaction vessels were charged with 100 mg. (1 mole) of malonic acid and 25 ml. (300 mmoles) of p-dioxane. To decrease the scatter in the primary data, isotope ratios obtained on experimental samples were compared directly with that of a quantity of carbon dioxide obtained by combustion of the starting material, rather than through a working standard of tank carbon dioxide.

Calculations.—The standard notation for the experimental isotope effect is that of Bigeleisen and Friedman[5]

$$C^{12} \pm C^{12} \pm C^{12} \xrightarrow{k_1/2} C^{12} + C^{12} = C^{12} \quad (1)$$

$$C^{13} \pm C^{12} \pm C^{12} \xrightarrow{k_3} C^{13} + C^{12} \pm C^{12} \quad (2)$$

$$C^{12} \pm C^{12} \pm C^{13} \xrightarrow{k_4} C^{12} + C^{12} \pm C^{13} \quad (3)$$

The intramolecular isotope effect is the deviation from unity of (k_4/k_3). The methylene and carboxyl carbon atoms of the starting material used in this research are known[1] to have the same isotopic constitution; in this situation

$$(k_4/k_3)_{obsd} = 2(X_D/X_C') - 1 \quad (4)$$

where 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 total carbon dioxide effluent.[6]

Results

The corrected carbon isotope ratios R_C' for each experimental sample are collected in Table I along with the values of $(k_4/k_3)_{obsd}$ to which they correspond. For convenience in presentation the R_C' values shown are referred to an arbitrary R_D of 0.010875; during the course of the study the

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

(6) Considerable extra decomposition time was allowed so that the reaction would have achieved a very high degree of completion since incomplete reaction affects the results calculation through eq. 4. For example, in the data to be recorded later the average span at one temperature of the $10^6X_C'$ values is 10; if the reaction were actually only 99% complete, the difference between $10^6X_C'$ observed and what it would be at 100% decomposition is just this great and corresponds to an error in $(k_4/k_3)_{obsd}$ of +0.0020.

range of R_D, due to variations in the response of the mass spectrometer, was 0.010829–0.010918. The uncertainty in any R tabulated is ± 2 in the last digit; the appended errors are average deviations. The values of $L(k_4/k_3)_{obsd}$[7] obtained from the last column of Table I are plotted versus $1000/T$ in

TABLE I

CORRECTED ISOTOPE RATIOS OF EXPERIMENTAL SAMPLES; CALCULATED INTRAMOLECULAR ISOTOPE EFFECTS

Run temp., °C.	Expt.	$R_C' \times 10^5$	(k_4/k_3) obsd.	Av. $(k_4/k_3)_{obsd}$
89.5	1	10672	1.0376	
	2	10678	1.0365	
	3	10688	1.0346	
	4	10685	1.0352	
	5	10682	1.0358	1.0359 ± 0.0011
99.5	24	10707	1.0311	
	25	10696	1.0332	
	26	10700	1.0324	
	27	10697	1.0329	
	28	10704	1.0316	
	29	10700	1.0324	1.0323 ± 0.0005
109.6	16	10712	1.0322	
	17	10705	1.0315	
	18	10707	1.0310	
	19	10703	1.0317	1.0316 ± 0.0004
119.9	20	10725	1.0276	
	21	10724	1.0277	
	22	10722	1.0283	
	23	10722	1.0283	1.0280 ± 0.0004
128.6	6	10732	1.0263	
	7	10732	1.0263	
	8	10729	1.0269	
	9	10731	1.0265	
	10	10739	1.0250	1.0262 ± 0.0005
139.5	11	10762	1.0208	
	12	10755	1.0220	
	13	10756	1.0218	
	14	10752	1.0225	
	15	10748	1.0234	1.0221 ± 0.0007

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

$$L(k_4/k_3)_{obsd} \, D = (3.77 \pm 0.17)(1000/T) - (6.87 \pm 0.44) \quad (5)$$

(The errors appended here are standard errors. The standard deviation of experimental points from the fitted line is ±0.10.) For comparison, earlier results on the intramolecular isotope effect in quinoline solvent[8] are plotted as the upper band in the figure. The quinoline (Q) data are represented well by the line

$$L(k_4/k_3)_{obsd} \, Q = (3.53 \pm 0.23)(1000/T) - (5.52 \pm 0.60) \quad (6)$$

The standard deviation of experimental points from the computed line is ±0.10.

(7) $L(x) = 100 \ln (x)$.

(8) P. E. Yankwich and R. L. Belford, THIS JOURNAL, 76, 3067 (1954).

Discussion

Reaction Coördinate Motion; Temperature Independent Factor.

From eq. 5 and 6, the temperature dependence of the intramolecular isotope effect observed in dioxane is similar to that reported earlier for quinoline solvent.[8] The previous studies of the intermolecular effect[1,2] suggested that the reaction coördinate motion in the decomposition was not affected by quinoline complexing. This conclusion was based on the finding that the temperature-independent factor (TIF) in the observed isotopic rate constant ratio was nearly the same in the two-solvent systems. The experimental errors associated with the value of $(k_4/k_3)_{obsd}$ obtained from eq. 4 are double those associated with $(k_1/2k_3)_{obsd}$ (to which the intermolecular isotope effect is related), so the TIF values computed by the method which we have described in an earlier publication[9] have little merit in the absolute. The effect of solvent change upon these values may, however, serve to establish a limit upon the structural effects of complexing, since a variation in TIF is the reflection in the reaction coördinate motion of changes in binding about the isotope site due to complex formation.

For the intramolecular isotope effect, the 3-particle and 9-particle models[9] yield the same result: that $\text{TIF}(k_4/k_3)_Q - \text{TIF}(k_4/k_3)_D = 0.012 \pm 0.012$. [For $(k_1/2k_3)$ the corresponding difference was 0.002 ± 0.005.] It may be adopted as a rough rule that the effect of TIF variation on the related temperature-dependent factor (TDF) in the isotopic rate constant ratio is linear. The large observed temperature dependence of (k_4/k_3)-obsd and $(k_1/2k_3)_{obsd}$ requires that the corresponding TIF values be very low.[10] In this situation a change in TIF due to variation of the reaction coördinate is accompanied by a change in temperature-dependent factor (TDF) which is 5–8 times as large. The smallest TDF effect in the systems under study would be connected with $(k_1/2k_3)$ and would amount to 0.010–0.016 on this basis, whereas the maximum effect of solvent change on the observed isotope effect, at $1000/T = 2.75$, is 0.008. If, nevertheless, one assumes this effect of solvent on reaction coördinate motion to be real, the equilibrium effect of complex formation becomes smaller than the structural effect, a situation hardly likely to obtain. The solvent effect on the TIF values computed for (k_4/k_3) leads to even more implausible situations.

These considerations support the earlier conclusion that the reaction coördinate motion is essentially the same for the decarboxylations in quinoline and dioxane solutions. To the extent that this is true, the contribution of the kinetic process (motion in the reaction coördinate) to TDF will be the same for both solvents. The observed solvent effect is thus ascribed wholly to complex formation in quinoline.

Complexing Model. Equilibrium Constants.

The most satisfactory model for the situation in quinoline[1] involves formation of complexes in which one or both carboxyl groups are hydrogen bonded to solvent molecules. Decarboxylation does not occur at an uncomplexed carboxyl group to any appreciable extent. In general the observed rate constant ratios, their kinetic components and the effects of complex formation, are related as

$$(k_1/k_2)_{obsd} = (k_1/k_3)\cdot P \qquad (7)$$

$$(k_4/k_3)_{obsd} = (k_4/k_3)\cdot P' \qquad (8)$$

(As a convenience in discussion, the values of these quantities employed below are all for the temperature $1000/T = 2.75$.[11])

The difference between the two plots in Fig. 1 is $L(P_Q') - L(P_D')$. We have argued previously that $P_D = P_D' = 1.000$. Under these circumstances

$$P_Q/P_D = P_Q = \frac{K_1(1 + SK_3 + SK_4 + S^2K_3K_4)}{2K_3(1 + SK_1 + S^2K_1^2/4)} \qquad (9)$$

$$P_Q'/P_D' = P_Q' = K_4/K_3^{12} \qquad (10)$$

where S is the concentration of complexing agent, here quinoline. These equations may be expressed in terms of two ratios of isotopic equilibrium constants, $(K_1/2K_3)_Q$ and $(K_4/K_3)_Q$.

From kinetics data[13] it is estimated that the maximum value of $K_{1Q} = 0.0384$ at $99.6°$. Earlier we assumed that $(K_1/2K_3)_Q = (K_4/K_3)_Q$; for the maximum value of K_{1Q} we found $(K_1/2K_3)_Q = 1.0093 \pm 0.0015$ for $P_Q = 1.0080 \pm 0.0013$. From (5) and (6), at $1000/T = 2.75$, $P_Q' = 1.0069 \pm 0.0014$, which is just $(K_4/K_3)_Q$ at this temperature. When this value is substituted into (9) a corrected value for the intermolecular equilibrium effect is obtained: $(K_1/2K_3)_Q = 1.0098 \pm 0.0015$.[14]

Bigeleisen and Wolfsberg[15] have predicted that, in general, $(K_1/2K_3)$ should be somewhat larger than (K_4/K_3), and the results above confirm this prediction. The magnitudes of these equilibrium isotope effects agree with still earlier predictions of Bigeleisen.[16]

Secondary Intermolecular Isotope Effect.

It is interesting to note that the secondary intermolecular isotope effect $(k_1/2k_4)_{obsd\ D}$ exhibits reverse temperature dependence such as was found earlier[4] for $(k_1/2k_4)_{obsd\ Q}$. The magnitude of this effect (which can be judged from the comparison plots in Fig. 2) seems larger than the experimental error; it probably originates in the strengthening

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

(10) For (k_4/k_3) the calculated TIF values are 0.96–0.98. The difficulties associated with TIF's less than unity have been pointed out in the preceding paper[1]; the present discussion does not hinge on this point.

(11) The k's in an *observed* ratio are defined by eq. 1–3. Those to the right in (7) and (8) are defined in terms of rates of $C^{12}O_2$ and $C^{13}O_2$ formation, the apparent difference being a symmetry number effect; $(k_1) = (k_1/2)_{obsd}$.

(12) K_1, K_3 and K_4 are, respectively, the formation constants for the monocomplexes $C^{12}C^{12}C^{12}S$, $C^{12}C^{12}C^{13}S$ and $SC^{12}C^{12}C^{13}$; the formation constants for the bi-complexes have been expressed in terms of these in the derivation of 9 and 10.[1]

(13) G. Fraenkel, R. L. Belford and P. E. Yankwich, THIS JOURNAL, 76, 15 (1954).

(14) It is important to note here that the sense with respect to unity of these isotopic equilibrium constant ratios and their magnitudes depend upon the model assumed for the decarboxylation and the strength of the solvent as a complexing agent. If the estimated K_{1Q} is too high, the calculated $(K_1/2K_3)_Q$ is too high also (its lower limit is P_Q), while $(K_4/K_3)_Q$ is unaffected. In the models rejected in the previous paper, $(K_4/K_3)_Q$ and the corrected values of $(K_1/2K_3)_Q$ have opposite senses with respect to unity, a seeming impossibility.

(15) J. Bigeleisen and M. Wolfsberg, *Adv. Chem. Phys.*, 1, 15 (1958).
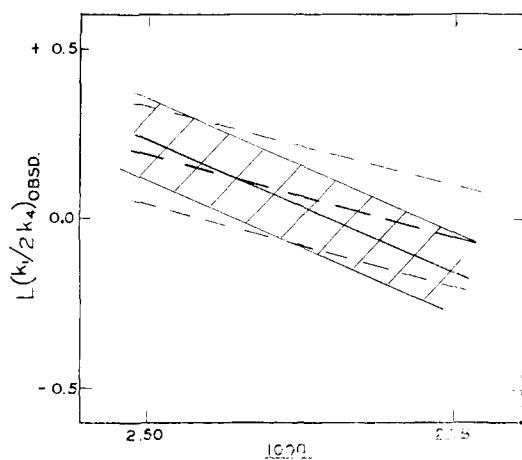
(16) J. Bigeleisen, *J. Phys. Chem.*, 56, 828 (1952).

Fig. 2.—Temperature dependence of the calculated intermolecular isotope effect $(k_1/2k_4)$: ————, dioxane solvent; ————, quinoline solvent (the light shading and outlines represent the smoothed average deviations in the original data).

of one C–C bond in the activated complex during rupture of the other, but exactly how the reverse temperature dependence is made manifest is a mystery to us.

Theoretical Models.—The great temperature dependence exhibited by these isotope effects requires that TIF be very little different from unity. It is not possible, then, to treat the decarboxylation of malonic acid in dioxane or quinoline in terms of Slater's simple model[17] since it requires that TIF be approximately 1.02. Both the 3-center treatment of Bigeleisen and Wolfsberg[18,19] and the 4-center approach described in one of our earlier publications[4] are capable of yielding TIF values closer to unity for parameter values which correspond to chemically reasonable reaction coördinate motions. However, for both 3- and 4-center systems, reduction of TIF to below 1.005–1.007 requires the assumption of a reaction coördinate in which C–C bond formation is more important than C–C bond rupture.

Bigeleisen and Wolfsberg[15] have proposed a slight change in Slater's two-center model which does yield TIF values very near unity; they suggest the use of the masses of the disjunct molecular fragments rather than those of originally connected

(17) N. B. Slater, Proc. Roy. Soc. (London), A194, 112 (1948).
(18) J. Bigeleisen and M. Wolfsberg, J. Chem. Phys., 21, 1972 (1953).
(19) J. Bigeleisen and M. Wolfsberg, ibid., 22, 1264 (1954).

atoms in the two-particle reduced mass calculations. The maximum TIF for (k_1/k_3) is 1.0062, and for (k_4/k_3) is 1.0026 on this basis. The use of molecular fragment masses is subject to criticism on several grounds, the most important of which seems to be that it requires treatment of the product rule expressions for normal molecules and activated complexes to be different. In any case, the imprecision in our data does not permit fruitful comparison of these several methods for TIF calculation which yield values little different from unity.

At temperatures above approximately 100°, (k_1/k_3) is apparently larger than (k_4/k_3), as is expected[15]; in the lower temperature range, however, the greater temperature dependence of the intramolecular isotope effect results in (k_4/k_3) rising above (k_1/k_3). This situation is just as troublesome on theoretical grounds as an apparent TIF less than unity, because both must have the same origin. It may be (we have no evidence for this) that these difficult situations arise in a general *medium effect*. We have shown above that dioxane, for example, is without particular (*i.e.*, complexing) effect on the decarboxylation, but any condensed phase furnishes a very different environment to the malonic acid (or complex) molecule than a vacuum, and it does not seem unreasonable to assume the existence of some effect ascribable to the hindrance of many of the internal vibrations in the reagent species.

It is not clear how such hindrance would modify the reaction coördinate motion to produce a very low TIF, and implicit in our mention of the medium effect is the assumption of its *generality*—perhaps it should be called a *density effect*. In this regard it is interesting to recall that the temperature dependence observed in the monoanion decarboxylation isotope effects[3,4] is nearly normal in magnitude; further, $(k_1/2k_4)_{obsd\ Q(anion)}$ is greater than unity and normal in temperature dependence over the entire range of temperatures investigated. It would be interesting to compare the acid and monoanion decarboxylations in water, where the solvation of negative ions is much less than that of positive ions; it seems likely that such studies would shed some light on the existence of a medium effect.