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

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

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The intermolecular carbon isotope effect in the decarboxylation of the mono-anion of malonic acid in quinoline solution has been investigated over the temperature range 67.5 to 119°. From consideration of the effects of solvent and added 1-butylpiperidine on the rate of decarboxylation and the position of the carbonyl absorption band, it is concluded that there may be in the system studied some observable isotope effect due to the impression upon the bond rupture process of equilibria antecedent to it involving the anionic solute and the quinoline solvent. The effect of possible non-random distribution of C^{13} among the various anionic species is considered also.

Introduction

The kinetics of the decarboxylation of the mono-anion of malonic acid in water solution were studied first by Fairclough,[1] whose observations were carried out on aqueous sodium hydrogen malonate. The concurrent decompositions of the free aqueous acid and the mono-anion in such a solution were untangled by Hall,[2] who found that near 90° the decarboxylation of the free acid was the faster by tenfold. The kinetics of the decarboxylation of the free acid and the mono-anion in quinoline solution were the subjects of a previous paper from this Laboratory,[3] in which certain differences traceable to influence of the solvent were pointed out.

Bigeleisen and Allen[4] measured the carbon isotope effect in the decomposition of aqueous normal trichloroacetate at 70.4°, but no other ion seems to have been studied similarly. The intramolecular[5] and intermolecular[6] carbon isotope effects in the case of free acid decarboxylation in quinoline have been determined, the common temperature range over which experiments were carried out being 86–118°. In this paper we report the results of an investigation of the intermolecular carbon isotope effect in the decomposition of the mono-anion of malonic acid; quinoline solutions were employed and the reaction was run at temperatures between 67.5 and 119°.

Experimental

Materials.—The malonic acid used was Eastman Kodak Company white label grade. Preliminary tests indicated that it was of high purity and the material was used as received. The carboxyl and methylene carbon atoms of the acid were compared as regards their isotopic constitution by carrying out decarboxylation of the acid under standardized conditions for which the intramolecular isotope effect is known; this sample of malonic acid was found to be homogeneous throughout in the carbon isotopes.

The quinoline employed was Eastman Kodak Company white label grade (synthetic). It was found to have been dried thoroughly, but since very small samples of malonic acid were to be employed, the quinoline was purified by distillation *in vacuo* immediately before a series of runs was started.

Preliminary experiments in which 1-ethylpiperidine was employed as the weak base (this material was used in the kinetics investigation[3]) yielded effluent carbon dioxide samples which could not be freed completely of impurities except through use of very tedious procedures. For this reason, 1-butylpiperidine, which boils 45° higher, was employed in these experiments. The material was prepared by reaction of piperidine and *n*-butyl iodide or chloride in the presence of aqueous potassium hydroxide; the product was twice distilled *in vacuo*, and that finally used boiled at 176.2° (literature 175.8°), and had a refractive index of 1.4461 at 20° (literature 1.4467).

Apparatus and Procedure.—The apparatus and general procedure have been described previously[7]; two modifications were instituted for this work. No trap was used between the reactor and the gas collection system. The effluent carbon dioxide was freed of volatile impurities by two distillations: the first from a Dry Ice–alcohol bath at −78° to a trap cooled in liquid nitrogen; the second from that trap held between −155 and −145° to one cooled in liquid nitrogen.

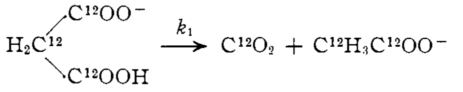
In a typical experiment 80 ml. of quinoline and 1.2 ml. (7 mmoles) of 1-butylpiperidine were mixed and brought to the desired temperature, as was 312 mg. (3 mmoles) of malonic acid. The acid was then combined with the mixed solvent and effluent gas collection started. The sweep rate of preheated, carbon dioxide-free helium was approximately 100 cc. per min. Samples of the effluent gases were taken at intervals, these ranging in length from 10 minutes at 67.5° to 7 seconds at 120°.

Isotope Analyses.—The procedures employed have been described in detail in previous publications from this Laboratory.[5,6]

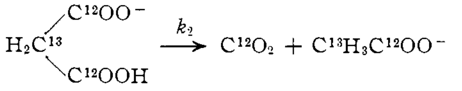
A. **Samples.**—Successive samples of effluent carbon dioxide collected in a given run are designated A, B and C, and amount to about 0.03 mmole of carbon dioxide in most cases. Since the clean-up of the reaction mixture by the helium sweep occurs at the very beginning of the sample collection, we believe that the A samples must be rejected since carbon dioxide derived from impurities in the reagents and solvent will be concentrated there.

Calculations

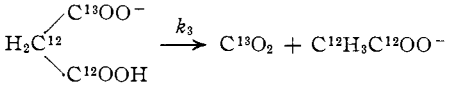
We adopt here a variant of that notation introduced by Bigeleisen and Friedman[8] and now in common use for description of carbon isotope effects in malonic acid decarboxylation



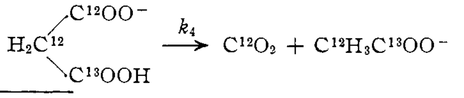
$$H_2C^{12}\begin{matrix}C^{12}OO^-\\ C^{12}OOH\end{matrix} \xrightarrow{k_1} C^{12}O_2 + C^{12}H_3C^{12}OO^- \quad (1)$$



$$H_2C^{13}\begin{matrix}C^{12}OO^-\\ C^{12}OOH\end{matrix} \xrightarrow{k_2} C^{12}O_2 + C^{13}H_3C^{12}OO^- \quad (2)$$



$$H_2C^{12}\begin{matrix}C^{13}OO^-\\ C^{12}OOH\end{matrix} \xrightarrow{k_3} C^{13}O_2 + C^{12}H_3C^{12}OO^- \quad (3)$$



$$H_2C^{12}\begin{matrix}C^{12}OO^-\\ C^{13}OOH\end{matrix} \xrightarrow{k_4} C^{12}O_2 + C^{12}H_3C^{13}OO^- \quad (4)$$

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[1] R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

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

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

[4] J. Bigeleisen and T. L. Allen, *J. Chem. Phys.*, **19**, 760 (1951).

[5] P. E. Yankwich and R. L. Belford, THIS JOURNAL, **76**, 3067 (1954).

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

[7] P. E. Yankwich, R. L. Belford and G. Fraenkel, *ibid.*, **75**, 832 (1953).

[8] J. Bigeleisen and L. Friedman, *J. Chem. Phys.*, **17**, 998 (1949).

Explicit in this notation is the assumption that the carbon dioxide originates from the ionized end of the molecule; the opposite assumption could have been made equally well (and will be considered below), for the likely rapid exchange of protons between solvent and solute makes either completely arbitrary for purposes of calculation, at least to the approximation that there is no isotope effect in the formation of the ions (*vide infra*). The stability of the malonic acid di-anion is not proof that the carbon dioxide here originates from the carboxyl group, though that mechanism may seem quite reasonable and be accessible to demonstration. The deviation from unity of the ratio $k_1/2k_3$ is a measure of an intermolecular isotope effect, and it is with this quantity that the present research is concerned. The deviation from unity of the specific rate constant ratio 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.

In these experiments the mole fraction of C^{13} in the carbon dioxide evolved, X_C, is compared with that of the carboxyl carbons in the intact diacid. Where the carboxyl and methylene carbons are homogeneous in the carbon isotopes, as in the present research, $(k_1/2k_3)_{\text{obsd.}} = (X_D/X_C)$, where X_D is the mole fraction of C^{13} in the carbon dioxide obtained from combustion of malonic acid, and where X_C is determined on carbon dioxide resulting from no more than about 5% decomposition. Where the carbon isotope contents of the methylene and carboxyl carbons of the parent compound differ, one may employ the relation $(k_1/2k_3)_{\text{obsd.}} = (3X_D - X_M)/(2X_C)$ in which the subscript M refers to the methylene position. In this study, no results will be used which were obtained from decomposition greater than 4.5% and corrections to zero reaction are smaller than experimental error in these circumstances.

The corrected carbon isotope ratios, R, for each sample are collected in Table I, along with the values of $(k_1/2k_3)_{\text{obsd.}}$ to which they correspond. The uncertainty in any R is ±2 in the last digit, or less. All appended errors are average deviations.

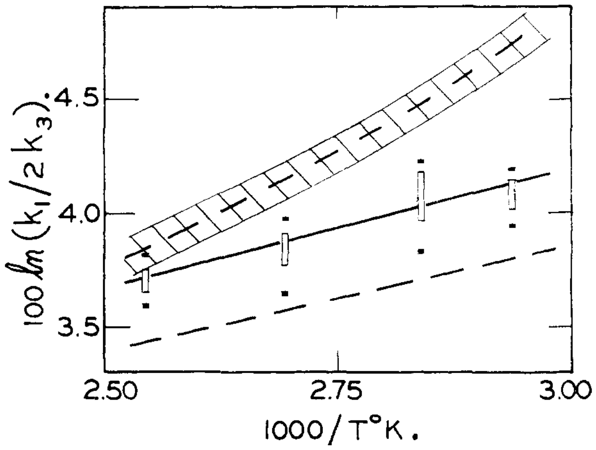

Fig. 1.—Influence of temperature on the intermolecular carbon isotope effects: —, this research; — — —, calculated for single bond rupture model, ω_{C-C} = 900 cm.$^{-1}$; - - - -, free acid in quinoline[6] (the shading represents the smoothed average deviations in the original data).

TABLE I

CORRECTED ISOTOPE RATIOS OF EXPERIMENTAL SAMPLES; CALCULATED INTERMOLECULAR ISOTOPE EFFECTS

A. Samples from decarboxylations[10]

Run temp., °C.	Sample	De-carbox., %	$R_C \times 10^6$	$(k_1/2k_3)$obsd.	Av., $(k_1/2k_3)$obsd.
67.5	22A[9]	0.00–1.92	10434		
	22B	1.92–3.01	10405	1.0416	
	22C	3.01–3.91	10398	1.0423	
	23A	0.00–0.69	10432		
	23B	0.69–2.25	10419	1.0402	
	23C	2.25–3.31	10407	10.414	
	24A	0.00–1.63	10429		
	24B	1.63–2.61	10406	1.0415	
	24C	2.61–3.56	10397	1.0424	
	25A	0.00–1.20	10441		
	25B	1.20–2.06	10410	1.0411	
	25C	2.06–2.81	10391	1.0428	1.0417 ± 0.0006
79	1B	1.92–3.33	10409	1.0412	
	1C	3.33–4.48	10387	1.0434	
	3B	1.60–2.70	10414	1.0407	
	3C	2.70–3.58	10430	1.0391	
	4B	1.32–2.37	10416	1.0405	
	4C	2.37–3.37	10396	1.0431	
	5B	0.96–1.87	10424	1.0397	
	5C	1.87–2.71	10393	1.0428	
	14B	1.34–2.24	10403	1.0418	
	14C	2.24–3.02	10409	1.0412	
	15B	1.63–2.91	10416	1.0405	
	15C	2.91–4.15	10411	1.0410	
	16B	1.38–2.51	10395	1.4026	
	16C	2.51–3.48	10391	1.0430	1.0415 ± 0.0011
98	17B	0.91–2.16	10426	1.0395	
	17C	2.16–3.94	10426	1.0395	
	18B	0.55–1.56	10449	1.0372	
	18C	1.56–2.71	10436	1.0385	
	19B	1.07–2.36	10426	1.0395	
	19C	2.36–3.73	10416	1.0405	
	20B	0.40–0.85	10431	1.0390	
	20C	0.85–1.86	10428	1.0393	1.0391 ± 0.0007
119	7B	0.42–1.35	10432	1.0389	
	9B	1.79–2.69	10441	1.0380	
	9C	2.69–3.72	10450	1.0371	
	10C	2.69–3.71	10453	1.0368	
	11B	1.73–2.63	10444	1.0377	
	11C	2.63–3.73	10440	1.0381	
	12B	0.80–1.50	10440	1.0381	
	12C	1.50–2.35	10450	1.0371	1.0377 ± 0.0005

B. Samples from combustion of malonic acid[11]

	$R_D \times 10^6$
Cb-3	10840
Cb-4	10846
Cb-5	10840

C. Samples from decarboxylation of liquid malonic acid at 140.5°

	$X_D \times 10^6$ Obsd.	$X_D \times 10^6$ Calcd.	$X_M \times 10^6$ (calcd.)[12]
D1C	10686		
D1Ac	10924	10728	10730
D2C	10688		
D2Ac	10924	10729	10729
D3C	10683		
D3Ac	10922	10726	10730
D4C	10677		
D4Ac	10915	10719	10722

Results

The values of 100 ln $(k_1/2k_3)_{\text{obsd.}}$ calculated from the last column of Table I are plotted *versus* 1000/T in Fig. 1. The vertical rectangles encompass the

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(9) The rejected A sample data at this temperature are typical and included for comparison.

(10) Carbon dioxide evolved.

(11) Carbon dioxide from combustion of acetic acid produced.

(12) Calculation based on (k_4/k_3) = 1.0292 under the conditions employed. P. E. Yankwich and A. L. Promislow, THIS JOURNAL, **76**, 4648 (1954).

calculated 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 lower dashed line is calculated from Bigeleisen's revised model[13] for the free acid with ω_{C-C} taken as 900 cm.$^{-1}$; almost the same result is obtained from the model proposed in a previous publication from this Laboratory.[5] The upper band is plotted from the data of Yankwich and Belford[6] for $(k_1/2k_3)_{\text{obsd.}}$ in the decarboxylation of free malonic acid in quinoline solution; the shading represents the smoothed average deviations of the experimental points.

The infrared absorption spectrum of malonic acid was determined in quinoline and dioxane, in the presence and absence of added 1-butylpiperidine (NBP). In all cases a prominent carbonyl band is found near 1720 cm.$^{-1}$; in the presence of the added base, the carbonyl absorption is reduced strongly and the characteristic carboxylate band[14] near 1600 cm.$^{-1}$ appears, as does a broad one at about 1485 cm.$^{-1}$. (The latter is likely unusually diffuse because both dioxane and quinoline absorb strongly in this region.) There is no indication of any appreciable quantity of a charged species other than the simple mono-anion in the presence of added base.

Discussion

Although the average deviations at each temperature in the data in Table I are relatively small, they are unfortunately large for a situation such as that found, where the variation with temperature of the isotope effect is itself small. That the intermolecular isotope effect in the decarboxylation of the mono-anion is different from that for the free acid is definite, however. It is interesting that the slope of the line through the experimental points in Fig. 1 is so close to that of the line calculated for the Bigeleisen model, and that the two lie not far apart; a similar plot with ω_{C-C} between 955 and 1095 cm.$^{-1}$ falls within the span of the results, and, in particular, the calculated for $\omega_{C-C} = 985$ cm.$^{-1}$ matches the least-squares line over its length to within ± 0.0003 in $(k_1/2k_3)_{\text{obsd}}$. This agreement is probably fortuitous, and data with less scatter might yield a curve with slope slightly smaller or slightly larger.

Extending the argument employed in interpretation of the temperature dependence of the isotope effects observed in free acid decarboxylation, we assume that any marked deviation of the effects observed for anion decomposition from those calculated on the basis of one of the successful simple models is due to an influence of the negative charge on the carboxylate, to solvent modification of the state of bonding about the isotopic carbon atom position in the ion, or to an isotope effect in the production from a single substrate type of the two varieties of the reagent anions in equations 3 and 4; any or all of these may operate in the system studied.

TABLE II

CARBONYL ABSORPTION MAXIMA AND APPARENT FIRST-ORDER RATE CONSTANTS FOR DECARBOXYLATION

Solvent	Carbonyl frequency, cm.$^{-1}$	Apparent rate constant at 99.6° $k \times 10^4$, sec.$^{-1}$
Quinoline (Q)	1705	4.6
Quinoline + NBP[15]	1715	2.7
Dioxane (D)	1732	0.066
Dioxane + NBP	1727	2.10
0.27 M Q in D		0.28
0.53 M Q in D		0.43
1.59 M Q in D	1715	1.18
4.24 M Q in D	1710	2.95
Quinoline (extrapolated)		(6.0)

In Table II are collected some observations on the rate of decomposition and position of the carbonyl absorption band for malonic acid in several media. The lowering of the C═O frequency accompanying the addition of quinoline to dioxane solutions of the free acid is indicative of a strong interaction between acid and weak base, presumably carboxyl solvation. The small decrease in carbonyl frequency observed when NBP is added to malonic acid in dioxane resulting in anion formation is a normal negative-charge effect.[16] The 10 cm.$^{-1}$ increase in the frequency of this band observed upon the addition of NBP to quinoline solutions of the diacid is probably the result of combination of these two effects—a decrease of about 5 cm.$^{-1}$ due to the assumption of negative charge, and an increase of about 15 cm.$^{-1}$ due to weakening of the carboxyl solvation by quinoline.

The rate of malonic acid decarboxylation in quinoline–dioxane exhibits first-order dependence upon quinoline concentration; there is no evidence for similar catalysis of anion decomposition.[3] The change of solvent from dioxane to quinoline has an accelerative effect upon anion decarboxylation ($k_D = 2.1 \times 10^{-4}$, $k_Q = 2.7 \times 10^{-4}$, sec.$^{-1}$). The effect of the same solvent change upon the rate of free acid decarboxylation must be inferred, since both general solvent and specific catalytic roles are played by quinoline; comparison of the extrapolated and observed rates of reaction ($k_{Q\text{extrap}} = 6.0 \times 10^{-4}$, $k_{Q\text{obs}} = 4.6 \times 10^{-4}$, sec.$^{-1}$) suggests that the general influence of quinoline is decelerative, *i.e.*, that carboxyl solvation in the free acid, though apparently a necessary prerequisite to the specific catalytic action of quinoline (as evidenced by the variation with temperature of $k_1/2k_3$), is intrinsically inhibitive to the course of the decarboxylation. These observations are in accord with the picture derived from the investigation of the carbonyl absorption band in similar solutions.

The direct influence of the quinoline is probably on the hydrogen atom of the carboxyl group, an interaction resulting in a hydrogen-bonded structure of the type O–H . . . N. As previously[5] we define equilibrium constants for the formation of these species as

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

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

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

(14) F. Douville, C. Duval and J. Lecomte, *Bull. soc. chim.*, **9**, 548 (1942).

(15) Malonic acid and 1-butylpiperidine (NBP) concentrations were the same as in the isotope effect runs.

(16) R. C. Gore, R. B. Barnes and E. Petersen, *Anal. Chem.*, **21**, 382 (1949).

For free acid decarboxylation in quinoline the contribution to $(k_1/2k_3)_{\text{obsd.}}$ of (K_1/K_3) may be estimated as the difference between the upper shaded band and the lower dashed curve in Fig. 1, provided one assumes that the simple bond rupture model is adequate to describe $(k_1/2k_3)$; 100 ln (K_1/K_3) varies from 0.4 to 0.9 over the temperature span of the present study. $(K_1/K_3)_{\text{anion}}$ is probably somewhat different from $(K_1/K_3)_{\text{acid}}$; in the limiting case of very small K values the effective ratio would be unity, and we believe that that direction of change starting from the ratio applicable to free acid decomposition is indicated in the anion case by the shifts observed in the C=O band position upon anion formation (*i.e.*, $(K_1/K_3)_{\text{anion}} < (K_1/K_3)_{\text{acid}}$). It is also apparent that the influence of this equilibrium constant ratio upon the observed isotope effect will depend upon which end of the anion yields the carbon dioxide as a consequence of activation: if the carbon dioxide originates from the carboxyl group, $(K_1/K_3)_{\text{anion}}$ (which is presumably greater than unity) operates to increase the observed $(k_1/2k_3)$,[17] while if the carboxylate group is the source of the carbon dioxide there is approximately no equilibrium effect since the K ratio applicable in that situation is just (K_1/K_1).

The general influence of the negative charge on the carboxylate group in the mono-anion is to lower appreciably the characteristic frequencies of the intact carboxyl; in a solvent the magnitude of this effect is certainly modified through polarization of the medium, but the direction is the same. If such a charge effect were the only influence of anion formation one would expect the experimental temperature dependence curve to lie somewhat below that calculated for the simple models; this negative deviation would be smaller if the carbon dioxide originated from the intact carboxyl group than if it were produced from the carboxylate, provided the effect were appreciable at all.

It is possible that there is an isotope effect in the formation of the ionic species on the left in equations 3 and 4. We represent their relative concentrations as $(2 - Z)$ and (Z), respectively; then, $K_x = (Z)/(2 - Z)$ is the equilibrium constant for the isotopic exchange reaction

$$\text{HOOC}^{12}\text{C}^{12}\text{H}_2\text{C}^{13}\text{OO}^- \rightleftharpoons {}^-\text{OOC}^{12}\text{C}^{12}\text{H}_2\text{C}^{13}\text{OOH} \quad (5)$$

The influence of this equilibrium upon the values of $(k_1/2k_3)_{\text{obsd.}}$ depends also on the source of the carbon dioxide: (ignoring for the moment the isotope effect due to solvation equilibria just discussed) $(k_1/2k_3)_{\text{obsd.}} = (k_1/2k_3)/(2 - Z)$ for the carboxylate source model, and $= (k_1/2k_3)/(Z)$ for the carboxyl source model. The values of K_x, and hence of Z, over the range of temperature covered by these experiments can be estimated using methods developed by Bigeleisen and Mayer[18]; in the region 70–120°, the deviation from unity of K_x is certainly small,[19] perhaps so small that its influence on the isotope effect observed can be ignored.

For the sake of argument, let us first assume that the carboxylate negative charge has inappreciable influence on the C–C vibrational frequencies; then all of the k's for both mono-anion models become identical with those for the free acid model, provided a similar activated complex is assumed. Then, for the carboxylate source model $(k_1/2k_3)_{\text{obsd.}} = (k_1/2k_3)/(2 - Z)$, and we estimate from Fig. 1: 100 ln $(2 - Z)^{-1} = +0.3 \pm 0.1$, whence $K_x = 1.006 \pm 0.002$. Since the effect of negative charge would be to lower slightly the frequency of the C–C bond across which dissociation occurs, and thereby calculated $(k_1/2k_3)$ for the model, consideration of that effect would result in higher calculated values for K_x. For the carboxyl source model:$(k_1/2k_3)_{\text{obsd.}} = (k_1/2k_3)\ (K_1/K_3)/(Z)$. In this situation, provided our estimate of the direction of deviation from unity of K_x is correct, about the most that one can say is that the isotope effect due to solvation equilibria and ion formation appear to be opposite in direction and apparently nearly compensatory, the influence here of the negative charge being smaller than in the previous case.

Investigation of the intramolecular isotope effect under similar conditions may permit more detailed speculation as to the nature and extent of these several possible contributing isotope effects in the monoanion decomposition system.

Acknowledgments.—We are indebted to Mrs. Beverly Thomas who performed the mass spectrometric analyses, and to Mrs. Louise Griffing for the infrared spectra. This research was supported by the A. E. C.

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[17] In comparing various models we employ the general definition of this rate constant ratio: $k_1/2$ = specific rate constant for C^{12}–C^{12} bond rupture in the species with skeleton 12–12–12; k_3 = specific rate constant for C^{12}–C^{13} bond rupture in the species with skeleton 12–12–13.

[18] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

[19] A referee has suggested that $K_x = 1.01$. We believe that this estimate is correct in direction but somewhat large in magnitude. Although the value 1.01 is comparable to some found reasonable by Bigeleisen[18] for typical acid–base isotopic exchange reactions, those involved a difference in the number of atoms bonded to carbon in the exchanging species, while in the case at hand the number of bonded atoms is the same but the nature of the bonding about the carbon atom is modified. An extreme situation, but one which illustrates our point, is seen with the equilibrium constants calculated by Urey[20]: for carbon and nitrogen exchange in the HCN–CN⁻ system: in both cases the heavier isotope concentrates in the acid molecule; the equilibrium constant (at 298.1°K.) is 1.030 for C^{12}–C^{13} exchange, but 1.001 + for N^{15}–N^{14} exchange.

[20] H. C. Urey, *J. Chem. Soc.*, 562 (1947).