[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Intramolecular Carbon Isotope Effect in the Decarboxylation of Liquid Malonic Acid Near the Melting Point

BY PETER E. YANKWICH AND ALBERT L. PROMISLOW

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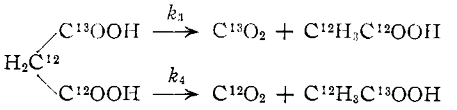
The intramolecular isotope effect in the decarboxylation of liquid malonic acid has been investigated at 140°. The product acetic acid was degraded *via* the Schmidt reaction in order to ascertain and permit correction for carbon isotope inhomogeneity in three-carbon malonic acid skeleton. The best results lead to $k_4/k_3 = 1.029_2 \pm 0.000_7$, a value in agreement with the prediction of Yankwich and Belford ($1.028_4 \pm 0.001_2$), but not with that of Bigeleisen (1.0198).

There have been published the results of several investigations designed to determine the magnitude of the intramolecular carbon isotope effect in the decarboxylation of malonic acid at temperatures slightly above its melting point. The rate constants may be defined[1] as



$$H_2C^{12}\begin{cases} C^{13}OOH \xrightarrow{k_3} C^{13}O_2 + C^{12}H_3C^{12}OOH & (1) \\ C^{12}OOH \xrightarrow{k_4} C^{12}O_2 + C^{12}H_3C^{13}OOH & (2) \end{cases}$$

In Table I are collected average values of the isotope effect expressed as $100\,[(k_4/k_3) - 1]$; the appended errors are average deviations and were computed by the present authors.

TABLE I

SUMMARY OF INTRAMOLECULAR ISOTOPE EFFECT RESULTS: $100[(k_4/k_3) - 1]$

T, °C.	Calcd. based on MA and CO$_2$	HAc	Av. of all results	Oxidn. method	Ref.
138	1.9 ± 0.1 (2)[a,b]	...		W[c]	1
138	2.9 ± 0.4 (4)	2.2 ± 0.2 (3)	2.5 ± 0.4	D[d]	2
	2.4 (1)	3.1 (1)	2.8 ± 0.3	W	
137	2.9 ± 0.3 (3)	2.5 (1)	2.8 ± 0.3	D	3

[a] (n) = number of experiments. [b] Only one introduction of CO$_2$ to mass spectrometer in one expt. [c] W = oxidation of MA or HAc by Van Slyke-Folch or similar wet combustion technique. [d] D = oxidation of MA or HAc over CuO at 700–800°.

The agreement among the various sets of results summarized in Table I is not too good; furthermore, the internal consistency of any given set (results calculated on the basis of carbon dioxide or acetic acid analyses should be the same) is little better. It is difficult to find likely specific causes of the observed discrepancies.

In some of the experiments[2,3] an inert gas sweep was employed to remove decarboxylation products from the reaction vessel; acetic acid (HAc) and carbon dioxide were later separated and purified by distillation. (Bigeleisen and Friedman[1] give no details of their method of product collection.) In all cases a malonic acid was employed which had been shown to be isotopically homogeneous in carbon by means of the soda lime–acetate pyrolytic degradation which yields the methylene carbon atom of malonic acid as methane. The wet oxidations were quantitative, presumably; one could then ignore an isotope effect of the type noted by Evans and Huston.[4]

The present study was conceived in such a manner as to: (a) make possible the determination of both the carboxyl and methyl carbon isotope ratios for such carbon in acetic acid product; (b) eliminate any possible but unrecognized effect on the results due to the use of a continuous collection (sweep) procedure; (c) obtain data for carbon dioxide and acetic acid products in each run. To these ends, we have carried out the decarboxylation of malonic acid just above its melting point in sealed reactors (batch process), and have employed a degradation procedure for acetic acid based on the Schmidt reaction[5] in order to establish the carbon isotope distribution in the original malonic acid.

Experimental

The analyses were divided into three series. Series A was a test of the batch decarboxylation procedure; the evolved acetic acid was burned over copper oxide. The acetic acid was degraded in all experiments of series B; but the results indicated that further improvement of the degradation procedure was desirable. In series A and B the malonic acid employed was Eastman Kodak Co. white label grade; preliminary tests showed that the purity of the material (99.9 ± 0.1% by acidimetric titration, m.p. 135°) was not increased significantly by recrystallization, and it was used without further purification other than careful drying.

In series C the improved degradation procedure was employed. The malonic acid used was a synthetic material prepared by the method described by Yankwich and Stivers.[3] The product was twice recrystallized from acetone–benzene mixtures, then sublimed *in vacuo* (at 90–100°).

Decarboxylation Apparatus and Procedure.—The batch reactor is shown in Fig. 1. It consists essentially of a chamber B, provided with a cold finger F, a break-off seal H, and tubes A and E for vacuum system connections. The sample size was chosen so that the final partial pressure of acetic acid vapor at the temperature of the decomposition was much less than the vapor pressure of the liquid acetic acid.

The reactor is connected to a high vacuum system through A and warmed with a Bunsen flame during evacuation. After the reactor is cool, dry CO$_2$-free air is admitted through A and the vessel removed from the vacuum system. A weighed sample of dry malonic acid is shaken through the constriction C into the body of the reactor B; the bulb is then connected to the vacuum system and evacuated for 2–3 hours, after which period it is sealed at C while under vacuum.

By means of a clamp placed at E, the whole bulb is immersed for 15–18 hours in an oil-bath thermostated at 140.5 ± 0.5°. (The reaction was found to be more than 98% complete in 12 hours. From the data of Hinshelwood, *vide infra*, one would expect 98% decarboxylation in about 4 hours.) The bulb is then taken from the bath, the supporting tube cut at G and a standard taper joint attached there. The breaking magnets are inserted through this joint and the reactor attached to the high vacuum system. When the connections are evacuated, a cold bath (Dry Ice–trichloroethylene) is raised about F to condense the acetic acid product, the seal H is broken, and the carbon dioxide product distilled from B to a liquid nitrogen-cooled finger

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

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

[3] P. E. Yankwich and E. C. Stivers, *J. Chem. Phys.*, **21**, 61 (1953).

[4] E. A. Evans and J. L. Huston, *ibid.*, **19**, 1214 (1951).

[5] K. F. Schmidt, *Ber.*, **57B**, 704 (1924).

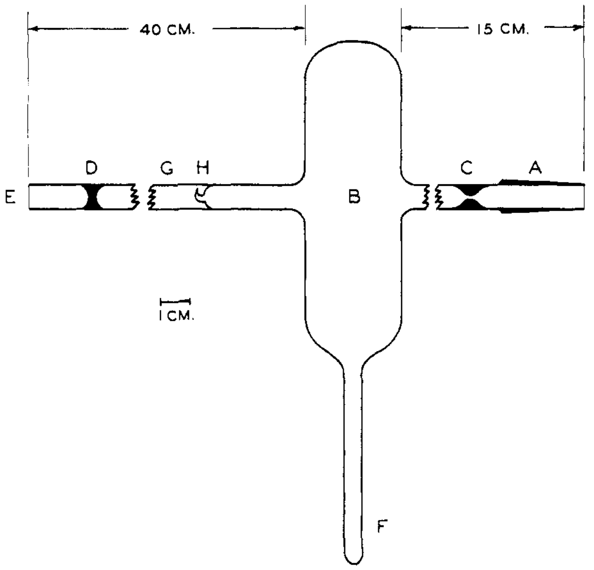

Fig. 1.—Batch-type decarboxylation vessel (letters refer to text).

on the vacuum line. The CO_2 is freed from traces of acetic acid by a second distillation; it is transferred finally to a mass spectrometer sample bulb. (In series C an additional purification consisting of solution of the CO_2 in carefully degassed distilled water was carried out.)

In the experiments in series A the cold finger F was broken off from B and acetic acid samples removed with a micropipet for combustion. In all other runs the acetic acid was vacuum transferred into an appropriate reaction vessel for degradation.

Degradation Apparatus and Procedure.—Acetic acid was degraded by procedures based upon Phares' application[6] of the Schmidt reaction,[5] which, in this case, may be written

$$HN_3 + CH_3COOH + H_2SO_4 \xrightarrow[30 \rightarrow 70°]{100\%\ H_2SO_4} N_2 + CO_2 + CH_3NH_2{\cdot}H_2SO_4 \quad (3)$$

The reaction trains used in this research are shown schematically in Fig. 2; the "B" train was employed in series B experiments, the "C" train in series C. As will be seen below, the isotope ratios obtained for carboxyl carbon when the "B" train was used were low and erratic. While the ratios obtained from methylamine combustion seem very reproducible, there is no guarantee that they are not in error also. A sweep of the mass spectrum of the samples showed that erratic behavior was always accompanied by a large (20–300 millivolts) background peak at m/q 30; it seemed likely that another impurity was present at m/q 44 (established at 20 volts for routine analyses) which affected the measured ion current ratio $(m/q\ 45)/(m/q\ 44)$, assumed to be due to isotopic forms of carbon dioxide only. Since these difficulties were removed, and internal consistency of the results established, by the introduction of the heated copper tube, they are presumed to have been due to oxides of nitrogen produced during the degradation and methylamine combustion.[7]

The reaction vessel is shown in Fig. 3. Into the pear-shaped flask J is placed *ca.* 50 mg. of reagent grade sodium azide and 0.3 ml. of *ca.* 100% sulfuric acid (3 parts concentrated reagent acid and 1 part 20% fuming acid); the flask is cooled in flaked ice until reaction ceases, then allowed to warm to room temperature. The flask J is then attached to the vacuum system and cooled to Dry Ice temperature while being evacuated (a small amount of gas evolution takes place before the solution freezes). The acetic acid in F is then distilled into J, which is then filled with dry CO_2-free air, removed from the vacuum system, and put into place in the degradation train. (While these operations are being carried out, the train is swept with a slow stream of helium.)

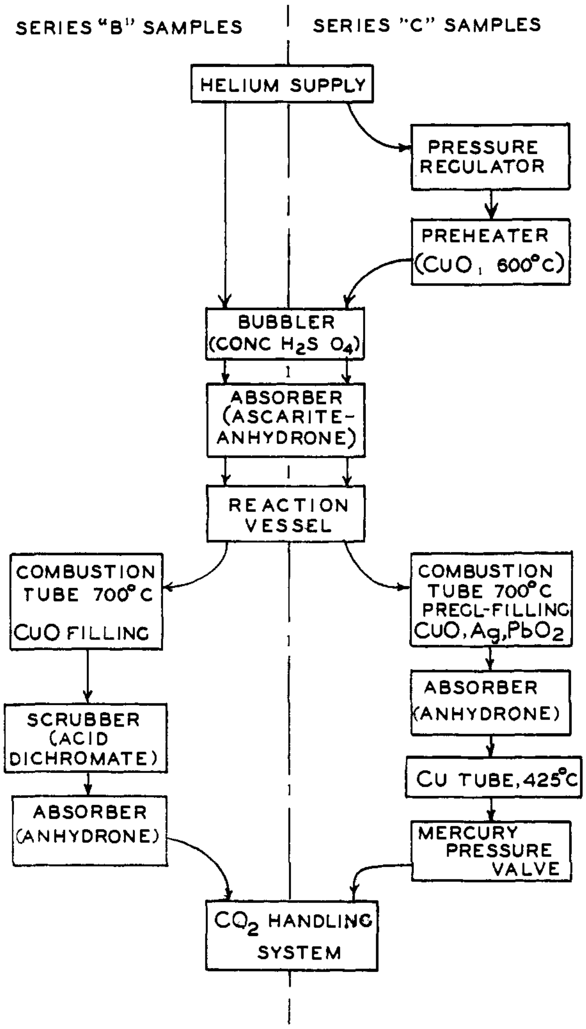

Fig. 2.—Block diagram of trains employed in acetic acid degradation.

A water-bath at 30° is placed about J; over a period of 10–15 minutes the temperature of the bath is increased to 70°, after which time the sweep is continued for one hour. The carbon dioxide collected, which is from the carboxyl carbon atom of the acetic acid, is trapped in the gas-handling system and removed for mass analysis (minimum yield 90%).

Flask J is cooled to room temperature, with the water-bath in place, and 5 ml. of 5 *M* carbonate-free sodium hydroxide introduced through L. The reactor is resealed and the water-bath temperature raised to 100°; the system is then swept for 40 minutes. The carbon dioxide collected, which is from the methyl carbon atom of the acetic acid, is trapped in the gas-handling system and removed for mass analysis. (The yield depends on the sweep time, exerts little effect on the carbon isotope ratio, and can be made equal to that in the previous step at will, by prolonging the sweep.)

As a test for occurrence of cross contamination of the carboxyl and methylene carbon atom samples, C^{14}-carboxyl-labeled acetic acid was degraded by the procedure used with C series samples. The carboxyl activity appearing in the methyl carbon sample depended upon the sweep time between collection of those samples and was of the order of 0.07% for 1–3 hours sweep.

Isotope Analyses.—The carbon isotope ratios of the various samples were obtained from measurements with a Consolidated-Nier Isotope-Ratio Mass Spectrometer. The carbon ratios of each sample were determined once on each

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(6) E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

(7) The background at m/q 30 was likely due to $N^{14}O^{16}$. The low carbon ratios were due probably to a contaminant at m/q 44, most likely $N^{14}N^{14}O^{16}$.

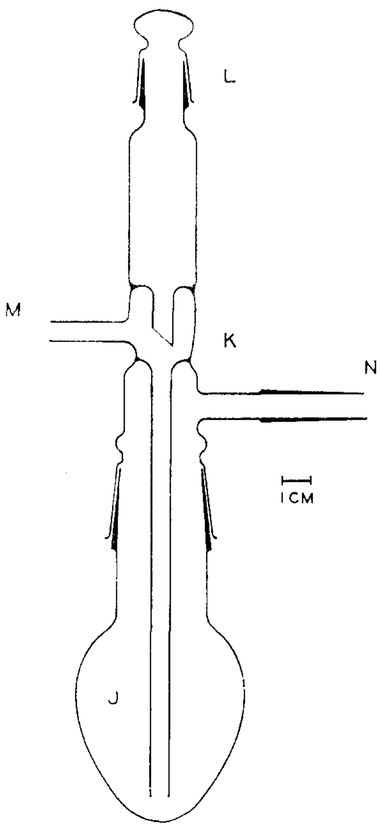

Fig. 3.—Reaction vessel used in acetic acid degradation (letters refer to text).

of at least three introductions of sample carbon dioxide into the manifold of the spectrometer. A triad of ratio determinations was considered satisfactory only if the average deviation from the mean ratio was 2×10^{-6} or less. Two working standards, one consisting of tank carbon dioxide, the other of carbon dioxide obtained from complete combustion of a small sample of malonic acid, were employed during the course of the work. Frequent cross checks were made among the effluent-gas samples and the working standards. In order to eliminate the effects of small variations in the response of the mass spectrometer, all measured ion current ratios were expressed in terms of that of the tank carbon dioxide standard.

The mass spectrum of each sample was obtained over the range *m/q* 26 to 48. The sample was rejected if this spectrum deviated appreciably from that of tank carbon dioxide which had been subjected to the same high vacuum manipulations.

The ratio of ion currents (*m/q* 45)/(*m/q* 44) was corrected for the contribution to the ion current at *m/q* 45 of the species $C^{12}O^{16}O^{17}$ by application of the value −0.000800 to the measured ratio of ion currents after the latter was corrected for incomplete resolution.

Calculations

The decarboxylation of liquid malonic acid has been shown to be first order with respect to the acid.[8,9] Rate constants for the reactions of interest here are defined in equations 1 and 2. In this paper five corrected isotope ratios, $R = (C^{13}O_2^{16})/(C^{12}O_2^{16})$, are employed in the evaluation of k_4/k_3: R_C, that of the effluent carbon dioxide; R_A, that of the carboxyl carbon atom of the product acetic acid; R_M, that of carbon dioxide obtained from the methyl carbon atom of product acetic acid; R_D, that of carbon dioxide obtained from complete combustion of the original malonic acid; R_B, that of carbon dioxide obtained from complete combustion of product acetic acid.

Any of these R values may be used to compute the mole fraction of C^{13}, X, in the particular sample, through the relation $X = R/(1 + R)$. If it is assumed that the concentration of species with carbon skeletons 12-13-13 and 13-12-13 may be neglected (*i.e.*, insignificant double labeling), then

$$k_4/k_3 = X_A/X_C \qquad (4)$$ [10]

Where X_A is not determined directly, the calculation of the isotope effect may be based on the observed ratios of the effluent carbon dioxide and the original malonic acid, in which case

$$k_4/k_3 = (2X_D - X_C)/X_C \qquad (5)$$

or on those of acetic acid and malonic acid, in which case

$$k_4/k_3 = (2X_B - X_D)/(3X_D - 2X_B) \qquad (6)$$

in both these relations the assumption of carbon isotope homogeneity in the three skeletal carbon positions is made.

Results

The corrected carbon isotope ratios, their averages and computed values for each X, are collected

TABLE II

CORRECTED ION CURRENT RATIOS AND CALCULATED C^{13} MOLE FRACTIONS

All R and X values have been multiplied by 10^6

Series A Run No.	R_C	R_B	R_D
1	10734	10971	10894
		10974	10891
2	10734	10968	
		10985	
3	10734	10974	
		10963	
4	10736	10970	
		10971	
5	10736	10974	
		10967	
Av. R	10735 ± 2	10972 ± 4	10893 ± 2
X	10621 ± 2	10853 ± 4	10776 ± 2

Series B Run No.	R_C	R_A	R_M
6	10745	11020	10859
7	10744	11043	10859
8	10744	11002	10856
Av. R	10744 ± 2	11022 ± 15	10858 ± 2
X	10630 ± 2	10902 ± 15	10741 ± 2

Series C Run No.	R_C	R_A	R_M	R_D
9	10724	11047	10843	10864
				10876
10	10722	11035	10840	10867
				10874
11	10722	11037	10834	
Av. R	10723 ± 2	11040 ± 5	10839 ± 3	10870 ± 5
X	10609 ± 2	10919 ± 5	10723 ± 3	10753 ± 5

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[8] C. N. Hinshelwood, *J. Chem. Soc.*, **117**, 156 (1920).

[9] J. Laskin, *Trans. Siberian Acad. Agr. Forestry*, **6**, 7 (1926).

[10] Detailed consideration of this matter reveals that the correction for double C^{13} labeling is approximately +0.0003 to k_4/k_3, which is about 1.03.

in Table II; the appended errors are average deviations from the mean value.

Internal Consistency of the Results.—Procedural deficiencies are frequently reflected in the several X values for a given series of experiments being in improper relationship to each other. Where the acetic acid is burned, as in series A, the X values should be related as

$$2X_B + X_C = 3X_D \qquad (7)$$

for that series, with the X's multiplied by 10^6 for convenience, we calculate: (21706 ± 8) + (10621 ± 2) = (32327 ± 8), while the value observed is (32328 ± 6).

Where the acetic acid is degraded, the X values are related as

$$X_A + X_M + X_C = 3X_D \qquad (8)$$

For the results obtained in the series B experiments we compute: (10902 ± 15) + (10741 ± 2) + (10630 ± 2) = (32273 ± 15), the observed value being (32328 ± 6). This discrepancy is believed to be due largely to the erratic results for carboxyl carbon in the acetic acid degradation. The data from the series C experiments are much more consistent; we calculate: (10919 ± 5) + (10723 ± 3) + (10609 ± 2) = (32251 ± 6), and observed (32259 ± 15).

Average Values for k_4/k_3.—Average values of $100[(k_4/k_3) - 1]$ calculated with equations 5 and 6 are given in Table III; the results from our series A are compared with those of Lindsay, Bourns and Thode[2] in which dry combustion procedures were employed. The mean value obtained from the former is 2.91 ± 0.08; that from the latter is 2.53 ± 0.27.

TABLE III

AVERAGE VALUES OF $100[(k_4/k_3) - 1]$ CALCULATED ON TWO BASES

	CO_2 basis eq. 5	HAc basis eq. 6
L, B and T	2.87 ± 0.36	2.20 ± 0.21
Series A	2.92 ± .04	2.90 ± .13

The most accurate results for the isotope effect should come from the series C experiments. In Table IV are given values of $100[(k_4/k_3) - 1]$ calculated with equation 4. The mean value obtained is 2.92 ± 0.05. If the calculation is based on average X values, a procedure which emphasizes the experimental error in the degradation, a value 2.92 ± 0.07 is found.

TABLE IV

VALUES FOR $100[(k_4/k_3) - 1]$ CALCULATED BY EQ. 4 FOR SERIES C

Run No.	X_C	X_A	$100[(k_4/k_3) - 1]$
9	10610	10926	2.98 ± 0.03
10	10608	10914	2.88 ± .03
11	10608	10917	2.91 ± .03
		Av.	2.92 ± .05

Discussion

Bigeleisen[11] has concluded that k_4/k_3 is temperature independent, which requires that its value for the C^{13} case at hand be 1.0198. The mean of all results obtained at 138° by Lindsay, Bourns and Thode[2] is 1.0253 ± 0.0027, carbon isotope homogeneity of the malonic acid being demonstrated. Our results at 140°, with the effect of carbon isotope inhomogeneity eliminated through the use of acetic acid degradation, are k_4/k_3 = 1.0292 ± 0.0007. It is interesting to note that an interpretation of related experiments in quinoline medium[12] leads to a prediction of k_4/k_3 = 1.0284 ± 0.0012 at 140°.

Acknowledgments.—This research was supported by the A. E. C. We are indebted to Professor Robert F. Nystrom for many helpful suggestions, and to Mrs. R. W. Hill for the mass spectrometer analyses.

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[11] J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

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

URBANA, ILLINOIS

[RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Radiation Chemistry of the Aliphatic Alcohols[1,2]

BY WILLIAM R. MCDONELL AND AMOS S. NEWTON

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The products formed in the irradiation of the liquid, air-free alcohols, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *s*-butyl, *t*-butyl, *n*-octyl and *n*-decyl, with 28 Mev. helium ions have been determined. The reduced products were hydrogen and saturated hydrocarbons with a total $G_{(\text{reduction})}$ of 7 to 8 equivalents per 100 e.v. in all cases. The oxidized products were aldehydes and glycols from primary alcohols, aldehydes, ketones and glycols from secondary alcohols and ketones with minor amounts of glycol from tertiary alcohols. Carbon monoxide and water were formed in all cases. The products are consistent with the principal bond rupture at the carbinol carbon atom, with the reactivity of such carbinol bonded groups exhibiting the order H > C_2H_5 > CH_3 in the alcohols studied. The mechanism of formation of some of the products has been discussed.

Introduction

Knowledge of the influence of structural and functional factors on the radiolytic behavior of organic compounds is necessary both for the development of a theoretical basis for the radiation chemistry of organic compounds and the uses of radiation chemistry in organic synthesis. Few systematic studies of the radiation chemistry of generic groups of pure compounds have been made. Lind and Bardwell[3] using α-particles, studied the saturated hydrocarbon gases methane to butane, and Honig and Sheppard[4] using both α-particles and deuterons

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(1) Much of the work presented here is from the University of California Radiation Laboratory Report UCRL-1378 (June 1951) by W. R. McDonell (declassified Ph.D. thesis).

(2) Presented in part at the Los Angeles Meeting of the American Chemical Society (March 1953).

(3) S. C. Lind and D. C. Bardwell, THIS JOURNAL, **48**, 2335 (1926).

(4) R. E. Honig and C. W. Sheppard, *J. Phys. Chem.*, **50**, 119 (1946).