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Revised

THE ISOTOPE EFFECT IN THE DECOMPOSITION OF OXALIC ACID[1,2]

by

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of Chemistry, University of California,
Berkeley

ABSTRACT

The C^{13} and C^{14} isotope effects in the decomposition of oxalic acid have been studied simultaneously at two different temperatures. In each case the C^{14} effect is approximately double the C^{13} effect, and both are in reasonable accord with theoretical calculations based on a simple postulated mechanism for the reaction.

For publication in The Journal of Physical Chemistry

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(1) The work described in this paper was sponsored by the U.S. Atomic Energy Commission.

(2) This paper was abstracted from part of the thesis submitted by Arthur Fry to the Graduate Division of the University of California in partial fulfillment of the requirements for the Ph.D. degree, June 1951.

(3) Present address: Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.

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Introduction

Lindsay, McElcheran and Thode[4] have studied the C^{13} isotope effect

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(4) J.G. Lindsay, D.E. McElcheran and H.G. Thode, J. Chem. Phys., 17, 589 (1949).

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in the decomposition of oxalic acid in concentrated sulfuric acid at 100°C. The results were reported as ratios of rate constants for the equations;

$$(COOH)_2 \xrightarrow{k_1} CO_2 + CO + H_2O \qquad (1)$$

$$\begin{matrix}{}^{*}\mathrm{COOH} \\ \mathrm{COOH}\end{matrix} \xrightarrow{k_2} {}^{*}\mathrm{CO_2} + \mathrm{CO} + \mathrm{H_2O} \qquad (2)$$

$$\begin{matrix}{}^{*}\mathrm{COOH} \\ \mathrm{COOH}\end{matrix} \xrightarrow{k_3} \mathrm{CO_2} + {}^{*}\mathrm{CO} + \mathrm{H_2O} \qquad (3)$$

The ratio k_2/k_3, where $^{*}C$ indicates C^{13}, was found to be 1.032, while $k_1/(k_2 + k_3)$ was 1.034.

Similar experiments have now been carried out using oxalic acid-1,2-C_2^{14}, and both the C^{13} and the C^{14} isotope effects have been determined on the same samples. In addition, the decompositions have been carried out at two different temperatures, and the differences in energy and entropy of activation for decomposition by equations (2) and (3) have been calculated for both C^{13} and C^{14}.

Experimental

Preparation of Oxalic Acid-1,2-C_2^{14} : - The oxalic acid-1,2-C_2^{14} used was prepared by the reaction between carbon dioxide-C^{14} and potassium on sand at 360° followed by extensive purification.[5] Carbon dioxide generated *in vacuo* from 3.318 g. of barium carbonate (2.75 μc) with hot concentrated sulfuric acid was dried and stored in a bulb for later use. A sample of sand was boiled with *aqua regia* and thoroughly washed and dried in order to remove metallic and organic impurities. A 50 cc. round bottomed flask with a neck about four inches long was filled about half full with the purified sand. To this was added 2.4 g. of freshly cut ether-washed potassium, and the flask was connected to the vacuum

(5) F. A. Long, J. Am. Chem. Soc., 61, 570 (1939).

line by a tygon tube to facilitate shaking. After evacuation, the flask was heated in a Woods metal bath to about 360°C, and shaken vigorously to spread the molten potassium over the surface of the sand. When the potassium melted a considerable quantity of volatile material was released which was pumped off. After the evacuation was complete, the temperature was maintained at 360°C, and the carbon dioxide-C^{14} was allowed to flow into the reaction vessel. The reaction proceeded rapidly and was facilitated by vigorous shaking and tapping on a corck ring. When the reaction was complete as shown by the drop in carbon dioxide pressure, the flask was allowed to cool and the excess potassium was cautiously decomposed by adding water. No trouble with fire was encountered in this decomposition, probably because the hydrogen quickly swept all the oxygen out of the flask; however, as a precaution, a vessel of liquid nitrogen into which the reaction vessel could be dipped was always kept handy in case the decomposition became too violent. The sand and some black carbonaceous material formed in the reaction was removed by filtration, and excess acetic acid was added. The solution was boiled to remove dissolved carbon dioxide which was recovered as barium carbonate of approximately the same specific activity as the starting material. Wt. barium carbonate recovered = 0.467 g. (14.1%). The black carbonaceous material above could also be burned and the carbon dioxide recovered as barium carbonate of high specific activity. Excess calcium chloride solution was then added to the acetic acid solution, and after digestion, the dirty grey calcium oxalate precipitate was removed by centrifugation. The precipitate was dissolved by adding a slight excess of concentrated hydrochloric acid and warming. This solution was then continuously ether extracted for three hours. The ether solution was evaporated over a small amount of water and the purification cycle was

repeated starting with the calcium oxalate precipitation. The final aqueous solution was concentrated to about 10 cc. and filtered, and the remaining water and hydrochloric acid were lyophilized off, leaving a pure white product of anhydrous oxalic acit, wt. = 0.3023 g., 39.9% yield. In other runs the yields ranged from 45-55%, with an additional 15-20% of the activity being recovered as carbon dioxide. While no extensive investigation of the reaction conditions was carried out, neither the amount of sand, the amount of potassium nor the exact temperature appeared to be at all critical. The yields could probably be improved somewhat by using freshly distilled potassium. Care was required in concentrating the final oxalic acid solution, since the acid will sublime away quite rapidly if evaporated to dryness on a steam bath with a stream of air passing over the surface. The lyophilization procedure was very satisfactory. The oxalic acid was checked for radioactive impurities by paper strip chromatography using a mixture of t-amyl alcohol and benzene saturated with 3 M hydrochloric acid as the solvent. No radioactive spots were found except for the oxalic acid spot, and an upper limit of 0.5% was set for the amount of radioactive impurity. The purity of an inactive sample prepared by the above procedure was checked by titrations with standard base and standard permanganate. A sample of 0.1927 g. of the oxalic acid required 4.33 cc. 1.000 M sodium hydroxide, giving an equivalent weight of 44.9 (theory = 45.0), and 21.50 cc. 0.2000 N potassium permanganate, giving an equivalent weight of 89.8 (theory = 90.0). For use in the decomposition experiments, 0.2230 g. of the oxalic acid-1,2-C_2^{14} prepared above was diluted with 14.77 g. of purified inactive oxalic acid by dissolving the two samples together, filtering and lyophilizing off the water. Base and permanganate titrations on the product gave theoretical values for the equivalent weight. The inactive oxalic acid was purified by recrystallizing Baker's C.P. oxalic acid two times from water.

In each recrystallization only about half the product was recovered, with both the first and last quarter of the crystals being discarded.

Preparation of ~100% Sulfuric Acid. - The ~100% sulfuric acid used was prepared by adding 100 cc. of 30% fuming sulfuric to 150 cc. of ordinary concentrated sulfuric acid in a glass stoppered flask. The solution was shaken vigorously and allowed to stand overnight. A sample of 1 cc., wt. = 1.8214 g., was diluted with water and upon titration with standard 1 M sodium hydorxide required 36.92 cc. for neutralization, giving a molecular weight of 97.5 (99.4% of theory). This same sulfuric acid stock was used in all the decomposition experiments.

Decomposition Experiments. - The decompositions were carried out using 99.4% sulfuric acid in the apparatus shown in Figure 1. Approximately one gram samples of oxalic acid were placed in the decomposition chamber, B. The apparatus was assembled, using the 99.4% sulfuric acid to lubricate the joints and stopcocks. Ten cc. of the 99.4% sulfuric acid was pipetted into the preheater, C, and dry carbon dioxide-free oxygen was allowed to sweep through the system for about one hour. The gas from the outlet of the assembly shown in Figure 1 was conducted, in turn, through a spiral trap cooled by a dry ice-isopropyl alcohol mixture, a spiral bubbler filled with 2 M sodium hydroxide to remove the carbon dioxide, a copper oxide packed furnace at ~700°C to burn the carbon monoxide to carbon dioxide, and another sodium hydroxide filled bubbler to absorb this carbon dioxide. When the oxygen had been sweeping through the apparatus for about an hour, the spiral bubblers were filled with 2 M sodium hydroxide, and the liquid in flask A was heated to reflux by means of a Glascol mantle. The vapor of the boiling liquid served as a constant temperature bath to heat the sulfuric acid and oxalic acid to the desired reaction temperature. The boiling point of the

liquid in flask A determined the temperature of decomposition. Dioxane and carbon tetrachloride were chosen to give temperatures of 103.0°C and 80.1°C, respectively. When the liquid in flask A had been refluxing vigorously for approximately one-half hour, the stopcock was opened and the sulfuric acid was allowed to flow onto the oxalic acid. At 103.0°C the reaction was very vigorous and care had to be exercised in adding the sulfuric acid to avoid frothing. In all cases the sulfuric acie was added as rapidly as possible. The oxygen sweep served to stir the oxalic acid-sulfuric acid mixture. The sweep was continued until gas bubbles were no longer observed in the sulfuric acid solution, and then for additional hour and one-half. The carbonate in the two bubblers was collected and weighed as barium carbonate. The yields of barium carbonate from the carbon dioxide and carbon monoxide were quantitative, and the blanks were negligible.

Isotopic Composition Measurements. - The C^{14} activity measurements were made using an ionization chamber and vibrating reed electrometer connected to a Brown recorder. The ionization chambers were filled to a standard pressure with carbon dioxide generated in a vacuum system from the barium carbonate samples with concentrated sulfuric acid. A sample of this same carbon dioxide was stored in a bulb for later mass spectrometric analysis. The samples from the carbon monoxide and carbon dioxide from a given run were measured in immediate succession in the same ionization chamber and on the same instrument in order to reduce to a minimum any variations in the procedure and instruments. Several independent measurements were made on each sample from each decomposition, starting with the barium carbonate in each case.

The C^{13} measurements[6] were made on a Consolidated Type 21-102 mass

(6) Thanks are due to Dr. A. Newton and Dr. L. Tolman of this laboratory for these measurements.

spectrometer, using a magnetic sweep to scan the peaks at m/q = 44 and 45. Several independent scannings of each sample were made. In several cases, the entire low m/q mass spectrum was taken using a voltage scan, and no peaks were found except those of the normal carbon dioxide pattern. Samples of normal carbon dioxide were also run during the sample determinations to check the reproducibility of the mass spectrometer. The m/q = 45 peak height was corrected for the O^{17} content of the carbon dioxide.

Results

The $C^{14}O_2$ specific activities and $C^{13}O_2$ mole fractions obtained in the various runs are shown in Table I. In all cases, the values given are averages of several measurements, and the indicated errors are average deviations of these measurements.

The C^{13} measurements were made at two different times, runs 1-4 and normal carbon dioxide 1 and 2 (carbon dioxide from dry ice) being measured at one time and runs 5-8 and normal carbon dioxide 3 and 4 (same stock sample of carbon dioxide) being measured somewhat later. Since in the subsequent calculations, only the relative $C^{13}O_2$ fractions are used, the variation in the normal carbon dioxide value between the two times is not serious since the difference is reflected in the values from both the carbon monoxide and carbon dioxide. The C^{14} measurements were made using different instruments and at different times

Table I

$C^{14}O_2$ Specific Activities and $C^{13}O_2$ Mole Fractions from the Decomposition of Oxalic Acid-1,2-C_2^{14}

$H_2C_2O_4$ Decomposition Run No.	Temp.	C^{13}		C^{14}	
		Mole Fraction $\frac{C^{13}O_2}{C^{12}O_2 + C^{13}O_2} \times 10^5$ *		Specific Activity ** -- Drift Rate, Volts/min. x 10^3	
		CO_2 Fraction	CO Fraction	CO_2 Fraction	CO Fraction
1	103.0°C	1089±6	1065±3	4585±40	4336±29
2		1092±0	1058±2	4535±39	4277±37
Normal CO_2 1		1115±1			
3		1088±2	1059±4	4554±39	4328±68
4		1091±3	1062±5	4504±27	4286±29
Normal CO_2 2		1116±1			
Permanganate oxidation		1074±2		4442±36	
5	80.1°C	1114±1	1076±3	4507±21	4203±36
6		1110±2	1078±6	4636±43	4335±31
Normal CO_2 3		1137±3			
7		1107±3	1073±3	4531±11	4247±20
8		1110±2	1075±3	4614±17	4352±24
Normal CO_2 4					

* Corrected for presence of $C^{12}O^{17}O^{16}$.

** Actual specific activity = ~30 dis./min./mg. $BaCO_3$

which probably accounts for the variations in specific activity from run to run. However, the carbon dioxide and carbon monoxide fractions from the same run were measured in immediate succession on the same instrument, to reduce this variation as much as possible within a given run.

In the following calculations only the monolabeled oxalic acid is considered although the oxalic acid actually used is called oxalic acid-1,2-C_2^{14}, since by its method of preparation both carbon atoms would be labeled if pure $C^{14}O_2$ were used. Actually, the number of dilabeled molecules was calculated to be a very negligible fraction of the total.

Referring to equations (1), (2) and (3) and assuming that the reaction is first order with respect to oxalic acid, the specific activities or mole fractions of the carbon dioxide and carbon monoxide are given by the following equations:

$$\frac{{}^{*}CO_2}{{}^{*}CO_2 + CO_2} = \frac{k_2}{k_2 + k_3} \cdot \frac{Ox^{*}\left(1 - e^{-(k_2 + k_3)t}\right)}{Ox\left(1 - e^{-k_1 t}\right) + Ox^{*}\left(1 - e^{-(k_2 + k_3)t}\right)}$$

and

$$\frac{{}^{*}CO}{{}^{*}CO + CO} = \frac{k_3}{k_2 + k_3} \cdot \frac{Ox^{*}\left(1 - e^{-(k_2 + k_3)t}\right)}{Ox\left(1 - e^{-k_1 t}\right) + Ox^{*}\left(1 - e^{-(k_2 + k_3)t}\right)}$$

Combining the above equations gives equation (4):

$$\frac{\dfrac{{}^{*}CO_2}{{}^{*}CO_2 + CO_2}}{\dfrac{{}^{*}CO}{{}^{*}CO + CO}} = \frac{k_2}{k_3} \qquad (4)$$

It should be noted that k_2/k_3 calculated in this manner is independent of time, and hence of the amount of reaction, while comparing the specific activity of the carbon dioxide or carbon monoxide to that of the oxalic acid is not.

For ease of tabulation and convenience of reference, the percentage isotope effect may be defined as $100\ (k_2/k_3 - 1)$. The percentage isotope effect values calculated by equation (4) from the data in Table I are given in Table II. The data of Lindsay, McElcheran and Thode[4] have been recalculated in this manner, and show a much narrower spread than using their method of calculation, although the average values are the same. These recalculated values are also shown in Table II.

Table II

C^{13} and C^{14} Isotope Effect in the Decomposition of Oxalic Acid

Decomposition Run No.	Temp.	Percent Isotope Effect $100\ (k_2/k_3 - 1)$	
		C^{13}	C^{14}
1	103.0°C	2.3	5.7
2		3.2	6.0
3		2.7	5.2
4		2.7	5.1
average		2.7 ± 0.22	5.5 ± 0.30
5	80.1°C	3.5	7.2
6		3.0	6.9
7		3.2	6.7
average		3.25 ± 0.15	6.7 ± 0.35
Lindsay, McElcheran and Thode*	100°C		
1		2.9	
2		3.5	
average		3.2	

* Recalculated from the original data using equation (4)

Discussion

The C^{13} isotope effect values shown in Table II are thus in very satisfactory agreement with the results obtained by Lindsay, McElcheran and Thode[4]. The C^{14} effect is approximately double the C^{13} effect at each temperature.

The differences in energy and entropy of activation caused by the isotopic substitution can be calculated from the theory of absolute rates.[7]

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(7) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", 1st. ed., McGraw-Hill Book Company, New York, New York (1941).

For equation (2), and temperature T_1,

$$(k_2)_{T_1} = \frac{kT_1}{h} e^{\Delta S^{\neq}_2/R} e^{-\Delta H^{\neq}_2/RT}$$

and for equation (3), and T_1,

$$(k_3)_{T_1} = \frac{kT_1}{h} e^{\Delta S^{\neq}_3/R} e^{\Delta H_3^{\neq}/RT}$$

Combining,

$$\left(\frac{k_2}{k_3}\right)_{T_1} = e^{(\Delta S^{\neq}_2 - \Delta S^{\neq}_3)/R} e^{-(\Delta H^{\neq}_2 - \Delta H^{\neq}_3)/RT} \qquad (5)$$

In a similar manner an equation is set up for T_2, and when this equation is combined with (5), equation (6) results.

$$\frac{(k_2/k_3)_{T_1}}{(k_2/k_3)_{T_2}} = e^{\frac{-(\Delta H^{\neq}_2 - \Delta H^{\neq}_3)}{R} \cdot \frac{T_2 - T_1}{T_1 T_2}} \qquad (6)$$

From the data observed in Table II, $(\Delta H^{\neq}_2 - \Delta H^{\neq}_3$* can be calculated by equation (6), and this value can be substituted back into equation (5), and $(S\Delta^{\neq}_2 - \Delta S^{\neq}_3)$ can be calculated. The calculated values are shown in Table III.

Table III

Energy and Entropy of Activation Difference between Equations (2) and (3)

Isotope	$-(\Delta H^{\neq}_2 - \Delta H^{\neq}_3)$	$\Delta S^{\neq}_2 - \Delta S^{\neq}_3)$
C^{13}	61 cal/mole	-0.11 e.u.
C^{14}	131 cal/mole	-0.24 e.u.

The presence of the isotope effect measured here allows some rather specific conclusions to be drawn concerning the mechanism of the decomposition.[8] At complete reaction, all of the carbon-carbon bonds in all the

(8) The authors wish to express their thanks to Professor Richard Powell for a fruitful discussion of the mechanism of the decomposition.

molecules are broken, so the isotope effect observed cannot be due to isotopic discrimination in the rate of rupture of the carbon-carbon bonds.

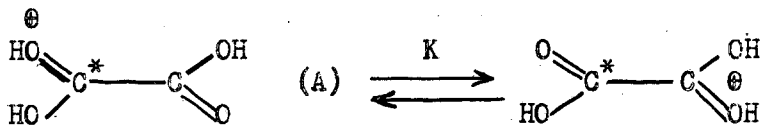
Therefore, if the observed isotopic fractionation is due to an isotope effect in the rate determining step of the reaction, the rate determining step must be the breaking of a carbon-oxygen bond, since the association of hydrogen

with oxygen is commonly considered to be rapid and reversible.

However, the observed isotope effect might also be due to some equilibrium step. An isotope effect is conceivable in rapid steps following the rate determining step only under very special circumstances. These require a symmetrical starting molecule and either a symmetrical product of the rate determining step or products which are rapidly interconvertable compared to the irreversible following reactions, in which the isotope selection is made. If an equilibrium process occurs before the rate determining step, an isotope effect in the equilibrium could multiply an isotope effect in the rate determining step.

Such a multiplication of effects could conceivably lead to either a larger or smaller overall effect, depending on whether the equilibrium constant was greater or less than one. Several such pre-equilibria might be involved in some cases.

In the present case a reasonable equilibrium prior to the rate determining step might be the association of a hydrogen ion with one of the carbonyl groups of the acid as shown in equation (7).



(7)

A simple calculation of the equilibrium constant, K, may be made using the equations derived by Bigeleisen and Mayer[9] or by Urey[10]. For lack of complete data, we

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(9) J. Bigeleisen and M. G. Mayer, J. Chem. Phys., 15, 261 (1947).

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

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have assigned the frequence of 1750 cm.$^{-1}$ to the C=O vibration, 1100 cm.$^{-1}$ to the normal C—C vibration and 1500 cm.$^{-1}$ to the two C····OH vibrations which are hybridized by resonance. The isotopic shifts are then calculated using the approximation of simple harmonic oscillators. Using these values the equilibrium constant at 100° is calculated to be 0.988 for C^{14} substitution and 0.995 for C^{13} substitution. Thus this particular equilibrium decreases the calculated isotope effect, but it is conceivable that in other cases the effect would be in the opposite direction.

In calculating the ratio k_2/k_3, the above vibrational frequencies are assigned to the normal molecules (A) and (B). For the transition state we take a model in which water has been lost from the carbon originally attached to two OH groups and the carbon-

carbon bond is greatly weakened leaving nearly free molecules of carbon dioxide and $\overset{\ominus}{C}OOH$. The carbon monoxide is assigned its accepted frequency of 2170 cm.$^{-1}$ and the carbonyl and hydroxyl frequencies in $\overset{\ominus}{C}OOH$ are assumed to be unchanged. The force constant for the C·····OH bond which is broken is set equal to zero. The ratio k_2/k_3 is then calculated using equation (8), as derived by Bigeleisen[11].

(11) J. Bigeleisen, J. Chem. Phys., 17, 675 (1949).

$$\frac{k_2}{k_3} = \left(\frac{\mu_3}{\mu_2}\right)^{1/2} \left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i \longrightarrow \sum_1^{3n-7} G(u_i^{\neq})\Delta u_i^{\neq}\right] \quad (8)$$

The function G(u) is defined by Bigeleisen and Mayer[9] who have tabulated values of G(u) as a function of u. The reaction coordinate reduced mass, μ, is assumed to be the reduced mass of the atoms forming the bond being broken. The symbol $\neq$ refers to the activated complex.

The rate ratio, k_2/k_3, calculated in this manner, when multiplied by the equilibrium constants calculated above, give overall isotope effects of 6.0% for C^{14} substitution and 3.1% for C^{13} substitution at 100°. These compare to the values of 5.5% and 2.7% measured experimentally. The corresponding calculated values at 80° are 6.3% and 3.4% compared to the experimental values of 6.7% and 3.25%[12]. The agree-

(12) We have recently learned, by private communication, of experiments in two other places (Research Chemistry Division, Atomic Energy Project, National Research Council, Chalk River, Canada; and Department of Chemistry, University of Illinois) in which the isotope effect in a chemical reaction was determined for both C^{13} and C^{14} simultaneously on the same reaction. In both of these cases the reported C^{14} effect is much more than twice the C^{13} effect. The results for the decomposition of mesitoic acid given by Stevens, Pepper and Lounsbury (Canada), J. Chem. Phys., 20, 192 (1952), are as follows: k_{12}/k_{13} 1.038 ±.003; k_{12}/k_{14} 1.101 ± .005. Here the C^{14}/C^{13} ratio is almost three. The results reported by Yankwich, Stivers and Nystrom (Illinois) at

the Berkeley meeting of the American Physical Society in December, 1951 and mentioned in the Abstract appearing in the Bulletin of the American Physical Society, 26, No. 8, Paper B5 give values for both the C^{13} and C^{14} effects corresponding with those previously reported. Here the C^{14} effect is about four times the size of that for C^{13}. This latter report was for the decarboxylation of malonic acid at its melting point. It is clear that from these three compariative studies, if results are accepted on their face value, that there are isotope factors involved in the determination of the rate of these decarboxylation reactions of which we are not yet cognizant, since it is difficult to see how a change in mass from C^{13} to C^{14} could chance the mechanism of the reaction, unless perhaps nuclear spin were involved in some way.

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ment in magnitude is quite satisfactory, but the calculated temperature coefficient is not large enough to explain that observed experimentally. Perhaps a better choice of frequencies and model would lead to a more satisfactory calculation. Ultimately the study of isotope effects in chemical reactions should enable us to elucidate all of the intimate details of the mechanism of the reaction. When the proper equilibria and rate determining steps are chosen, the calculated isotope effect should coincide with that observed experimentally. The choice of a molecule which reacts at one of two chemically identical groups, such as oxalic or malonic acid, is a fortunate one, since net isotope effects are observed at complete reaction, thus making it unnecessary to study the isotopic composition of the products as a function of the amount of reaction.

The presence of an isotope effect does not unequivocally establish the mechanism of the decomposition, but it does offer very strong evidence that the rupture of the carbon-carbon bond is not rate determining, and, consequently, that the rate determining step in this medium is the rupture of the carbon-oxygen bond. Actually the rupture of the carbon-oxygen bond and of the carbon-carbon bond is probably all part of a concerted reaction with the loss of hydroxyl (or water) from one carboxyl or the other being the initiating step. The essential steps of what is considered to be the most likely mechanism for the decomposition are shown in Chart I.

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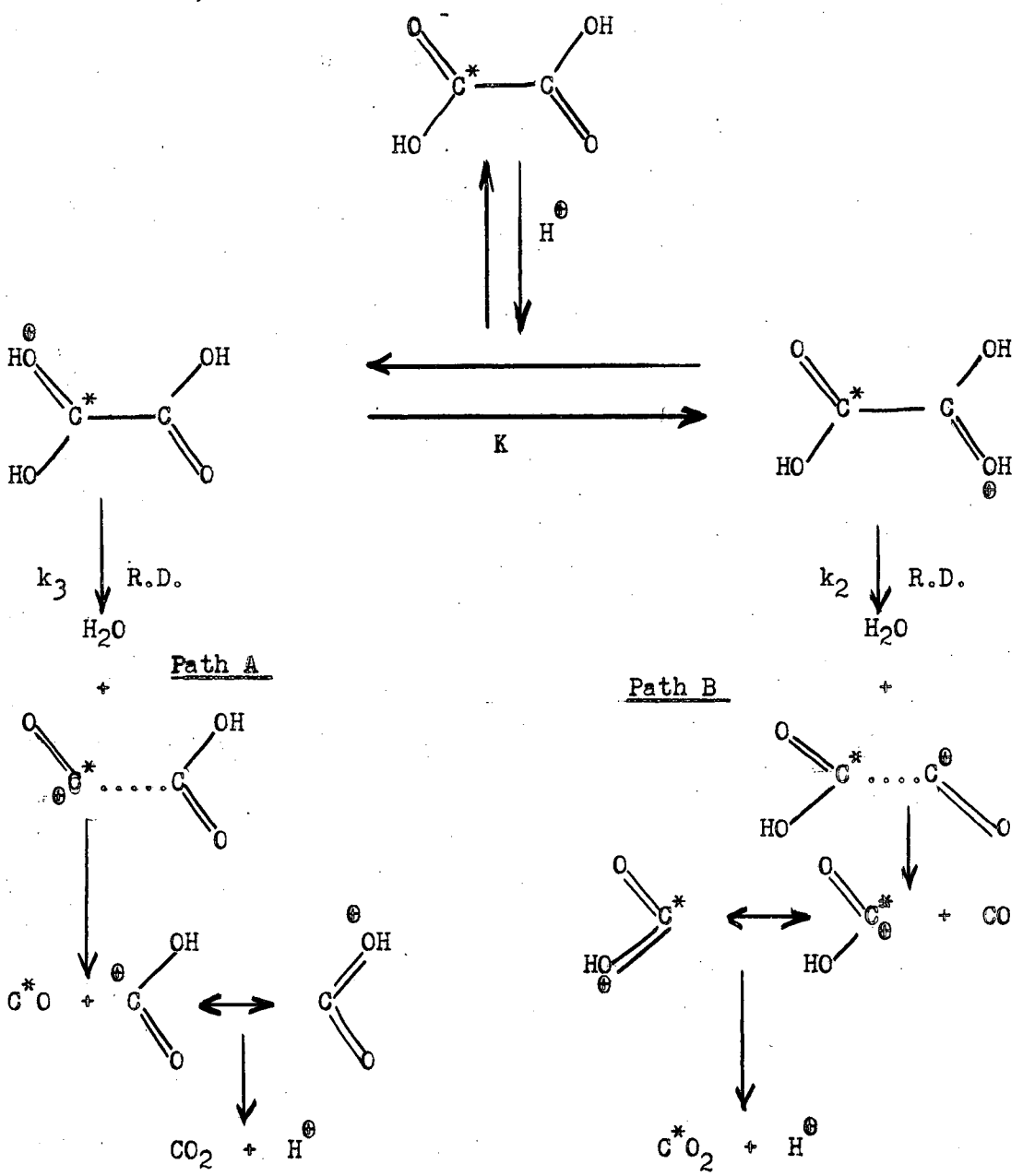
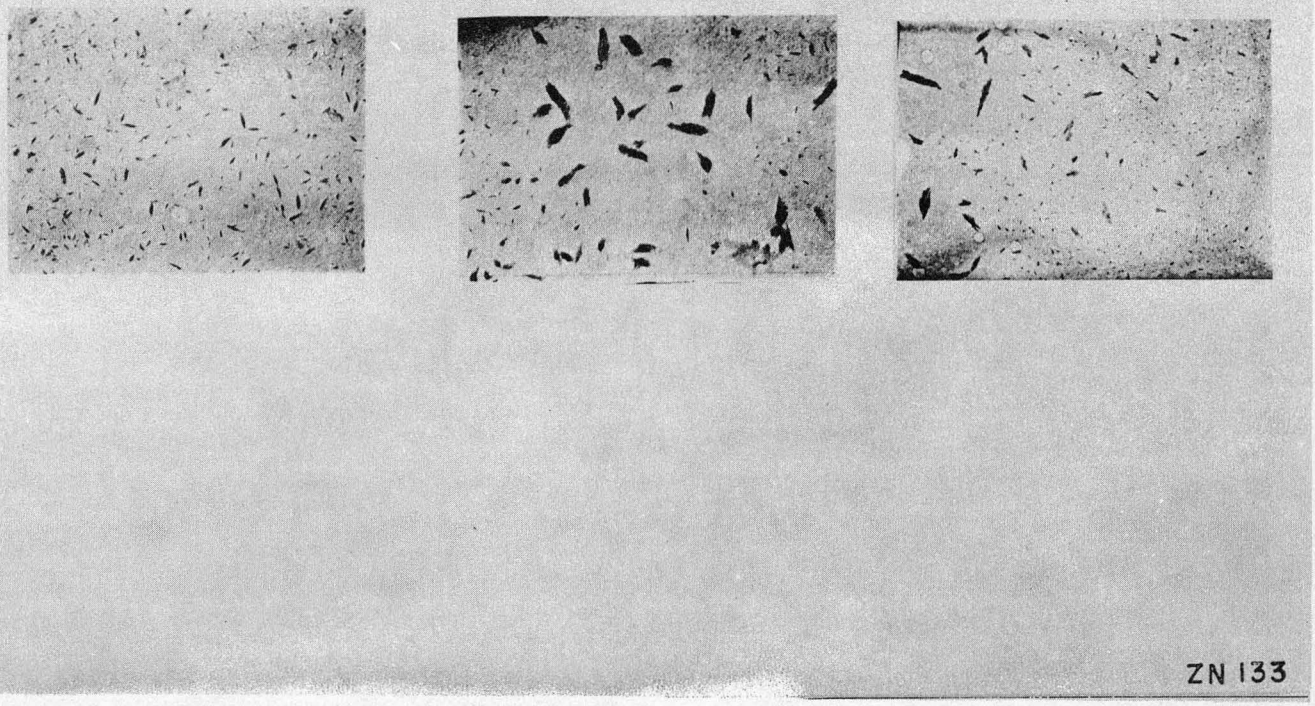
Chart I. - - Mechanism of the Decomposition of Oxalic Acid in 100% Sulfuric Acid



Path A is seen to be less likely than Path B, since we observe an enrichment of labeled atoms in the carbon dioxide.

Ultimately, the study of isotope effects in chemical reactions should enable us to elucidate all of the intimate details of the mechanism of the reaction. In the case of the decomposition of oxalic acid by sulfuric acid, sufficient data will make it possible to determine just which mode of vibration results in decomposition. Presumably, when the proper choice is made, all of the factors in equation (7) will be known and the calculated values, when combined with the proper equilibrium constants, will coincide with the experimental values. The choice of a molecule which reacts at one of two chemically identical groups, such as oxalic or malonic acids, is a fortunate one, in that the term $\sum_{i}^{3N-6} G(U_i)\Delta U_i$ in equation (7) is always identically zero, thus affording a considerable simplification in the calculations for the rate determining step.



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