ISOTOPE EFFECTS IN CHEMICAL REACTIONS

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ABSTRACT

The effect on reaction rates caused by substitution of C^{13} for C^{12} has been measured for two organic decomposition reactions. Isotope effects have been found in the thermal decarboxylation of malonic acid and in the decomposition of oxalic acid in concentrated sulfuric acid. Malonic and oxalic acid molecules containing only C^{12} carbon atoms were found to decarboxylate about 5.5% faster than those containing a C^{13} isotope in a carboxyl position. It was found that C^{13} did not distribute itself equally among the decomposition products of oxalic acid, but showed a 3.3% preference for the carbon dioxide rather than carbon monoxide. A 2.1% greater probability of rupture of C^{12}-C^{12} over C^{12}-C^{13} bonds in the decarboxylation of malonic acid was observed. The effect of temperature on the isotope effects in malonic acid was investigated. The magnitude of the effects was found to be constant in the temperature range studied.

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INTRODUCTION

General Introduction

The discovery of isotopes has had a tremendous effect on the history of Science. Separated isotopes are becoming increasingly available and their use is becoming widespread. They are now rapidly finding their place in instruments of destruction, as in the Atomic and Hydrogen bombs, and as a useful tool in industrial control and fundamental research. In the latter field isotopes, both stable and radioactive, are of great importance in the elucidation of many problems in medical, biological, geological and chemical research. We now know that the isotopes of an element, although chemically very similar, are not identical. In the course of millions of years the small differences in chemical properties have caused a fractionation of isotopes in nature. This fractionation, although small, has aided us in our knowledge of geological and biological processes which occurred millions of years ago. Moreover, the small differences in the chemical properties of isotopes have made possible their separation by chemical means.

Separated stable isotopes, because of their similarity in chemical properties and also because of improved equipment for their detection and measurement, are admirably suited to act as tracers to tag the path of an element or compound in a complex chemical reaction. In order to achieve maximum success in the use of isotopes to determine reaction mechanisms or to interpret data involving isotopic tracers, it is necessary to know that differences do exist in the chemical behavior of isotopes and the magnitudes of these differences.

The purpose of this thesis is to review the relatively new field of investigation concerning the effect of isotopic mass on the rates of chemical reactions, and to report on the isotope fractionation which occurs in the decomposition of oxalic and malonic acids containing normal abundances of C^{13}.

Historical

It is interesting to note that although isotope effects as we shall consider them here are restricted to the light elements, the existence of isotopes was first recognized by "isotope effects" in the heavy elements. In the fifteen years following Becquerel's discovery of radioactivity (1) several pairs of radioactive elements, namely ionium and thorium, mesothorium and radium and radium-B and lead were found to be chemically inseparable and indeed spectroscopically identical. (2)-(7). In 1913 Soddy suggested the name isotopes for these pairs of elements as they occupied the same place in the periodic table. Since the radioactive decay chains of the thorium and uranium series end in the lead isotopes of mass numbers 208 and 206 respectively, it was to be expected that the atomic weight of lead might vary, depending on whether it was found associated with thorium or uranium deposits. This hypothesis was shown to be correct by T. W. Richards (8) who found that the lead associated with thorium ores had a higher atomic weight than that found among uranium deposits.

Shortly after this, Sir J. J. Thomson (9) suggested that the light elements of the periodic table might consist of mixtures of isotopes. He built an instrument for the analysis of positive rays formed in a discharge tube and obtained direct evidence that neon consisted of two

isotopes. Following World War I, the development and use of the mass spectrograph by F. W. Aston led to the identification and determination of the abundances of the isotopes of a large number of elements. During this period, however, the isotopes of an element were believed to be chemically identical since their abundances were found to be remarkably constant in nature (10) and since all efforts to separate them by chemical means had failed.

Following the prediction of a rare heavy isotope of hydrogen (11) and the discovery of the rare isotopes of carbon (12), nitrogen (13) and oxygen (14) about 1930, differences in the physical properties of the light elements became increasingly evident. Calculations based on Debye's theory of specific heatsof solid substances indicated that differences might be expected to occur in the vapor pressures of the isotopes of hydrogen. By evaporating 4000 cc. of liquid hydrogen down to a residue of about one cc, Urey, Brickwedde and Murphy (15) were able to sufficiently concentrate the hydrogen isotope of mass two to make its detection possible spectroscopically. Keesom and Van Dijk (16) achieved a considerable separation of the neon isotopes by fractionally distilling liquid neon at -248.4°. Also Lewis and Cornish (17) showed that vapor pressure differences existed between the isotopic molecules H_2O^{16}, H_2O^{18} and D_2O^{16}.

Early in 1932 Urey and Rittenberg calculated that the percent dissociation of hydrogen iodide should depend on whether the light or heavy isotope of hydrogen was used (18). Later they were able experimentally to check the predictions of the theory and secured

exact agreement between theory and experiment.

Shortly after, Urey and Grieff (20) calculated equilibrium constants for a number of isotopic exchanges involving elements in the first period of the periodic table. The calculated equilibrium constants differed slightly from unity, indicating that the isotopes of these light elements differed significantly in their thermodynamic properties. For example, the equilibrium constant for the isotopic exchange reaction $C^{13}O_2^{16} + H_2O^{18} \rightleftarrows C^{13}O_2^{18} + H_2O^{16}$ was calculated to be 1.044 at 0°C. Weber, Wahl and Urey (21) experimentally determined the equilibrium constant to be 1.046 at 0°C. At 25°C. the carbon dioxide was found to contain 3.5% more O^{18} than the water with which it was in equilibrium. Many of Urey and Grieff's calculated equilibrium constants have now been determined experimentally and in all cases agreement with theory has been excellent (22)-(27). In several cases the differences found in the chemical properties of the different isotopes of the lighter elements have been sufficiently great to enable the partial separation of the isotopes by chemical means. Using counter-current exchange columns for the system Hg/NH_4^+ Thode and Urey (23) were able to produce concentrations of N^{15} up to 72%. By similar exchange reactions C^{13}, N^{15} and D are now being produced commercially by the Eastman Kodak Company, Rochester, N.Y. (29).

Closely related to the differences observed in the chemical properties of isotopes is the question of the constancy in nature of the isotopic composition of the lighter elements. It was to be expected on the basis of Urey and Grieff's calculations that

equilibrium conditions occurring in nature would cause a fractionation of the isotopes of the light elements. H. T. Emelius (30) in 1934 had reported variations in the density of water from various sources of up to 4.4 p.p.m. Dole and co-workers (31)-(35) using densimetric methods, and Thode and Smith (36) using a mass spectrometer, found variations in the abundance of the oxygen isotopes of 3-4%, depending on the source of the oxygen. Nier and Gulbransen (25) and Nier and Murphy (26) have reported similar variations for the carbon isotopes. Briscoe in 1925 reported small variations in the atomic weight of boron (37). Later, Thode, Macnamara, Lossing and Collins (38) found variations up to 3.5% in the ratio of the boron isotopes, depending on the source of boron.

More recently variations in the abundances of isotopes have been found for elements in the second and third periods of the periodic table. Thode, Macnamara and Collins have extensively investigated the variations found in nature of sulfur isotopes (39). Their most recent findings, up to 6.5% variation in the $\frac{S^{32}}{S^{34}}$ ratio, and over 3% variation in the $\frac{S^{32}}{S^{33}}$ ratio have led them to predict a variation of 13% in the $\frac{S^{32}}{S^{36}}$ ratio (40). These variations are surprising in view of the relatively large atomic weight of sulfur. Smaller variations have also been found in the abundance of the germanium isotopes by Graham, Macnamara, MacFarlane and Crocker (41).

These natural variations in the abundances of isotopes in nature must mean that natural processes are continually fractionating isotopes. It follows that if the isotopic equilibrium constants differ from unity, the isotopes of an element must react at different rates. This was observed from the beginning in the case of hydrogen and deuterium. One of the first

methods used to concentrate deuterium was the electrolysis of water (42). Deuterium was evolved at the cathode at a relatively slower rate than hydrogen and hence D_2O was concentrated in the residue. As a rule deuterium compounds react slower or are more stable than their hydrogen analogues. Gerd and Schmidt showed that deuterides were more stable than hydrides (43). Wynne-Jones (44) found the ionization rate of protium to be ten times that of deuterium. Jungers and Taylor (45) found in the mercury photosensitised decomposition of the deuterammonias that NH_3 decomposed about ten times faster than ND_3. Recently T. W. Newton and G. K. Rollefson (46) investigated the relative rates of photochlorination of $CHCl_3$ and $CDCl_3$. For the reactions

$$CHCl_3 + Cl \xrightarrow{k_1} HCl + Cl_3$$

$$CDCl_3 + Cl \xrightarrow{k_2} DCl + CCl_3$$

The ratio of the rate constants $\frac{k_1}{k_2}$ was found to be $1.4 \pm .2\ e^{\frac{710 \pm 90}{RT}}$. Further evidence along this line was found in the relative rates of reaction of HI and DI with Methyl iodide (47). In this case, for the reactions

$$HI + CH_3I \xrightarrow{k_1} CH_4 + I_2$$

$$DI + CH_3I \xrightarrow{k_2} CH_3D + I_2$$

$\frac{k_1}{k_2}$ turned out to be 1.42.

One apparent exception is reported by Schröer and Lutgert (48). They found that $(COOD)_2$ in D_2O decomposed 20% faster than $(COOH)_2$ in H_2O.

Recently it had been shown that differences in the reactivities of isotopic molecules are not limited to compounds of hydrogen and deuterium. H. C. Urey (49) reported that algae contained 2.07% less C^{13} than the $C^{13}O_2$ content of the nutrient solution in which they were grown,

indicating again that the C^{12} was used in synthesis at a faster rate than the heavier isotope. However, Myerson and Daniels (50) found that urea labelled with C^{14} hydrolyzed faster than the unlabelled urea.

Isotope effects have also been observed in dissociation of isotopic molecules under electron impact in a mass spectrometer. Although this is not a chemical process as we ordinarily think of the term, the effects found here have pointed the way for investigation of bond rupture probabilities of isotopic molecules in chemical reactions. Since the historical backgrounds for the two phenomena are so related it is well to consider here some of the isotope effects observed for dissociation electron impact.

Considerable differences in the dissociation probabilities have been observed for C-H and C-D bonds in deuterated carbon compounds. Evidence of this effect has been found in ethene-1,2 d_2 (51), methane-d (52), acetylene-d_1, acetylene-d_2 (53) propane-1-d, propane-2-d (54) and acetaldehyde deuterated in the aldehyde group (55). Evans, Bauer and Beach (52) in their investigations on methane-d in a mass spectrometer observed two effects:

(1) A decreased probability of the process

$$CH_3D \qquad CH_3^+ + D + \epsilon$$

(2) An increased probability of the process

$$CH_3D \qquad CH_2D^+ + H + \epsilon$$

both relative to the probability of the process

$$CH_4 \qquad CH_3^+ + H + \epsilon$$

The first effect is well known and its explanation is based on the differences in zero-point energy of the two isotopic molecular

process $C_2HD + \epsilon \rightarrow C_2D^+ + H + 2\epsilon$ .....(d)

on the same scale is 1.2.

Since the decrease in the specific probability of process (b) is greater than the increase in (d), we conclude that the decrease in amplitudes of oscillation in the heavy acetylenes is more important than the lowering of the zero point energy of C_2D^+ in determining the mass spectra. Further evidence to the effect that the decrease in the amplitudes of oscillation of the heavy acetylenes is the major factor in the isotope effect is found in the fact that the process (c) is less probable than (a). These effects are understandable since only about 20% of the $C_2H_2^+$ ions dissociate. We would predict that the larger the amount of dissociation the greater would be the effect of the zero point energy of the dissociated fragment on the mode of dissociation. The same reasoning can be applied to explain Evans, Bauer and Beach's results on deuterated methane.

For the case of diatomic molecules as in the dissociation of H_2, D_2, and even N_2, the effect of the lowered amplitudes of oscillation of the heavier isotope and the Franck-Condon principle determine the mode of dissociation. As to be expected, we find that $\frac{H^+}{H_2^+} > \frac{D^+}{D_2^+}$ (57) (58), and that $\frac{N^{14+}}{N^{14}N^{14+}} > \frac{N^{15+}}{N^{15}N^{15+}}$ (59).

In 1948 while investigating the mass spectra of propane containing a 53% excess of C^{13} in an end position, Beeck, Otvos, Stevenson and Wagner (60) found that the dissociation probability of the C^{12}-C^{12} bond in propane-1-C^{13} was increased by 7% and the dissociation probability of the C^{12}-C^{13} bond decreased by 12% relative to a propane molecule containing only C^{12} carbon atoms. In this case we have

$$C^{12}H_3 - C^{12}H_2 - C^{12}H_3 \xrightarrow{k_1} C^{12}H_3 - C^{12}H_2^+ + C^{12}H_3$$

$$C^{12}H_3 - C^{12}H_2 - C^{13}H_3 \xrightarrow{k_2} C^{12}H_3 - C^{12}H_2^+ + C^{13}H_3$$

$$\xrightarrow{k_3} C^{13}H_3 - C^{12}H_2^+ + C^{12}H_3$$

The dissociation probabilities of these three processes are in the ratio 1:.38:1.07. Here the decrease in zero point energy of the $C^{12}-C^{13}$ ion fragment increases its probability of formation with respect to the corresponding dissociation process in the $C^{12}-C^{12}-C^{12}$ molecule more than the decrease in amplitude in the ground state decreases the total dissociation probability.

As a result of this investigation the same group sought a similar isotope effect in the thermal cracking of propane-1-C^{13}. Here again an 8% more frequent rupture of $C^{12}-C^{12}$ bonds than $C^{12}-C^{13}$ bonds observed (61).

Shortly after this, Yankwich and Calvin (62) observed that in the thermal decarboxylation of malonic and bromomalonic acids labelled with C^{14} in a carboxyl position, the specific activity of the carbon dioxide evolved was less than that of the starting material. They compared the activities of the carbon dioxide evolved, the starting diacid and the monacid produced. From their results they concluded that the ratio of probability of rupture of $C^{12}-C^{12}/C^{12}-C^{14}$ bonds was 1.12 for malonic acid and 1.4 for bromomalonic acid.

Following Yankwich and Calvin's report on the isotope effect found in C^{14} malonic acid there was considerable skepticism regarding the magnitude of the effect. It was decided at that time to convince ourselves that such was actually the case. Malonic acid was a convenient substance to work with as it is readily decarboxylated above its melting

point of 136.5° to produce carbon dioxide and acetic acid. The availability of a mass spectrometer and the high precision attainable with it as compared with the less accurate techniques necessary when using C^{14} suggested the use of C^{13} malonic acid. Consequently malonic acid containing an 18% C^{13} enrichment in a carboxyl position was synthesized. Several decarboxylations were carried out but inability to obtain consistent results necessitated turning to malonic acid containing a normal abundance of C^{13}.

During the same period experiments were carried out to measure the distribution of C^{13} in the carbon monoxide and carbon dioxide formed as products in the decomposition of oxalic acid in concentrated sulfuric acid. The results obtained (63) were rather surprising and are reported here in detail.

Soon after, a number of papers, both experimental and theoretical, appeared in the literature on the topic of isotope effects in chemical reactions. J. W. Weigl and M. Calvin (64) during an investigation into the mechanism of photosynthesis found that barley seedling plants utilize $C^{12}O_2$ faster than $C^{14}O_2$.

Stevens and Attree (65) investigated relative rates of hydrolysis of methyl benzoate containing C^{14}. They found that the normal molecule hydrolyzed about 12% faster than the C^{14} labelled ester. These authors (66) also found an isotope effect in the benzilic acid rearrangement of benzil labelled with C^{14} in one carboxyl group. The migration of the phonyl group which results in the formation of a C^{14}-C bond was found to take place preferentially.

Bigeleisen (67) treating the formation of ions in a mass spectrometer as a rate process attempted to find a theoretical basis for

the data of Stevenson et al on propane-1-C^{13}. Applying the methods of statistical mechanics to the theory of absolute reaction rates he calculated ratios of rate constants for the dissociation processes of propane shown previously (page 10). At 777° the calculated values for the ratios $\frac{k_1}{k_2}$ and $\frac{k_1}{k_3}$ turned out to be 1.043 and 1.023 respectively. Although the calculated values are much smaller than the experimental values, a more significant discrepancy is that the ratio $\frac{k_1}{k_3}$ is experimentally found to be less than unity. Bigeleisen points out that it is difficult to see how any mechanism which treats the production of ions as a rate process will remove this discrepancy. Using the same approach Bigeleisen (33) calculated ratios of rate constants for the decarboxylation of C^{14} malonic acid. His calculations predicted a 4% effect compared with the 12% effect found experimentally. Not satisfied with this, Bigeleisen and Friedman (39) repeated Calvin's experiment using malonic acid containing a normal abundance of C^{13}. Their results in part checked their theoretical calculations. Since work was proceeding on this problem simultaneously in this laboratory, their results will be considered in greater detail later.

K. S. Pitzer (70), using the same theoretical approach but making different approximations, arrived at a theoretical value for the ratio of rate constants for the isotopic species of malonic acid which supported Yankwich and Calvin's results.

The present type of investigation promises to be one of fundamental importance in that it throws light on not only the mechanism of chemical reaction, but also on the nature and behavior of the activated complex and the influence of the products on the way in which the activated complex

breaks up. In this thesis isotope effects in oxalic and malonic acids have been measured as well as the previously uninvestigated effect of temperature on the isotope effects in malonic acid. The results obtained regarding both the magnitude of the effect and its relation to temperature have theoretical significance.

Theoretical

According to the theory of absolute reaction rates* in order for a molecule to decompose, its energy first increases to a maximum and then decreases as the products of the reaction separate. The difference between the zero point energy of the reactant and the position of maximum energy is the activation energy for the process. In the position of maximum energy the molecule forms what is known as an activated complex. These complexes are considered to lie on top of the energy barrier between the initial and final states. The rate of reaction is given by the velocity with which the activated complexes travel over the top of the barrier from the initial to the final state. The configuration corresponding to the activated complex has all the properties of an ordinary molecule except that one normal vibration frequency has an imaginary value. The activated complex may be regarded as having translational and rotational degrees of freedom and remaining stable for all vibrational modes but one, which corresponds to translational movement along the reaction co-ordinate and leads to decomposition. This translational degree of freedom takes the place of one vibrational degree in order to keep constant the total of 3n degrees of freedom. It may be treated statistically as a one dimensional translation.

*For a complete discussion of this theory see S. Glasstone, K. Laider and H. Eyring. The Theory of Rate Processes - McGraw Hill Book Co., New York and London, 1941.

The assumption is made that the activated complexes are always in equilibrium with the reactants. It can be easily shown that for a simple decomposition reaction

$$A \longrightarrow A^* \longrightarrow \text{products}$$

the rate for this reaction may be given as

$$k_r = K\frac{C}{C_A}\left(\frac{kT}{2\pi m^*}\right)^{\frac{1}{2}}\frac{1}{\delta} \qquad \ldots\ (1)$$

where K is the transmission coefficient,

C_A and C^* are the equilibrium concentrations of A and activated complex respectively.

m^* is the effective mass of the activated complex along the co-ordinate of decomposition.

δ is a hypothetical quantity considered as being the length of a potential box containing the activated state.

Since the activated complex is postulated as being in equilibrium with the reactant, it is possible to write an equilibrium constant for the system as

$$K_c = \frac{C^*}{C_A} \qquad \ldots\ (2) \text{ assuming ideal behavior.}$$

The equilibrium constant is related to the standard free energy change by the well known equation

$$-RT \ln K_c = \Delta F^o \qquad \ldots\ (3)$$

where ΔF^o is the standard free energy change in going from reactants to products.

In this case the equation may be written as

$$-RT \ln K_c = F^{o*} - F_A{}^o \qquad \ldots\ (4)$$

The free energy is related to the partition function by the following

equation:

$$F = E_o + RT \ln N - RT \ln Q \qquad \ldots\ (5)$$

where E_o is the zero point energy of the molecule,

N is Avogadro's number,

Q is the complete partition function for the molecule.

If we consider the standard state to be for one molecule (instead of one mole) in unit volume, the N's drop out and the equilibrium constant may be written in terms of the respective partition functions, i.e.,

$$K_c = \frac{Q^{\ddagger}}{Q_A} e^{-\frac{(E_o^{\ddagger} - E_{oA})}{RT}} \qquad \ldots\ (6)$$

$$k_r = K \frac{Q^{\ddagger}}{Q_A} e^{-(E_o^{\ddagger} - E_{oA})} \left(\frac{kT}{2\pi m^{*}}\right)^{\frac{1}{2}} \frac{1}{\delta} \qquad \ldots\ (7)$$

Consider now the decomposition of a compound A having two isotopic varieties A_1 and A_2, where A_1 and A_2 are the light and heavy varieties respectively. The rate constants for the two species are:

$$k_1 = K_1 \frac{Q_1^{\ddagger}}{Q_{A_1}} e^{-(E_{o1}^{\ddagger} - E_{oA1})} \left(\frac{kT}{2\pi m_1^{*}}\right)^{\frac{1}{2}} \frac{1}{\delta_1} \qquad \ldots\ (8)$$

$$k_2 = K_2 \frac{Q_2^{\ddagger}}{Q_{A_2}} e^{-(E_{o2}^{\ddagger} - E_{oA_2})} \left(\frac{kT}{2\pi m_2^{*}}\right)^{\frac{1}{2}} \frac{1}{\delta_2} \qquad \ldots\ (9)$$

The zero of the energy scale for the normal molecules is best chosen as the minimum in the potential energy curve of the normal molecules. The minimum in the saddle of the potential energy surface of the activated complex is a suitable zero for the calculation of the ratio of the partition functions of the isotopic activated complexes (72) (73). Since the potential energy surfaces are believed to be identical for isotopic molecules, the ratio of the rate constants becomes:

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} \frac{Q_1^{\ddagger}}{Q_2^{\ddagger}} \frac{Q_{A_2}}{Q_{A_1}} \left(\frac{m_2^*}{m_1^*}\right)^{\frac{1}{2}} \qquad \ldots\ (10)$$

Letting $f' = \frac{Q_{A_2}}{Q_{A_1}}$ and $f^{\ddagger'} = \frac{Q_2^{\ddagger}}{Q_1^{\ddagger}}$,

we have

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} \frac{f'}{f^{\ddagger'}} \left(\frac{m_2^*}{m_1^*}\right)^{\frac{1}{2}} \qquad \ldots\ (11)$$

For a complete treatment the quantum mechanical tunnel effect should be considered. The effect is known to be small and need not be considered for elements heavier than hydrogen.

A fair approximation to the complete partition function is given as (74):

$$Q = ge\ gn \left\{\frac{(2\pi MkT)^{3/2}}{h^3} \cdot \frac{RT}{P}\right\} \left(\frac{8\pi^2 (8\pi^3 ABC)^{\frac{1}{2}} (kT)^{3/2}}{\sigma h^3}\right) \prod_i (1-e^{-u})^{-1} \qquad \ldots\ (12)$$

where M is the molecular weight of the molecule considered,

A,B,C are the three principal moments of inertia,

σ is the symmetry number,

ge, gn are the electronic and nuclear statistical weights respectively.

$u = \frac{hc\omega}{kT}$ where ω is the molecular vibrational frequency in $cm.^{-1}$.

In our case we are dealing with the ratios of partition functions for isotopic molecules. Thus we have

$$= \left(\frac{M_2}{M_1}\right)^{3/2} \left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{\frac{1}{2}} \frac{\sigma_1}{\sigma_2} \frac{e^{-\frac{u_{2i}}{2}}}{1-e^{-u_{2i}}} \frac{1-e^{-u_{1i}}}{e^{-\frac{u_{1i}}{2}}} \qquad \ldots\ (13)$$

and similarly for $f^{\ddagger}$.

The ratios of the moments of inertia are usually unknown for polyatomic molecules and are difficult to calculate. It has been the general practice to make use of the Teller-Redlich theorem (75). From this rule we find the

relationship

$$\left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{m_1}{m_2}\right)^{\frac{3}{2n}}\left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{\frac{1}{2}}\prod\frac{u_{1i}}{u_{2i}}=1 \qquad \ldots. (14)$$

where m_1 and m_2 are the atomic weights of the isotopic atoms being considered and n is the number of isotopic atoms reacting per molecule.

Using the result of equation (14) in equation (15), we define a new partition function ratio

$$f=\left(\frac{m_1}{m_2}\right)^{3/2}f'=\frac{\sigma_1}{\sigma_2}\prod_i\frac{u_{2i}}{u_{1i}}\;\frac{e^{\frac{-u_{2i}}{2}}}{1-e^{-u_{2i}}}\cdot\frac{1-e^{-u_{1i}}}{e^{\frac{-u_{1i}}{2}}} \qquad \ldots. (15)$$

This equation for the partition function ratio for two isotopic molecules has been simplified by Urey (75) and Bigeleisen and Mayer (76).

Urey has defined quantities x_i and δ_i such that

$$x_i=\frac{u_{1i}+u_{2i}}{2} \qquad \delta_i=\frac{u_{1i}-u_{2i}}{2}$$

and expanding in terms of the δ's he obtains

$$\ln f=\ln\frac{Q_2}{Q_1}=\ln\frac{\sigma_1}{\sigma_2}+\sum_i\ln\frac{u_{2i}}{u_{1i}}+\sum_i\left[\coth x_i\delta_i+\frac{1}{12}x_i\;(\coth^2 x_i-1)\delta^2\right] \qquad \ldots. (16)$$

Bigeleisen and Mayer have used a slightly different simplification. We shall use their equations here.

Let $u_{1i}=u_{2i}+\Delta u_i$ where u_{1i} corresponds to the lighter molecule. Then Δu_i is always positive and equation (15) becomes

$$f=\frac{\sigma_1}{\sigma_2}\prod_i\frac{u_{2i}}{u_{2i}+\Delta u_i}\cdot e^{\frac{u_i}{2}}\cdot\frac{1-e^{-(u_{2i}+\Delta u_i)}}{1-e^{-u_{2i}}} \qquad \ldots. (17)$$

For the case when Δu_i is small, which is true for every case but hydrogen, equation (17) can be simplified to give:

$$f=\frac{\sigma_1}{\sigma_2}\left[1+\sum_i\left(\frac{1}{2}-\frac{1}{u_{2i}}+\frac{1}{e^{u_{2i}}-1}\right)\Delta u_i\right] \qquad \ldots. (18)$$

$$=\frac{\sigma_1}{\sigma_2}\left[1+\sum_i G(u_{2i})\Delta u_i\right] \qquad \ldots. (19)$$

Where $G(u)=\left(\frac{1}{2}-\frac{1}{u_{2i}}+\frac{1}{e^{u_{2i}}-1}\right)$

Tables of G (u) values have been calculated by Bigeleisen and Mayer for u ranging from 0 to 25. Applying this value for f in equation (11) we obtain

$$\frac{k_1}{k_2} = \frac{\sigma_1}{\sigma_2} \cdot \frac{\sigma_2}{\sigma_1} \cdot \frac{K_1}{K_2} \cdot \left(\frac{m_2^*}{m_1^*}\right)^{\frac{1}{2}} \left[1 + \sum G(u_{21}) \Delta u_i - \sum G(u_{21})^{\ddagger} \Delta u_i^{\ddagger}\right] \quad (20)$$

for the case when Δu_i is small.

By making several approximations this equation may be used in calculating ratios of rate constants for isotopic molecules (67)(68)(77). For isotopic atoms heavier than hydrogen the ratio of the transmission coefficients is considered to be unity. In the present instance the symmetry numbers are considered to be the same for the isotopic molecule and its activated complex. We know very little about the molecular vibrations in the activated state so we neglect the term $G(u)^{\ddagger} \Delta u^{\ddagger}$. This in effect considers the activated state to consist of essentially free atoms. The value thus calculated will give an upper limit for the $\frac{k_1}{k_2}$ ratio. In certain cases involving a unimolecular decomposition, $\left(\frac{m_2^*}{m_1^*}\right)^{\frac{1}{2}}$ can be calculated assuming a simplified model of the activated complex. It is assumed that the m^*'s are merely the reduced mass of the two atoms involved in the bond being broken (78). If the fundamental vibration frequencies of the normal molecule and the isotopic shift caused by substitution by the heavier isotope are known, or can be calculated it is therefore possible to calculate approximate ratios of rate constants. Equation (20) has been used in this thesis to calculate a theoretical value for the isotope effect in C^{13} malonic acid.

PART I

C^{13} ISOTOPE EFFECT IN THE DECARBOXYLATION OF NORMAL MALONIC ACID

THEORY

Malonic acid containing a normal concentration of C^{13} consists of several isotopic varieties. The different species together with their approximate abundances are:

$C^{12}OOH$ | $C^{12}H_2$ | $C^{12}OOH$	97%	$C^{13}OOH$ | $C^{13}H_2$ | $C^{12}OOH$	0.02%
$C^{12}OOH$ | $C^{12}H_2$ | $C^{13}OOH$	2%	$C^{13}OOH$ | $C^{13}H_2$ | $C^{13}OOH$	0.0001%
$C^{12}OOH$ | $C^{13}H_2$ | $C^{12}OOH$	1%		

Those molecular species which occur to the extent of less than one percent are considered here as making a negligible contribution to the isotope effect.

The thermal decomposition of normal malonic acid may then be represented by the following equations:

$$C^{12}OOH\text{-}C^{12}H_2\text{-}C^{12}OOH \xrightarrow{k_1} C^{12}O_2 + C^{12}H_3C^{12}OOH \qquad (1)$$

$$C^{12}OOH\text{-}C^{13}H_2\text{-}C^{12}OOH \xrightarrow{k_2} C^{12}O_2 + C^{13}H_3C^{12}OOH \qquad (2)$$

$$\begin{array}{l} C^{13}OOH \\ | \\ C^{12}H_2 \\ | \\ C^{12}OOH \end{array} \xrightarrow{k_3} C^{13}O_2 + C^{12}H_3C^{12}COH \qquad (3)$$

$$C^{12}OOH \xrightarrow{k_4} C^{12}O_2 + C^{12}H_3C^{13}OOH \qquad (3')$$

The decomposition of malonic acid has been shown to be of first order (79) (80). Therefore at any time t

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3M_3^{\circ}(1-e^{-(k_3+k_4)t})}{(k_3+k_4)\left[M_1^{\circ}(1-e^{-k_1t}) + M_2^{\circ}(1-e^{-k_2t}) + \frac{k_4M_3^{\circ}}{k_3+k_4}(1-e^{-(k_3+k_4)t})\right]} \qquad (4)$$

where M_1°, M_2° and M_3° are the initial mole fractions of the different isotopic species of malonic acid in equations (1), (2), (3) and (3') respectively. When $t = \infty$, equation (4) becomes

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3M_3^{\circ}}{(k_3+k_4)\left[M_1^{\circ}+M_2^{\circ}+\frac{k_4M_3^{\circ}}{k_3+k_4}\right]} \qquad (5)$$

and when t is small, (4) becomes

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3M_3^{\circ}}{k_1M_1^{\circ} + k_2M_2^{\circ} + k_4M_3^{\circ}} \qquad (6)$$

Let α be the atom fraction of C^{13} occurring in the normal malonic acid used. If we assume that the ratio of the carbon isotopes is the same in the methylene and carboxyl positions (see p. 34) we can calculate the mole fraction of the three isotopic species of malonic acid in terms of α.

$$M_1^{\circ} = 1-3\alpha$$

$$M_2^{\circ} = \alpha$$

$$M_3^{\circ} = 2\alpha$$

Substituting these values in equations (5) and (6) and making the approximations $k_4 \approx k_3 \approx \frac{k_1}{2}$; $k_1 \approx k_2$ in the denominator we obtain

at $t = \infty$

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2k_3 \alpha}{(k_3+k_4)(1-\alpha)} \qquad (7)$$

or rearranging

$$\frac{k_4}{k_3} = \frac{2\alpha}{1-\alpha}\left[\frac{C^{12}O_2}{C^{13}O_2}\right] - 1 \qquad (7')$$

at t small

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2k_3\alpha}{k_1(1-\alpha)} \qquad (8)$$

or

$$\frac{k_1}{2k_3} = \frac{\alpha}{1-\alpha}\left[\frac{C^{12}O_2}{C^{13}O_2}\right] \qquad (8')$$

If the thermal decarboxylation of malonic acid is taken to completion, a mass spectrometric analysis of the CO_2 produced gives the values of $\frac{C^{12}O_2}{C^{13}O_2}$ in equation (7'). The ratio $\frac{\alpha}{1-\alpha}$ is obtained directly from the $\frac{C^{13}O_2}{C^{12}O_2}$ ratio in the CO_2 produced when a sample of the malonic acid is completely converted to CO_2. The ratio $\frac{k_4}{k_3}$ may be obtained in this way. The same ratio may also be obtained from a mass spectrometric analysis of the CO_2 formed on complete oxidation of the acetic acid produced. The equation obtained for the CO_2 of acetic acid oxidation is

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{\frac{2k_4\alpha}{k_3+k_4} + \alpha}{2(1-3\alpha) + \frac{2k_4\alpha}{k_3+k_4} + \frac{4k_3\alpha}{k_3+k_4} + \alpha} \qquad (9)$$

or solving for $\frac{k_4}{k_3}$

$$\frac{k_4}{k_3} = \frac{2 - \alpha\left[1 + \frac{C^{12}O_2}{C^{13}O_2}\right]}{3\alpha\left[1 + \frac{C^{12}O_2}{C^{13}O_2}\right] - 2} \qquad (9')$$

If the first CO_2 evolved from a decomposition experiment is collected and analyzed mass spectrometrically, the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio obtained may be substituted in equation (8') together with the previously determined value for $\frac{\alpha}{1-\alpha}$, and $\frac{k_1}{2k_3}$ obtained. Combination of the values obtained for $\frac{k_1}{2k_3}$ and $\frac{k_4}{k_3}$ will allow the calculation of $\frac{k_1}{k_3 + k_4}$ which is a measure of the relative reaction velocities of the two isotopic molecular species M_1^o and M_3^o.

It has been pointed out by J. Bigeleisen (81) that the last fraction of CO_2 evolved from a complete decarboxylation may be used to evaluate $\frac{k_1}{k_3 + k_4}$. If we consider the amounts of the relative species M_1^o, M_2^o and M_3^o remaining at time $t_{\infty-\epsilon}$ where ϵ is small, the abundance now becomes

$$M_{1_{t_{\infty-\epsilon}}} = M_1^o e^{-k_1 t} = (1-3\alpha)e^{-k_1 t}$$

$$M_{2_{t_{\infty-\epsilon}}} = M_2^o e^{-k_2 t} = \alpha e^{-k_2 t}$$

$$M_{3_{t_{\infty-\epsilon}}} = M_3^o e^{-(k_3 + k_4)t} = 2\alpha e^{-(k_3 + k_4)t}$$

Substituting these values in (5) and making the approximation $\alpha e^{-k_2 t} \approx \alpha e^{-k_1 t}$ in the denominator, we obtain on simplification

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{\frac{2\alpha}{1-2\alpha} e^{k_1 \frac{1-(k_3 + k_4)t}{k_1}}}{\left(1 + \frac{k_4}{k_3}\right)\left[1 + \left(k_4/k_3 \middle/ 1 + \frac{k_4}{k_3}\right)\frac{2\alpha}{1-2\alpha} e^{k_1\left[\frac{1-(k_3 + k_4)t}{k_1}\right]}\right]} \qquad ((10)$$

If the amount of malonic acid corresponding to the last CO_2 evolved is known, it is possible to get a further check on $\frac{k_1}{k_3+k_4}$ if the assumption is made that $k_1 \cong k$, the over-all rate constant.

EXPERIMENTAL

Apparatus and Reagents

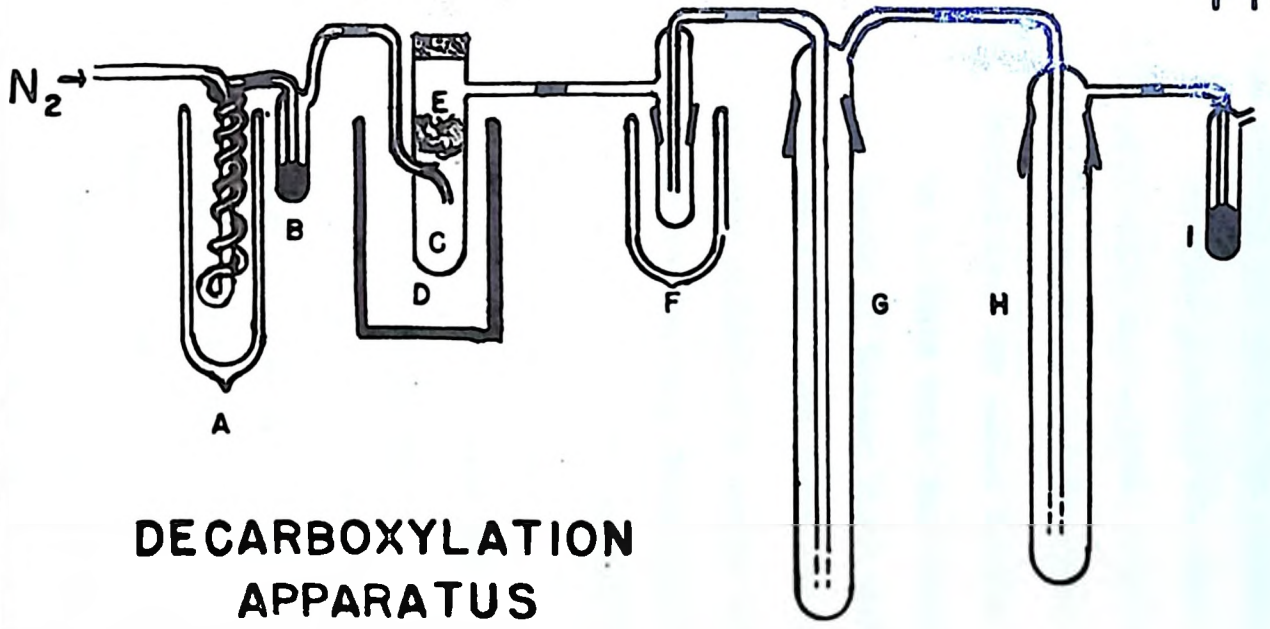
The decarboxylation apparatus is shown in Fig. 1. It consisted essentially of a test tube-like reaction vessel C, cold traps A and F, two mercury bubblers B and I and two barium hydroxide bubblers G and H. An oil bath controlled to $\pm 0.5^{\circ}C$ of the reaction temperature was also used.

The dry oxidation train used for preparing carbon dioxide samples from organic compounds is shown in Fig. 2. It consisted of a potassium hydroxide bubbler A, cold trap B, a quartz combustion tube containing copper oxide E, together with a micro-combustion boat C, a furnace D and two barium hydroxide bubblers F and G. A mercury bubbler H was included at the end of the train.

A high vacuum line, Fig. 3, was used in the purification of carbon dioxide samples. It consisted of a manifold connected through a cold trap to a two-stage Mercury diffusion pump, which was backed by a Welch 1400 Duoseal rotary pump.

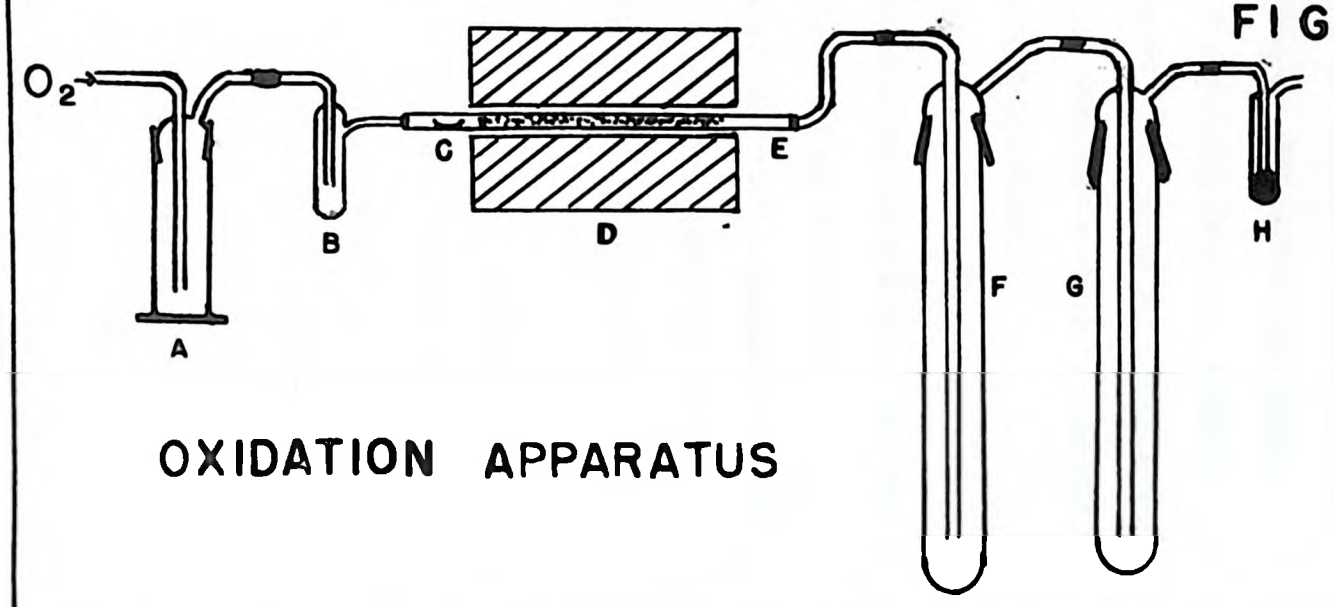
Attached to the manifold were traps T_1 and T_2 and a mercury manometer M. The manifold was fitted with ground glass joints so that special pieces of apparatus could be fitted on and removed when necessary. These require separate discussion. A is an apparatus for releasing carbon dioxide from barium carbonate, and B is used in the wet oxidation of organic compounds. Their operation will be discussed later.

FIG. 1



DECARBOXYLATION APPARATUS

FIG. 2



OXIDATION APPARATUS

raised around the reaction vessel. The acetic acid was collected in trap F and the carbon dioxide was collected in the barium hydroxide bubblers G and H. After allowing sufficient time for the reaction to go to completion (about three hours at 138°C) the barium hydroxide bubblers were removed and the barium carbonate filtered off, washed and dried.

Wherever possible the acetic acid resulting from the complete decarboxylation was oxidized over hot copper oxide to carbon dioxide and water. The analysis of this carbon dioxide provided a check on the ratio $\frac{k_4}{k_3}$ obtained from the carbon dioxide of decarboxylation.

In a single experiment designed to measure the $\frac{k_1}{k_3+k_4}$ ratio, a 100 gm. sample of Eastman Kodak certified chemical malonic acid was decomposed at 136°C. The first and last fractions of carbon dioxide evolved were collected as barium carbonate. In later experiments, 5 gm. samples of British Drug House malonic acid were decomposed at various temperatures between 137°C and 199°C. In these experiments the carbon dioxide only was collected.

In order to evaluate the quantity α, the C^{13} concentration of the starting malonic acid, two procedures were adopted. Samples of malonic acid used in Runs Z, 3F-8F and 3L-8L were oxidized to carbon dioxide by a wet oxidation procedure. The oxidizing solution was a modification (82) of that used by Van Slyke and Folch (83). The oxidation was accomplished on the high vacuum line (Fig. 3) using the wet oxidation reaction vessel B. This was attached to the vacuum line through a 12/30 ground glass joint J_1. Stopcock S-5 and the 19/38 ground glass joint J_2 were lubricated with a viscous solution of phosphoric anhydride in syrupy phosphoric acid. The oxidation solution was placed above

stopcock S-5. About 50 mg. of malonic acid were placed in the reaction vessel and the vessel evacuated. The reaction vessel was then shut off from the vacuum line and the oxidation solution added through stopcock S-5, care being taken to prevent air from getting in. The reaction vessel was gently warmed until the evolution of carbon dioxide seemed complete. After it had cooled somewhat, stopcock S-4 was closed and S-1 opened. The carbon dioxide was then frozen down in trap T_1 with liquid air. S-1 was closed and the oxidation apparatus removed from the line. Gases non-condensable in liquid air were pumped off and the carbon dioxide purified by two fractionations off dry ice-acetone baths. The purified carbon dioxide was then frozen down in a sample tube R equipped with a break seal, and removed for mass spectrometric analysis.

For the remainder of the runs, standard oxidation samples were prepared by oxidation of malonic acid in a quartz combustion tube containing copper oxide at 700-800°C by a method similar to that described by Rittenberg (84). The boat containing the malonic acid C (Fig. 2) was heated with a gas flame and the carbon dioxide and acetic acid vapor carried over the hot copper oxide by a stream of pure nitrogen. The carbon dioxide formed was again collected as barium carbonate.

In the oxidation of acetic acid from the decarboxylation runs to carbon dioxide and water, the dry oxidation procedure was adopted. The acetic acid was placed in the micro combustion boat and the procedure as outlined above was followed. As before, the carbon dioxide was collected as barium carbonate.

In order to check the validity of the assumption that the ratio of the carbon isotopes was the same in the methylene and carboxyl positions

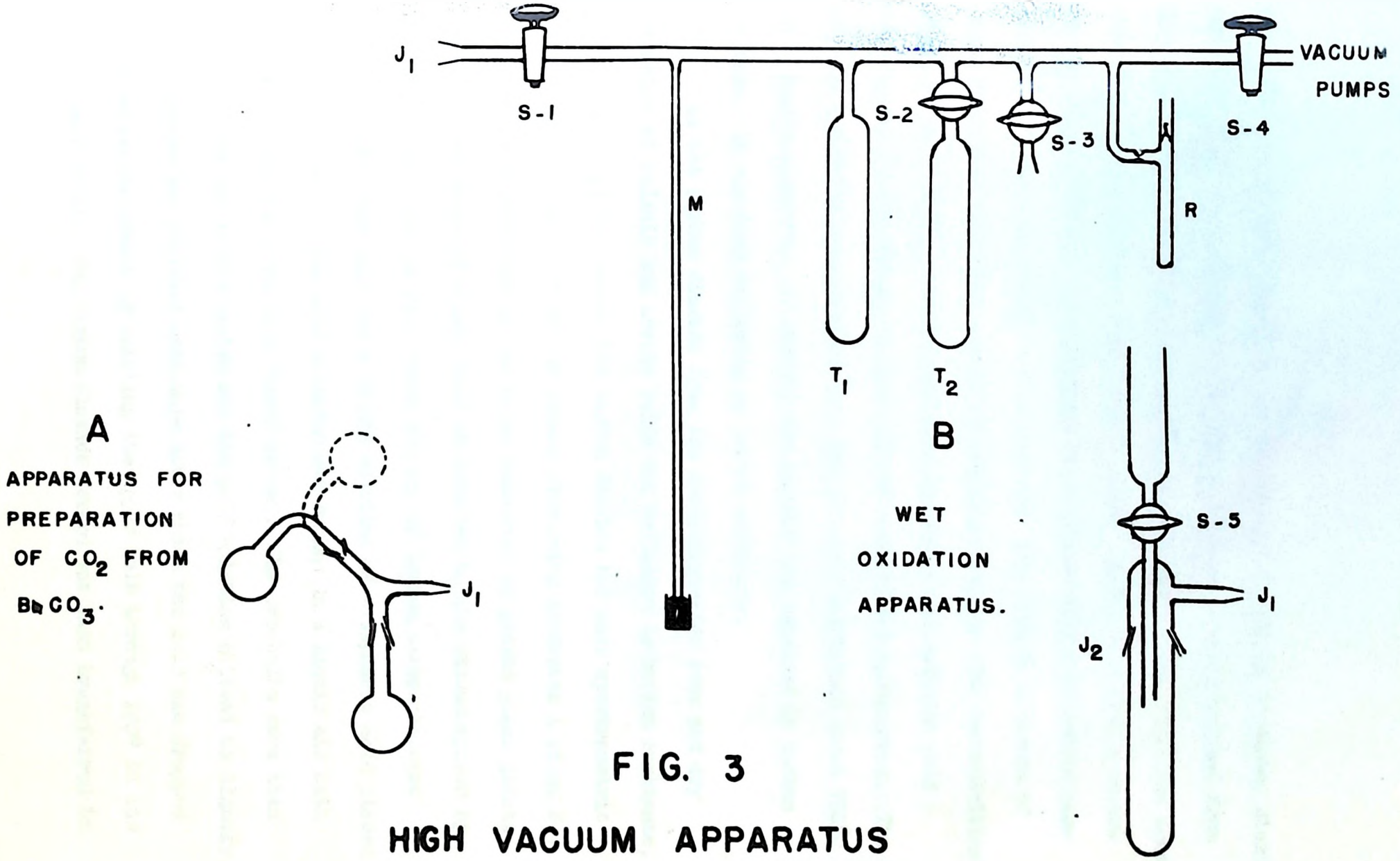


FIG. 3

HIGH VACUUM APPARATUS

of malonic acid, the methylene carbon atom was converted to carbon dioxide and its $\frac{C^{12}O_2}{C^{13}O_2}$ ratio compared with the average ratio as determined from the carbon dioxide obtained by oxidation of malonic acid. This was done stepwise, using Eastman Kodak malonic acid. Acetic acid from a decarboxylation experiment was converted to sodium acetate with sodium carbonate. The sodium acetate was heated with soda lime in a stream of pure nitrogen to produce methane of methylene origin. The decomposition products were passed through potassium hydroxide and sulfuric acid bubblers to remove carbon dioxide and any unsaturated hydrocarbon. The methane and nitrogen continued over copper oxide maintained about 750°C in a quartz tube (Fig. 2) whereby the methane was oxidized to carbon dioxide. It was then collected as barium carbonate.

As the carbon dioxide from the decarboxylation runs and dry oxidation of malonic and acetic acids was collected as barium carbonate, it was necessary to recover the carbon dioxide for mass spectrometric analysis. This was done on the vacuum line using apparatus A (Fig. 3). This apparatus consisted of two bulbs connected by ground glass joints to a Y-shaped coupling which could be attached to the vacuum system by a ground glass joint at J_1. About 100 mg. of barium carbonate were placed in the lower bulb and a dilute solution of phosphoric acid placed in the upper bulb. The acid solution was frozen in a liquid air bath and the system evacuated to a "hard" vacuum. The two bulbs were then shut off from the vacuum system and the acid solution allowed to liquefy. The procedure was repeated once more after which the acid was dropped on the barium carbonate by rotating the upper bulb through 180° in its ground glass joint. The carbon dioxide formed was then transferred to

trap T_1 and purified as before by two fractionations off a dry ice-acetone bath. It was then frozen down in a sample tube R and removed from the line for mass spectrometric analysis.

Mass Spectrometry

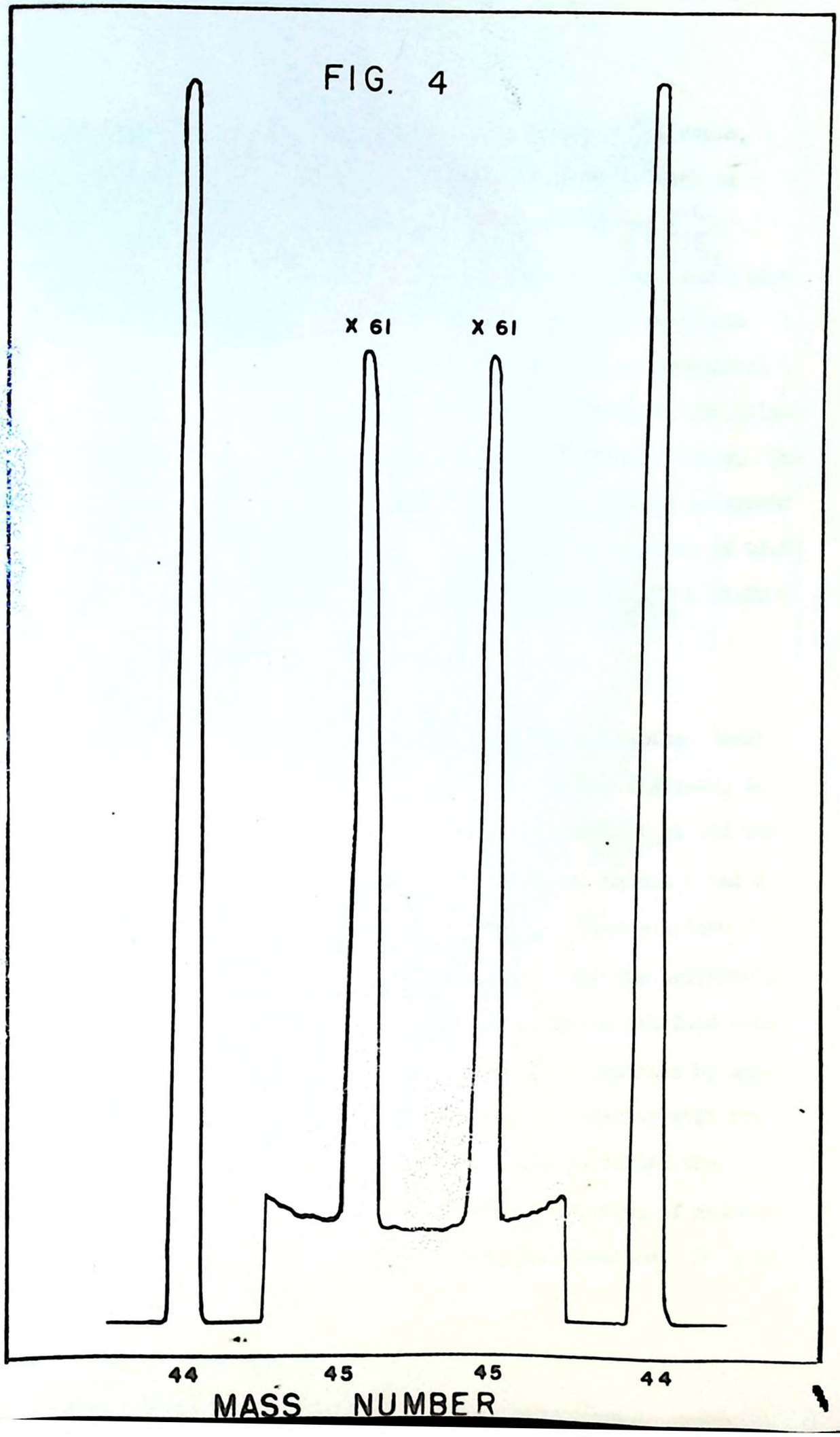
All carbon dioxide samples were analyzed with a 180° direction focusing high precision mass spectrometer. The ion currents were amplified by a total feedback D.C. amplifier, using a 954 electrometer tube in the first stage of amplification. The output was fed into a Leeds and Northrup Speedomax recorder. The $\frac{C^{12}O_2}{C^{13}O_2}$ ratio was obtained from the ratio of masses 44/45 ion currents after applying a suitable correction for the contribution to the mass 45 ion current by the molecular species $C^{12}O^{16}O^{17}$, i.e.,

$$\frac{C^{12}O^{16}O^{16}}{C^{13}O^{16}O^{16}} = \frac{1}{\frac{45}{44} - \frac{C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16}}} = \frac{1}{\frac{45}{44} - 0.0088}$$

Each carbon dioxide sample was measured relative to a standard sample, the standard in this case being carbon dioxide from an oxidation run on the malonic acid used. The procedure was to analyze the standard, the sample, and the standard again as rapidly as possible. The analysis was considered to be satisfactory only if the standards checked within 0.1‰, the precision of a single analysis. Automatic magnetic scanning was used throughout. A single analysis consisted of six or seven spectrograms, each spectrogram consisting of masses 44 and 45, and then by reversing the direction of scan, masses 45 and 44. A typical spectrogram is shown in Fig. 4.

By this method a relative precision of 0.1‰ was readily attainable

FIG. 4



between standard and sample. The absolute value of the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio, however, varied from day to day and from week to week by as much as one percent. It was assumed that the absolute value for the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio of the standard was a constant, and that the variations found were caused by fluctuations in the mass spectrometer. In order to relate mass spectrometer ratios obtained on different days, it was convenient to assign a suitable value to the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio of the standard, and relate the ratios obtained for the samples on different days to this value. The value of the ratio chosen for the standard was 92.77. Thus on a certain day, if a sample gave a $\frac{C^{12}O_2}{C^{13}O_2}$ ratio of 91.20 relative to a ratio of 92.50 for the standard, the value used for the sample would be $\frac{92.77}{92.50} \times 91.20$ = 91.47 relative to 92.77.

RESULTS AND DISCUSSION

The results obtained from the decarboxylation of Eastman Kodak malonic acid are shown in Table I. The mass spectrometer analyses, in terms of the $\frac{C^{12}}{C^{13}}$ ratio of the carbon dioxide of decarboxylation and the carbon dioxide from acetic acid oxidation are given in columns 2 and 3 respectively. The ratio $\frac{k_4}{k_3}$ in column 4 is calculated from equation (7'), p. 21, using the mass spectrometer ratio of column 2 and the previously determined ratio $\frac{\alpha}{1-\alpha}$, the $\frac{C^{13}}{C^{12}}$ ratio of the carbon dioxide obtained from malonic acid oxidation. The same ratio in column 5 is obtained by substituting the mass spectrometer ratio from column 3, together with the value of α in equation (9'), p. 22. This ratio will be called the "intramolecular effect" since it deals with only one species of malonic acid, namely, the one containing a C^{13} in a carboxyl position. It gives

TABLE I

Intramolecular Isotope Effect in Normal Malonic Acid*

Run	$\frac{C^{12}O_2}{C^{13}O_2}$**		$\frac{k_4}{k_3}$	
	CO_2 (Decarboxylation)	Acetic Acid	CO_2	Acetic Acid
50-1	93.96	-----	1.026	-----
50-2	93.87	-----	1.024	-----
50-3	94.22	92.33	1.031	1.019
50-4	94.43	92.24	1.036	1.023
II	-----	92.22	-----	1.024
Z-5	93.88	92.06	1.024	1.031
Mean			1.028	1.024
			1.026±	0.002

*Eastman Kodak malonic acid, runs at 139° ± 0.5°C.

**All $\frac{C^{12}O_2}{C^{13}O_2}$ ratios are relative to the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio in a normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e., $\frac{(1-\alpha)}{\alpha} = 92.77$.

a measure of the relative probabilities of rupture of a $C^{12}-C^{12}$ bond as compared with a $C^{12}-C^{13}$ bond in the same molecule. The deviation of this ratio from unity is a measure of the isotope effect.

The value of the $\frac{k_4}{k_3}$ ratio as obtained from the isotopic analysis of the carbon dioxide from oxidation of the acetic acid of decarboxylation (column 5) is seen to be lower than that obtained from the carbon dioxide of decarboxylation. An error of about 0.2% in the determination of $\frac{\alpha}{1-\alpha}$ could cause this variation. The average of the two values, namely, 1.026 ±0.002 should be more reliable than the results for either the carbon dioxide or acetic acid.

In Table II is shown the influence of temperature on the $\frac{k_4}{k_3}$ ratio, using certified chemical malonic acid supplied by the British Drug House. It is seen that this ratio is constant in the temperature range studied, a result which is in excellent agreement with theory.

Considering equation (3) and (3'), p. 20, the theoretical ratio $\frac{k_4}{k_3}$ is given by

$$\frac{k_4}{k_3} = \left(\frac{m_3^*}{m_1^*}\right)^{\frac{1}{2}} \left[1 + \sum G(u)_{3,4} (u_4-u_3) - G(u)^{\ddagger}_{3,4} (u_4^{\ddagger}-u_3^{\ddagger}) \right]$$

However, since we are dealing with only one molecular species, $u_4 = u_3$ and $G(u)_{3,4} (u_4-u_3) = 0$. As we know little about the behaviour of the activated complex, we shall neglect its contribution to the ratio of rate constants. As a first approximation then, $\frac{k_4}{k_3} = \left(\frac{m_3^*}{m_4^*}\right)^{\frac{1}{2}}$.

For this reaction we may represent the m^*'s as being the reduced mass of the two atoms involved in the bond being broken. Thus $m_3^* = \mu\, C^{12} - C^{13}$ and $m_4^* = \mu\, C^{12} - C^{12}$. Therefore $\frac{k_4}{k_3} = 1.020$.

TABLE II

Influence of Temperature on Intramolecular Effect*

Run	Temperature °C	$\frac{C^{12}O_2}{C^{13}O_2}$**	$\frac{k_4}{k_3}$
50-5	138° ± 0.5°	93.70	1.020
50-6	151° "	93.70	1.020
50-8	174° "	93.88	1.024
50-9	199° "	93.74	1.021
Mean			1.021 ± 0.001

*B.D.H. malonic acid

**All $\frac{C^{12}O_2}{C^{13}O_2}$ ratios are relative to the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio in a normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e., $(1-\alpha)/\alpha = 92.77$.

TABLE III

$\frac{C^{12}O_2}{C^{13}O_2}$ Ratio of Methylene Carbon in E.K. Malonic Acid

Run	$\frac{C^{12}O_2}{C^{13}O_2}$*	
	CO_2 from Malonic Acid Oxidation	CO_2 from Methylene Carbon
I	92.77	92.79
II	92.77	92.80

*All $\frac{C^{12}O_2}{C^{13}O_2}$ ratios are relative to the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio in a normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e., $\frac{1-\alpha}{\alpha} = 92.77$.

for $\frac{k_4}{k_3}$ gives $\frac{k_1}{k_3+k_4}$. It is implied that the amount of carbon dioxide taken is small enough so that the isotopic content of the remaining malonic acid remains unchanged. Deviations from unity of the ratio $\frac{k_1}{k_3+k_4}$ are a measure of the "intermolecular isotope effect", since we are dealing with the relative rates of reaction of two species of malonic acid, one containing only C^{12} carbon atoms and the other containing a C^{13} carbon in a carboxyl position.

The results of the single run made with E.H. malonic acid at 135° to determine the ratio $\frac{k_1}{k_3+k_4}$ are given in Table IV. The effect of temperature on this ratio is shown in Tables V and VI, using E.E.H. malonic acid. Tables V and VI both indicate that in the temperature range studied, the isotope effect is constant. It should be pointed out that the ratio $\frac{k_1}{k_3+k_4}$ found in Table VI is calculated from an isotopic analysis of the last fraction of carbon dioxide evolved in a decarboxylation run (see equation (10), p. 32). The results obtained here show a greater spread and an over-all lower isotope effect than that obtained from the first carbon dioxide evolved (Table V). Since any experimental errors would tend to diminish the isotope effect, the larger value found in Table V is thought to be more reliable.

The apparent lack of a temperature coefficient for the intermolecular effect is, at first, surprising since in this case we are comparing the rates of reaction of two isotopic species of malonic acid and temperature dependent terms do appear in the theoretical expression for the ratio of rate constants. For the reactions (1) and (3), pp. 19 and 20, $\frac{k_1}{2k_3} = \frac{K_1}{K_3}\left(\frac{m_3^*}{m_1^*}\right)^{\frac{1}{2}}\left[1+\sum G(u)_{3,1}(u_1-u_3)-\sum Gu_{3,1}^{*}(u_1^{*}-u_3^{*})\right]$

TABLE IV

Intermolecular Isotope Effect in Normal Malonic Acid*

Sample	$\frac{C^{12}O_2}{C^{13}O_2}$**	$\frac{k_1}{2k_3}$	$\frac{k_1}{k_3+k_4}$***
First CO_2 evolved	97.05	1.046	1.033
Last CO_2 evolved	86.83		

*Eastman Kodak malonic acid, runs at 138° ± 0.5°C.

**$\frac{C^{12}O_2}{C^{13}O_2}$ ratios are relative to malonic acid standard as 92.77.

***Assuming $\frac{k_4}{k_3} = 1.026$.

TABLE V

Influence of Temperature on Intermolecular Isotope Effect

Using First Carbon Dioxide Evolved*

Run	Temperature °C	$\frac{C^{12}O_2}{C^{13}O_2}$**	$\frac{k_1}{2k_3}$	$\frac{k_1}{k_3+k_4}$***
3F	137° ± 0.5°	95.94	1.034	1.023
5F	149° "	96.58	1.041	1.030
7F	173° "	95.88	1.034	1.023
8F	196° "	96.13	1.036	1.025
Mean			1.036 ± 0.001	1.025 ± 0.001

*B.D.H. malonic acid

**All $\frac{C^{12}O_2}{C^{13}O_2}$ ratios are relative to the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio in a normal malonic acid combustion sample assigned a value of 92.77, i.e., $\frac{1-\alpha}{\alpha} = 92.77$.

***Assuming $\frac{k_4}{k_3} = 1.021$.

Although the vibrational frequencies of malonic acid are not well known, approximate frequencies can be calculated from force constants and an approximate value for this ratio of rate constants obtained. It is found that the calculated ratio $\frac{k_1}{2k_3}$ is 1.0213 at 138°C and 1.0212 at 200°C (see appendix). Although the predicted value does not agree with the $\frac{k_1}{2k_3}$ ratio of 1.036 found experimentally, it does indicate that the variation with temperature of the $\frac{k_1}{2k_3}$ or $\frac{k_1}{k_3+k_4}$ ratio would be below the limits of detection in these experiments.

As with $\frac{k_4}{k_3}$, the experimental value obtained for $\frac{k_1}{k_4+k_3}$, using E.K. malonic acid (Table IV), is higher than that found using B.D.H. malonic acid at 138°C. The same explanation as before could be advanced, but since only one experiment was done using the E.K. acid, the difference cannot be considered too significant.

In Table VII, the results obtained in this investigation are compared with the results obtained by Bigeleisen and Friedman. It is seen that the results with B.D.H. malonic acid give rate ratios which closely check those of Bigeleisen and Friedman. (69)

The ratio $\frac{k_1}{2k_3}$, as we have mentioned earlier, is a measure of the rupture probability of a $C^{12}-C^{12}$ bond in the molecule containing only C^{12} carbon atoms as compared with the rupture probability of a $C^{12}-C^{13}$ bond in the molecule containing a C^{13} carboxyl carbon. The ratio $\frac{k_1}{2k_4}$ compares the rupture probabilities for the $C^{12}-C^{12}$ bond in the two molecular species considered. By simple arithmetic it is seen that $\frac{k_1}{2k_4} = 1.015$ for B.D.H. malonic acid. That is to say, there is a greater probability of rupture of the $C^{12}-C^{12}$ bond in the molecular species

TABLE VII

Comparison of Results

	Bigeleisen and Friedman	Present Work		Theory (Bigeleisen)
		B.D.H. Malonic	E.K. Malonic	
$\frac{k_1}{2k_3}$	1.057	1.036	1.046	1.021
$\frac{k_4}{k_3}$	1.020	1.021	1.026	1.020

containing only C^{12} carbon atoms than in the species containing the C^{13} carboxyl carbon. This result is interesting as Stevenson et al (60) found a lesser probability of rupture of the $C^{12}-C^{12}$ bond in $C^{12}H_3-C^{12}H_2-C^{12}H_3$ than in $C^{12}H_3-C^{12}H_2-C^{13}H_3$ in a mass spectrometer by electron impact, due consideration being given to the fact that there are two $C^{12}-C^{12}$ bonds in the former molecule. Stevenson has explained their results as being due to a greater increase in the probability of formation of the ion fragment $C^{13}H_3-C^{12}H_2^+$ in the propane 1-C^{13} than the decrease in the dissociation probability of propane 1-C^{13}. (56)

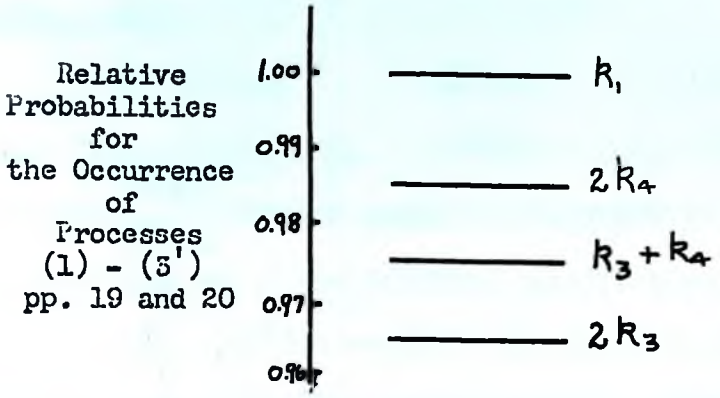
Stevenson's reasoning suggests an analogous situation in the unimolecular decomposition reaction. It is well known that the effect of increased isotopic mass is to lower the vibrational frequency of a molecule. This serves to increase the activation energy for a heavy isotopic species. Consider now our molecular isotopic species of malonic acid.

The ratio $\frac{k_1}{k_3+k_4}$ tells us that the lighter molecule reacts 2.5% faster than the heavier molecule. By the reasoning above, this is due to the lower zero point energy, or, if the molecules are not all in the zero level, the lower vibrational amplitudes of the heavier species. However, for the heavier species, there are two paths of decomposition from the activated state. The one which will be preferred will be the one which places the products in their lowest energy states. The $\frac{k_2}{k_3}$ ratio of 1.021 shows that the preference is given to the bond rupture which places the C^{13} in the acetic acid. This is analogous to saying that the $C^{12}-C^{12}$ bond is the weaker of the two in the C^{13} species of malonic acid. The activated complex is considered to have one vibrational

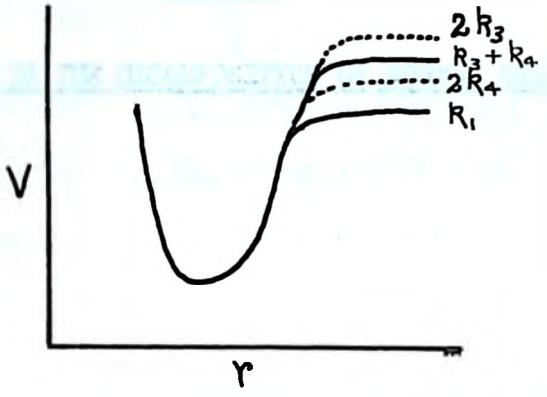
degree of freedom replaced by a translational degree of freedom along the reaction co-ordinate. The bond involved may be thought of as loosely bound, having no vibrational energy, and subject to decomposition at any instant. Now, depending on whether this loose bond is formed of a C^{12}-C^{12} linkage or a C^{12}-C^{13} linkage, there will be different zero point energies in the activated state for the two forms of the C^{13} molecule, and the bond rupture will be favoured which leaves the products with the lowest energy. This is equivalent to saying that the zero point energy of the products affects the way in which the complex breaks up, although the actual rate-controlling step occurs in the activated complex. By this mechanism, we can explain the effects found in malonic acid.

Two effects contribute to the $\frac{k_1}{2k_3}$ ratio. A higher activation energy for the heavier molecule decreases the reactivity of this molecular species. Of the heavier molecules which do react, the probability of rupture of the C^{12}-C^{13} bond is decreased as this bonding in the acetic acid formed gives a lower zero point energy. Consequently, we obtain the largest effect, 1.036, for $\frac{k_1}{2k_3}$. On the other hand, the $\frac{k_1}{2k_4}$ ratio is due to two opposing effects. The increased activation energy of the heavier molecule decreases its reactivity as before. However, of the reacting heavier molecules, the probability of rupture of the C^{12}-C^{12} bond will be increased due to the formation of a C^{12}-C^{13} bonding in the acetic acid. Thus the effect of increased activation energy will be decreased. As is to be expected, we find that $\frac{k_1}{2k_4}$ is smaller than either $\frac{k_1}{2k_3}$ or $\frac{k_1}{k_3+k_4}$.

The rupture probabilities of the different processes relative to process (1), p. 19, may be represented diagramatically as



Since the relative rupture probabilities are a function of the over-all activation energy, these results may be represented on a potential energy curve.



The effects of different zero point energies of the two molecular species have been incorporated into the potential energy curves. In this latter diagram, if the over-all activation energy for the process represented by k_1 is unity, the other processes $2k_4$, k_3+k_4, $2k_3$ will be represented as having successively larger activation energies.

It is conceivable that a reaction could occur where the effect of the zero point energy of the products is sufficient to compensate for the increased activation energy of the heavier molecule. If this were true in malonic acid, $\frac{k_1}{2k_4}$ would be less than unity.

PART II

C^{13} ISOTOPE EFFECT IN THE DECOMPOSITION OF NORMAL OXALIC ACID

THEORY

Normal oxalic acid consists of three isotopic species involving carbon, namely:

$$\begin{matrix} C^{12}OOH \\ | \\ C^{12}OOH \end{matrix} \qquad \begin{matrix} C^{12}OOH \\ | \\ C^{13}OOH \end{matrix} \qquad \begin{matrix} C^{13}OOH \\ | \\ C^{13}OOH \end{matrix}$$

Since the $\begin{matrix} C^{13}OOH \\ | \\ C^{13}OOH \end{matrix}$ species occurs to the extent of only 0.01%, its presence will be neglected in the following calculations.

Oxalic acid decomposes in the presence of concentrated sulfuric acid into carbon dioxide, carbon monoxide and water. For the two species considered we have:

$$\begin{matrix} C^{12}OOH \\ | \\ C^{12}OOH \end{matrix} \xrightarrow{k_1} C^{12}O_2 + C^{12}O + H_2O \qquad (1)$$

$$\begin{matrix} C^{12}OOH \\ | \\ C^{13}OOH \end{matrix} \xrightarrow{k_2} C^{13}O_2 + C^{12}O + H_2O \qquad (2)$$

$$\begin{matrix} C^{12}OOH \\ | \\ C^{13}OOH \end{matrix} \xrightarrow{k_3} C^{12}O_2 + C^{13}O + H_2O \qquad (2')$$

Since the decomposition is kinetically of the first order (85), we may write

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_2 Ox_2^o (1-e^{-(k_2+k_3)t})}{(k_2+k_3)\left[Ox_1^o (1-e^{-k_1 t}) + Ox_2^o (1-e^{-(k_2+k_3)t}) \frac{k_3}{k_2+k_3} \right]} \qquad (3)$$

where Ox_1^o and Ox_2^o are the two isotopic species considered in equation (1), (2) and (2') respectively. When $t = \infty$, we have

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_2 Ox_2^o}{(k_2+k_3)\left[Ox_1^o + \frac{k_3}{k_2+k_3} Ox_2^o \right]} \qquad (4)$$

and when t is small,

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_2 Ox_2^o}{k_1 Ox_1^o + k_3 Ox_2^o} \qquad (5)$$

If we let α equal the average concentration of C^{13} in the oxalic acid, we have

$$Ox_1^o = 1 - 2\alpha$$

$$Ox_2^o = 2\alpha$$

Substituting these values in (4) and (5) and making the approximations $k_2 \approx k_3 \approx \frac{k_1}{2}$ in the denominator, we have, for $t = \infty$

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2\ k_2\ \alpha}{(k_2+k_3)\ (1-\alpha)} \qquad (6)$$

or solving for $\frac{k_2}{k_3}$,

$$\frac{k_2}{k_3} = \frac{1}{\frac{2\alpha}{1-\alpha}\left[\frac{C^{12}O_2}{C^{13}O_2}\right] - 1} \qquad (6')$$

and for t small,

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2\ k_2\ \alpha}{k_1(1-\alpha)} \qquad (7)$$

or

$$\frac{k_1}{2k_2} = \frac{\alpha}{1-\alpha}\left[\frac{C^{12}O_2}{C^{13}O_2}\right] \qquad (7')$$

The same type of equations can be developed for the carbon monoxide produced. In this case we find for $t = \infty$,

$$\frac{k_2}{k_3} = \frac{2\alpha}{1-\alpha}\left[\frac{C^{12}O}{C^{13}O}\right] - 1 \qquad (8)$$

and for t small,

$$\frac{k_1}{2k_3} = \frac{\alpha}{1-\alpha}\left[\frac{C^{12}O}{C^{13}O}\right] \qquad (9)$$

The ratio $\frac{C^{12}O_2}{C^{13}O_2}$ in equation (6') is obtained from a mass spectrometric

analysis of the carbon dioxide produced when the decomposition is carried to completion. The same ratio in equation (7') is obtained from a similar analysis of the first carbon dioxide evolved in a decomposition experiment. A mass spectrometric analysis of the carbon dioxide produced when a sample of the oxalic acid used is completely oxidized, provides the value of $\frac{\alpha}{1-\alpha}$. Combination of equations (6') and (7') enabled the calculation of $\frac{k_1}{k_2+k_3}$.

EXPERIMENTAL

Apparatus and Reagents

The oxalic acid decomposition line is shown in Fig. 5. The decomposition vessel R consisted of two parts, a lower test tube-like reaction vessel for the oxalic acid, and an upper bulb for the sulfuric acid. The reaction vessel was connected through the trap T to two sample lines S_1 for collecting the carbon dioxide, and S_2 for oxidizing the carbon monoxide and collecting it as carbon dioxide. Both sample lines could be connected to a manifold containing a mercury manometer. The manifold was connected to the vacuum pumps through ST-1. The carbon monoxide sample line consisted of an ignition flask F and an oxygen generator O. The ignition flask was a 500 ml. bulb containing a nichrome filament sealed into a ground glass insert. The oxygen generator was a 250 ml. bulb containing potassium chlorate. The total volume of S_2 was purposely made large in order to remove as much of the carbon monoxide from the reactor as possible. The reaction vessel, heated by an oil bath, maintained to within $\pm 1^{\circ}C$ of the reaction temperature, by a Dekhotinsky thermo-regulator.

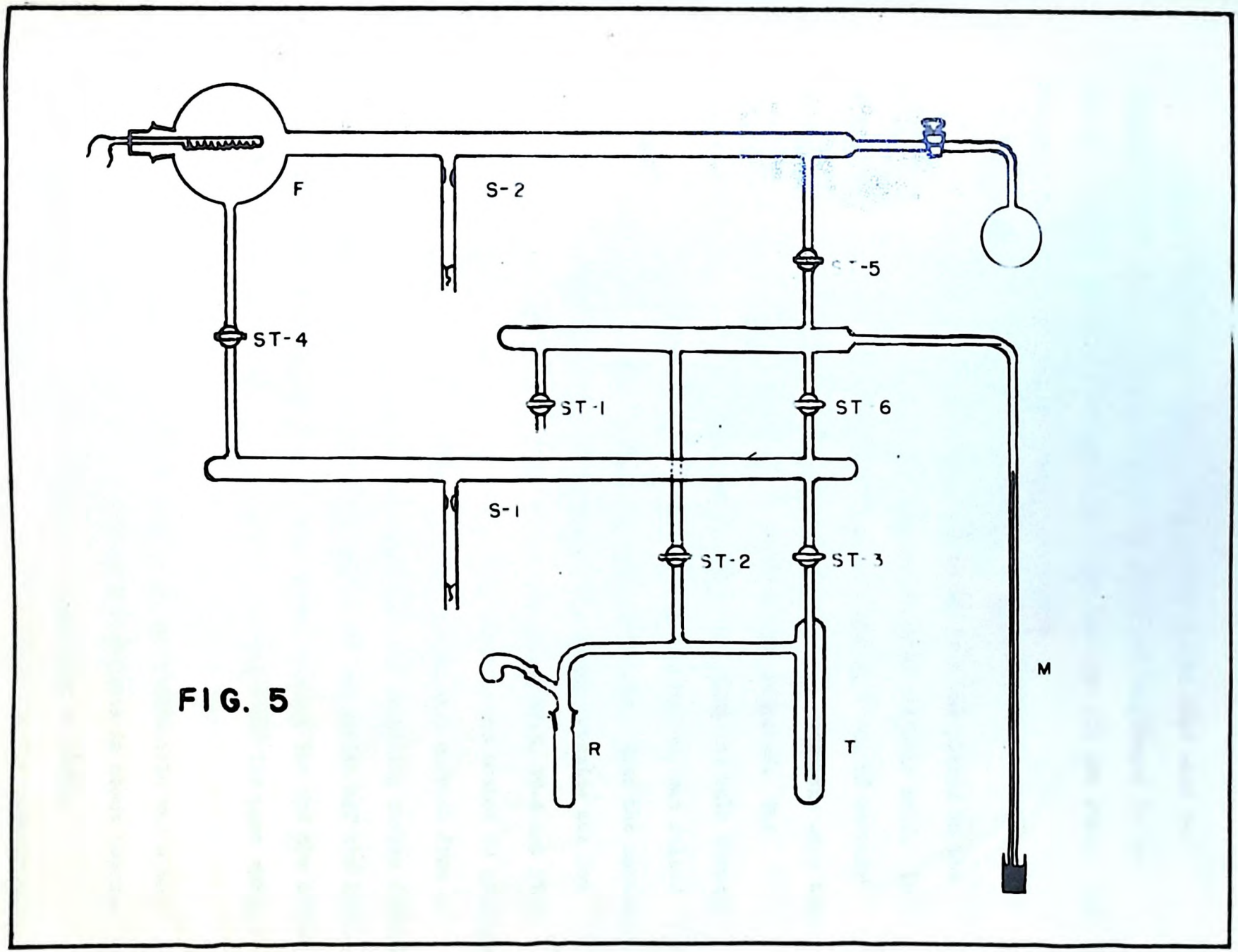


FIG. 5

OXALIC ACID DECOMPOSITION LINE

About 100 gm. of ordinary high-grade oxalic acid were recrystallized three times from distilled water and dehydrated in the vacuum line. This stock of oxalic acid was used for all the runs. The sulfuric acid used was the concentrated reagent.

Procedures

For a typical run, a sample of oxalic acid was placed in the reactor and the acid bulb filled with concentrated sulfuric acid. The entire line was evacuated to a pressure of about 10^{-5} mm. of mercury and a liquid air bath was placed around trap T. All stopcocks were then closed, but ST-2 leading from the reactor to the manometer. The sulfuric acid was added to the oxalic acid by rotating the bulb through 180°, and the oil bath, preset to the desired temperature, was raised around the reaction vessel containing the oxalic acid. When the manometer indicated that the reaction was complete, the carbon monoxide was let into S_2 through stopcocks ST-3 and ST-4. Stopcocks ST-3, ST-4 and ST-2 were closed and ST-5 opened. The potassium chlorate was heated to generate an excess of oxygen. The filament in F was heated with current from a 12-volt transformer to flash the gas mixture. The resulting carbon dioxide was frozen down in a sample tube S-2, pumped off and sealed off the line. The liquid air on the trap T was then replaced with dry ice and the carbon dioxide was frozen down in S-1, pumped on and sealed off for mass spectrometric analysis.

Preliminary runs indicated that 0.06 gm. oxalic acid was a convenient amount to use. The decomposition was complete in about twenty-four hours. Two runs were carried out to completion at 100°C.

In order to prepare a carbon dioxide sample for the determination

of the C^{13} concentration of the oxalic acid used, a sample of oxalic acid was oxidized to carbon dioxide, using the wet oxidation procedure described for malonic acid (p. 25).

One run was carried out to determine the ratio $\frac{k_1}{k_2+k_3}$. A 3 gm. sample of oxalic acid was decomposed in sulfuric acid at 100°C. The first two or three ml. of carbon dioxide were removed ten minutes after starting the run; the last few ml. of carbon dioxide formed at the end of the run were also collected. The carbon monoxide formed in these runs was not collected.

The procedure for the mass spectrometric analyses of the carbon dioxide samples was identical with that described for malonic acid, except that in this case all samples were compared with a carbon dioxide sample from oxalic acid oxidation. As before, the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio of the oxidation standard was assigned an arbitrary value, in this case, 92.35.

RESULTS AND DISCUSSION

The results of the oxalic acid decomposition runs have been tabulated in Table I. In Runs 1 and 2, the decomposition was carried to completion. In columns 3 and 4 are shown the $\frac{C^{12}O_2}{C^{13}O_2}$ ratios as determined mass spectrometrically for the carbon dioxide and carbon monoxide (converted to carbon dioxide) formed in the reaction. The ratio $\frac{k_2}{k_3}$ is given in columns 5 and 6 as calculated from equations (6') and (8), p. 45, respectively. The deviation from unity of this ratio is a measure of the intramolecular isotope effect. In Run 3, only the first and last fractions of carbon dioxide evolved were collected. Column 3 contains the $\frac{C^{12}O_2}{C^{13}O_2}$ ratios found in each case. Only one ratio of $\frac{k_1}{2k_2}$ was obtained and this

TABLE I

C^{13} Isotope Effect in Oxalic Acid Decomposition*

Run	Details	$\frac{C^{12}O_2}{C^{13}O_2}$**		$\frac{k_2}{k_3}$		$\frac{k_1}{2k_2}$	$\frac{k_1}{k_2+k_3}$
		CO_2	CO	CO_2	CO		
1	Complete	90.60	93.51	1.040	1.021		
2	Complete	90.85	94.06	1.054	1.037		
3	First CO_2 evolved	93.79				1.016	1.032
	Last CO_2 evolved	86.76					

*Temperature of runs, 100° ± 1°C

**All $\frac{C^{12}O_2}{C^{13}O_2}$ ratios are relative to the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio in a normal oxalic acid oxidation sample, arbitrarily chosen as 92.35, i.e., $\frac{1-\alpha}{\alpha}$ = 92.35.

was from the first carbon dioxide evolved. This ratio is shown in column 7. The calculated ratio $\frac{k_1}{k_2+k_3}$ is found in column 8. The deviation from unity of this latter ratio is a measure of the intermolecular isotope effect.

The average of the $\frac{k_2}{k_3}$ ratios turns out to be 1.033 ± 0.003. This indicates that there is a 3.3% greater probability of the C^{13} being found in the carbon dioxide rather than in the carbon monoxide. This value is believed to be more reliable than the variations would indicate due to the internal consistency found in the results from the carbon dioxide and carbon monoxide in Run 2.

The ratio $\frac{k_1}{k_2+k_3}$ indicates that the oxalic acid species containing only C^{12} carbon atoms reacts 3.2% faster than the molecule containing a C^{13} carbon atom. This may be explained as due to the lower zero point energies of the heavier molecule, causing it to have an increased activation energy. Of the heavier molecules which do decompose, there are two paths of decomposition whereby the C^{13} may be associated with one or two oxygen atoms. The path which will be preferred will be that one which will place the products in their lowest energy forms. The problem then resolves itself into which of the two combinations $C^{13}O_2 + C^{12}O$ or $C^{12}O_2 + C^{13}O$ has the lower over-all zero point energy. We would predict that the former combination would be favoured in view of the fact that the calculated equilibrium constant for the isotopic exchange reaction

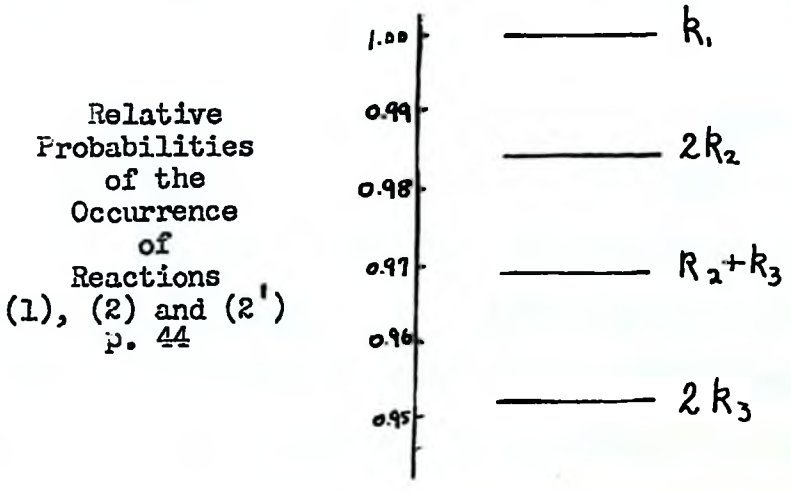
$$C^{12}O_2 + C^{13}O \rightleftharpoons C^{13}O_2 + C^{12}O$$

is 1.036 at 25°C, favouring the C^{13} in the carbon dioxide. Thus it is

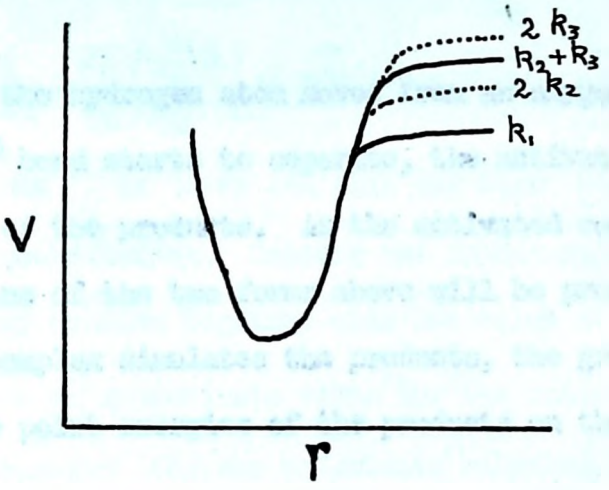
seen that if the products carbon dioxide and carbon monoxide have any bearing on the isotope effect in the decomposition of the heavy molecule, then C^{13} will be favoured in the carbon dioxide. The experimental results seem to indicate that the products of the reaction do have a bearing on the rates since $\frac{k_2}{k_3} = 1.033$.

The probability of occurrence of reaction (2), p. 44, will be influenced by two opposing effects. The lower zero point energy of the reactant molecule, and hence the higher activation energy, will tend to decrease the probability of occurrence of reaction (2). However, the lower zero point energies of the products of the reaction resulting in a lower activation energy will increase its probability. On the other hand, the probability of occurrence of reaction (2'), p. 44, will be influenced by two effects which are additive. As before, the lower zero point energy of the heavy molecule decreases the probability of occurrence of reaction (2'). Since the products have a higher zero point energy resulting in a higher activation energy, the probability of reaction (2') will be further decreased.

The relative probabilities of the occurrence of reactions (1), (2) and (2'), p. 44, may be represented as



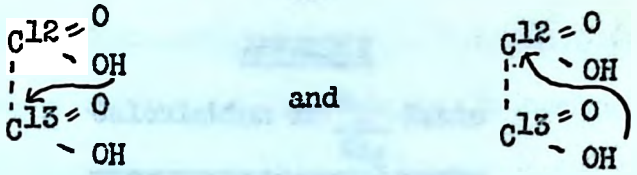
Also, since the relative probabilities of occurrence of these reactions are related to the over-all activation energies, we can, as in the case of malonic acid, represent our results on a potential energy diagram, i.e.,



As before, the effect of the differences in the zero point energy have been included in the height of the potential barrier.

In the preceding discussion we have attempted to relate the effect of the partition functions and thus the zero point energies of the products to the rates of reaction. Actually, the relative rates of these isotopic reactions must depend on the partition functions of the activated complex, and if the nature of the products would seem to influence the rates, it must be that the activated complex has already begun to simulate the products.

The activated complex behaves like a normal molecule except that one vibrational degree of freedom is replaced by a translational motion along the reaction co-ordinate. The mechanism of the decomposition of oxalic acid is thought to be a decarboxylation to formic acid followed by a rapid decomposition of formic acid to carbon monoxide and water. If this is the case, there would be two forms of the activated complex:



As the hydrogen atom moves from an oxygen to a carbon atom and the C^{12}–C^{13} bond starts to separate, the activated complex takes on the appearance of the products. As the activated complex tends toward the products, one of the two forms above will be preferred. The more the activated complex simulates the products, the greater will be the effect of the zero point energies of the products on the rates of reaction.

APPENDIX

Calculation of $\frac{k_1}{2k_3}$ Ratio

The ratio of the rate constants $\frac{k_1}{2k_3}$ is given as

$$\frac{k_1}{2k_3} = \frac{K_1}{K_3}\left(\frac{m_3^*}{m_1^*}\right)^{\frac{1}{2}}\left[\,1 + \sum G(u)_{3,1}(u_1 - u_3') - \sum G(u)^{\ddagger}_{3,1}(u_1^{\ddagger} - u_3^{\ddagger})\right]$$

We assume that $\frac{K_1}{K_3}$ is unity and that the term $G(u)^{\ddagger}_{3,1}(u_3^{\ddagger} - u_1^{\ddagger})$ makes a negligible contribution. Knowing the fundamental vibration frequencies for the heavy species together with the value of $u_1 - u_3 = \frac{hc(\omega_1 - \omega_3)}{kt}$, we can calculate an approximate value for the ratio $\frac{k_1}{2k_3}$.

Bigeleisen (68) has calculated relative rate constants for the decomposition of two species of malonic acid, the normal molecule, and the molecule containing a C^{14} in a carboxyl position. For his calculations he has calculated molecular frequencies and isotopic shifts for the symmetric molecular species $C^{14}OOH \cdot CH_2 \cdot C^{14}OOH$. His calculated frequencies are shown below:

Calculated Fundamental Vibration Frequencies of Malonic Acid

	ω cm^{-1}	$\Delta\omega$ cm^{-1}
ω_1	756	2.4
ω_2	230	4.4
ω_3	905	3.6

Bigeleisen uses the isotope shifts found for the symmetric molecule $C^{14}OOH \cdot CH_2 \cdot C^{14}OOH$ in the calculations involving the unsymmetric $C^{14}OOH \cdot CH_2 \cdot C^{12}OOH$ molecule, and then halves the calculated isotope effect.

If we make the assumption that the isotopic shift for the

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