THEORETICAL INVESTIGATION OF CARBON-13 ISOTOPE EFFECTS IN THE THERMAL ISOMERIZATION OF CYCLOPROPANE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Hans Paul Edward Sachse
1967

ABSTRACT

THEORETICAL INVESTIGATION OF CARBON-13 ISOTOPE EFFECTS IN THE THERMAL ISOMERIZATION OF CYCLOPROPANE

by Hans P. E. Sachse

The unimolecular reaction rate theories of N. B. Slater and of R. A. Marcus were applied to existing rate data for the unimolecular isomerization of cyclopropane. Complete vibrational calculations were carried out for cyclopropane, cyclopropane-d_6, cyclo-$C_2^{12}C^{13}H_6$ and cyclo-$C_3^{13}H_6$. In the course of the vibrational analysis of cyclopropane, an investigation of the ring modes of species E' resulted in the assignment of the 884(2) cm^{-1} frequencies to the ring vibrations rather than the 1050(2) cm^{-1} frequencies as some other workers have done.

The unimolecular reaction rate constants were calculated in the high-pressure limit and also as a function of pressure, using both the Slater and the RRKM theories. Then calculations were carried out to compute the kinetic isotope effect for carbon-13 substituted cyclopropane molecules at the high-pressure limit and as a function of pressure.

The vibrational analysis of the molecule allowed the necessary amplitude factors for the Slater theory to be calculated. The shapes of the curves for the pressure dependence

of the molecules were in agreement for high pressures; however, the shape of the fall-off of the carbon-13 isotope effect with pressure and the low-pressure limit could not be reconciled with the observed values, reflecting the incorrectness of the underlying assumptions of the Slater theory.

For the calculations of the kinetic isotope effect using the RRKM theory, a frequency pattern had to be determined for both unlabeled and isotopically substituted activated complexes. An empirical method was employed to fix the vibrational frequency pattern of the complexes and the complex geometry of Setser was used. The prescription used in assigning the complex frequencies involved: the removal of a C—H bond stretch as corresponding to the internal translational motion along the reaction coordinate; the changing of the three ring modes into a C—C and a C$\overset{\cdots}{-}$C bond stretch, and a C-C-C angle bend in the complex; the shift of the twisting frequencies to simulate hindered rotation of the end CH_2 groups in the complex; and, finally, other frequencies were unchanged or changed toward their corresponding propylene frequencies, the magnitudes being closer to the propylene frequencies as indicated by the large entropy of activation. The resulting complex frequencies were adjusted slightly so that the isotope effect would have the correct temperature dependence.

The isotope effect is a ratio of the isotopic rate constants at any pressure and thus small changes in the frequency pattern of the isotopically substituted complex relative to the unlabeled complex will change the value of k/k' at high pressures more than those at low pressures, which are essentially independent of the complexes. This has the effect of markedly altering the shape of the fall-off of the isotope effect as a function of pressure. It was not possible to construct a physically reasonable vibrational frequency pattern for the complexes by the above empirical method that would give reasonable agreement with experiment. The sensitivity of the calculated results to small changes in the complex vibrational frequency patterns indicate both that the isotope effect is a more sensitive test of the details of the theory than the isomerization rate constant results and that the empirical method which has been successful in analyzing the isomerization rate constant results and the deuterium isotope results cannot be used in the case of the relatively small carbon-13 kinetic isotope effect. Thus the more direct, but more complicated, approach of performing complete vibrational analyses of the isotopic complexes seems necessary for carrying out RRKM calculations of the carbon-13 kinetic isotope effect.

THEORETICAL INVESTIGATION OF CARBON-13
ISOTOPE EFFECTS IN THE THERMAL
ISOMERIZATION OF CYCLOPROPANE

By

Hans Paul Edward Sachse

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1967

To my parents

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. L. B. Sims for his guidance and encouragement during the course of this investigation.

TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

LIST OF TABLES

TABLE Page

I. INTRODUCTION

The thermal decomposition of a uniform gas is termed "unimolecular" if, at a fixed temperature, the rate expression is first-order in reactant concentration at high concentrations and becomes second-order at sufficiently low concentrations. The decrease of the so-called first-order rate constant with concentration from a limiting value at high concentrations to a concentration dependent second-order rate constant is referred to as the "fall-off." Early experiments revealed the existence of first-order reactions which apparently could not be explained by a second-order collisional activation mechanism. However, the strong temperature dependence shown by these first-order rate constants, making them expressible in the Arrhenius form, indicated that the dissociation of a molecule required it to have high energy. And yet, the apparent independence of the rate constant from concentration seemed to indicate that this energy was not acquired by collision.

It remained for Lindemann[16] to propose his mechanism whereby attention was focused on the internal motions of the molecule. At the time little was known about these motions except that they would probably prove to be complicated. Lindemann proposed that a collisional activation mechanism for the attainment of high energies would be possible if the time between collisions were significantly shorter than the lifetime of the high energy or activated molecule. In this manner, a steady-state concentration of active molecules could be maintained and their rate of dissociation would be limited by the concentration of reactant molecules; and the reaction is first-order. On the other hand, as the concentration is decreased, the situation would be encountered where the lifetime of the active molecules would be shorter than the time between collisions, such that the rate of reaction would be limited by the second-order collisional activation process. It should be noted that, in order for a molecule to exhibit unimolecular behavior, it must contain a sufficient number of energy "sinks" (i.e., it must be sufficiently polyatomic) to give rise to a time lag in the formation of the dissociation configuration that is long in comparison with the time between collisions.

All of the theories of unimolecular reactions assume that an active molecule will be deactivated on every collision (the strong collision assumption),[36] so that the rate of deactivation is the same as the collision frequency. The rate of spontaneous decomposition, on the other hand, is dependent on both the model for the active molecule and the criterion for the reaction. The difference in the various theories of unimolecular reactions arises then from their treatment of these factors. Thus, assumptions made concerning inter- and intramolecular energy transfer, anharmonicity of vibrations, and the randomness of the distribution of energy, which are of fundamental importance in the theory of reactions, can be tested by comparison of experimental data with theory.

With the focus on the internal motions of the molecule as significant in the description of the reaction, it can be seen that a study of the effects of isotopic substitution on the characteristics of the reaction would be a further aid in establishing the validity of the assumptions made in connection with the various theories of unimolecular reactions. Both of the theories under consideration, that of N. B. Slater[36] and that of R. A. Marcus,[17,18] attempt to establish a definite description of the activated complex in terms of its internal motions. The Slater theory assumes that a molecule may be represented as a collection of uncoupled classical harmonic oscillators which are described as the normal mode oscillators. The critical energy for reaction can, in the Slater theory, be equated to the high-pressure experimental activation energy. The theory of R. A. Marcus, referred to as the RRKM theory, is also dependent on the detailed vibrational characteristics of the molecule. However, the molecule is described as a collection of lightly-coupled quantum harmonic oscillators. The rate of reaction of an active molecule at a particular energy is viewed as proportional to the ratio of the density of states of the active molecule to that of the activated complex at the given energy. Thus, both theories reflect a dependence on molecular structure through the vibrational modes of the active molecule and of the complex.

Of the reactions known to exhibit gas phase unimolecular behavior, perhaps the most studied example is that of the thermal structural isomerization of cyclopropane to propylene.[6,20] Other examples include the isomerization of methyl isocyanide to acetonitrile[28,29] and the decomposition of nitrogen pentoxide.[19,14] The only mechanisms proposed for the isomerization of cyclopropane which have withstood the test of experiment and theoretical arguments are the two originally proposed by Chambers and Kistiakowsky.[6] One involves the migration of a hydrogen in the activated complex with the carbon skeleton essentially undeformed, and the other involves the formation of a tri-methylene-like activated complex accompanying an opening of the carbon ring. The first was used by Slater in his theoretical calculations, while the second is indicated by studies of the isomerization of deuterium-substituted cyclopropanes.[22,23,27,4,24] Investigations of the effect of changes in the complex structure on the calculated rate carried out by Schlag[27] and Setser[24] resulted in a complex structure involving both the hydrogen migration and the opening of the carbon ring. The frequencies of the complex which are sensitive to deuterium substitution were adequately defined by this comparison. Work by Weston[38] revealed a carbon-13 isotope effect in the thermal isomerization of cyclopropane. He felt the results could be explained on the basis of either mechanism.

In order to assess the importance of ring motions for the isomerizations, Sims and Yankwich[32] determined the carbon-13 isotope effect as a function of pressure at several temperatures. Their results indicate that the reaction coordinate is more complex than the hydrogen bridging coordinate originally proposed,[6] and they conclude, on the basis of the isotopic sensitivity of the magnitude of the isotope effect to the ring deformation frequencies, that the reaction coordinate includes considerable ring relaxation. However, the temperature and pressure dependence of the carbon-13 isotope effect have not been adequately interpreted, even though considerable information concerning the carbon-13 isotope sensitive vibrations of the complex could be obtained; this information is requisite to a vibrational analysis of the complex for a more complete understanding of the reaction.

The purpose of this study was to make comparisons between the experimental carbon-13 isotope effect and that calculated by the Slater and RRKM theories of unimolecular reactions.

II. GENERAL DEVELOPMENT OF THE THEORIES

A. Introduction

The temperature dependence of the rate constant of an elementary reaction can be described in terms of the Arrhenius expression

$$k = A \exp(-E_a/RT) \tag{1}$$

where A is the pre-exponential factor and E_a is the experimental activation energy. The usual interpretation of this strong dependence on temperature is that only molecules with high energy are capable of reaction and that there is a minimum energy, called the critical energy, necessary for reaction. Molecules which have a total energy greater than this critical energy are termed "active" molecules. Experimentally one observes an average rate constant over all molecules with energy greater than the critical energy.

If c_i is defined as the probability of reaction per unit time from state i, where i is an enumeration of the active energy levels (be they continuous or quantized) and f_i is the fraction of molecules in state i, the observed rate constant for the first-order reaction is

$$k = \sum_i c_i f_i \tag{2}$$

the sum being over all states i of the active molecule. The distribution of active molecules, f_i, is dependent on the experimental conditions (i.e., the method of excitation) and the specific decomposition rate, c_i, is dependent on the model used to describe the active molecule.

B. The Slater Theory

Slater proposed[33,34] that a polyatomic molecule may be described as a collection of non-interacting classical harmonic oscillators. The molecular motion is described by a set of internal (or symmetry) coordinates, q_r, which may, since the oscillators are harmonic and the potential energy expression is quadratic in the coordinates, be resolved into n normal modes of vibration with frequencies $\nu_1, \nu_2, \ldots, \nu_n$, energies $\epsilon_1, \epsilon_2, \ldots, \epsilon_n$ and phases $\phi_1, \phi_2, \ldots, \phi_n$. Each normal mode is associated with a normal coordinate Q_i, which is a linear combination of the internal coordinates. The frequencies are assumed independent; consequently, the energies and phases of the different modes of vibration will be constant in the free molecules and will change only on collision. Thus, there is no energy flow between oscillators. The reaction is said to occur when a specified coordinate q_r attains a critical value, q_{ro}.

The internal coordinates are related to the normal coordinates by the transformation

$$q_r = \sum_{i=1}^{n} \alpha_{ri} Q_i \qquad (3)$$

where the α_{ri} are the elements of the eigenvector matrix associated with the vibrational secular equation,

$$\left| \mathbb{G}\mathbb{F} - \lambda \mathbb{E} \right| = 0 , \tag{4}$$

where, in the notation of Wilson, Decius and Cross,[43] $\mathbb{G}$ is the inverse kinetic energy matrix, $\mathbb{F}$ is the force constant matrix, λ is the eigenvalue and $\mathbb{E}$ the identity matrix. For an harmonic oscillator, the normal coordinates are of the form

$$Q_i = K_i \cos 2\pi(\nu_i t + \phi_i). \quad (0 \leq \phi_i < 1), \tag{5}$$

Where the Q_i satisfy the energy relations[36]

$$T = \sum_{i=1}^{n} \dot{Q}_i^{\,2}/\lambda_i$$

$$\text{and} \qquad V = \sum_{i=1}^{n} Q_i^{\,2} \ . \tag{6}$$

The λ_i are related to the normal frequencies, ν_i, by

$$\lambda_i = 4\pi^2 \nu_i^{\,2} \tag{7}$$

These restrictions lead to interpretation of the coefficients K_i as

$$K_i = \sqrt{\epsilon_i} \tag{8}$$

where ϵ_i is the energy in the i^{th} normal mode. Finally, the expression for the internal coordinates becomes

$$q_r = \sum_{i=1}^{n} \alpha_{ri}\sqrt{\epsilon_i} \cos 2\pi(\nu_i t + \phi_i) \tag{9}$$

Now a molecule cannot react unless

$$q_r = \sum_{i=1}^{n} |\alpha_{ri}| \sqrt{\epsilon_i} \geq q_{ro} \tag{10}$$

where the cosine term is taken to have the maximum value of unity. The values of ϵ_i that satisfy this requirement and at the same time keep the total energy $E = \sum_i \epsilon_i$ content a minimum are

$$\epsilon_{io} = q_r^{2} \alpha_{ri}^{2}/\alpha^4 \tag{11}$$

where $$\alpha^2 = \sum_{i=1}^{n} \alpha_{ri}^{2} \qquad (\alpha > 0) \tag{12}$$

The minimum total energy for dissociation is therefore

$$E_o = q_{ro}^{2}/\alpha^2 \tag{13}$$

Note that it is not necessary that the reaction coordinate be one of the q_r. It may be a linear combination of the form

$$q_o = \sum_{r=1}^{n} \gamma_r q_r \tag{14}$$

The amplitude factors of equation 3 then would be

$$\alpha_{oi} = \sum_{r=1}^{n} \gamma_r \alpha_{ri} \tag{15}$$

Having established the minimum conditions for reaction, the distribution function and the specific rate constants of equation 2 must be determined. If it is assumed that the system is in effective equilibrium, then the population in the energized ranges $(\epsilon_i, \epsilon_i + d\epsilon_i)$, for $i = 1,2,\ldots,n$, where the ϵ_i satisfy equation 16, will be

$$C \exp(-E/k_bT) \prod_{i=1}^{n} \left(\frac{d\epsilon_i}{k_bT}\right) \tag{16}$$

where C is the total number of molecules in the system. The fraction of energized molecules with energies $\epsilon_1, \epsilon_2, \ldots, \epsilon_n$ reacting per second is L, the average frequency with which q_r attains the critical value q_{ro} . The collision frequency per molecule and hence the rate of deactivation is again assumed to have the classical form (strong collision assumption)

$$\omega = ZC \tag{17}$$

where

$$Z = 4\sigma^2 \left(\frac{\pi k_b T}{m}\right)^{½} \left(\frac{N}{RT}\right) \qquad \text{sec}^{-1}\ \text{mm}^{-1}$$

Hence the number of molecules raised in unit time into this energy range is

$$\omega C \exp(-E/k_bT) \prod_{i=1}^{n} \frac{d\epsilon_i}{k_bT} \qquad (18)$$

However, the population of activated molecules in any energy range will not correspond to the Boltzman distribution because of the depletion by reaction; it will be some smaller number, such as

$$Cg(\epsilon_1,\epsilon_2,\ldots,\epsilon_n)\ d\epsilon_1\ d\epsilon_2 \ldots d\epsilon_n \qquad (19)$$

where g is to be determined. Then the number of molecules reacting per unit time is

$$Cg\ L\ d\epsilon_1\ d\epsilon_2 \ldots d\epsilon_n \qquad (20)$$

and the number deactivated is

$$\omega Cg\ d\epsilon_1\ d\epsilon_2 \ldots d\epsilon_n \qquad (21)$$

In the steady state, the number of molecules activated by collision is equal to the number deactivated plus the number which react; hence

$$(L+\omega)g = \omega(k_bT)^{-n} \exp(-E/k_bT) \qquad (22)$$

which gives an expression for g. Now by integrating equation 20 over internal energies,

$$k = -\frac{1}{C}\frac{dC}{dT} = \int_{\epsilon_1}\cdots\int_{\epsilon_n} g\ L\ d\epsilon_1\ d\epsilon_2 \ldots d\epsilon_n\ , \qquad (23)$$

and substituting g,

$$k = \int_{\epsilon_1} \cdots \int_{\epsilon_n} \frac{L \exp(-E/k_bT)}{1 + L/\omega} \prod_{i=1}^{n} \left(\frac{d\epsilon_i}{k_bT} \right) \tag{24}$$

where the integral is over the energy range which corresponds to activation. By letting

$$b = E_o/(k_bT) \quad ,$$

$$\mu_i = |\alpha_i| / \alpha \qquad (\sum \mu_i^2 = 1) \tag{25}$$

and $$\nu = \sum_{i=1}^{n} \mu_i^2 \nu_i^2 \quad ,$$

the integral may be reduced to

$$k = \nu \exp(-b)\, I_n(\theta) \tag{26}$$

or

$$k/k_\infty = I_n(\theta) = \frac{1}{\Gamma(m)} \int_0^\infty \frac{x^{m-1}\, e^{-x}\, dx}{1 + x^{m-1}/\theta} \tag{27}$$

where $x = (E - E_o)/(k_bT)$

$$m = \frac{n+1}{2}$$

$$\theta = \frac{\omega}{\nu}\, b^{m-1}\, f_n$$

$$f_n = (4\pi)^{m-1}\, \Gamma(m) \prod_{i=1}^{n} \mu_i \quad .$$

and n is the number of effective or contributing modes.

If there exists more than one equivalent reaction coordinate, the rate constant must be multiplied by a statistical factor α corresponding to the number of equivalent coordinates, since the theoretical high-pressure rate constant is evaluated on the assumption that the reaction will occur whenever any one of the reaction coordinates exceeds its critical value. Thus, as Slater has shown,[35]

$$k_\infty = \sum_{r=1}^{\alpha} k_{\infty_r} \qquad (28)$$

where k_{∞_r} is the rate constant evaluated for one of the reaction coordinates.

Note that at high pressures the integral approaches the value of $\Gamma(m)$ and k/k_∞ approaches unity. At very low pressures, the value of the integral approaches θ and the rate constant becomes

$$k_o \cong \frac{\alpha \nu \theta \exp(-b)}{\Gamma(m)} = \alpha\omega(4\pi b)^{m-1} \exp(-b) \prod_{i=1}^{n} \mu_i \,. \qquad (29)$$

It is convenient to express the equations for the Slater α's in terms of the matrix notation of the molecular vibration problem as described by Wilson, Decius and Cross.[43] The transformation from internal coordinates R_i to the normal coordinates Q_i is given as

$$\mathbb{R} = \mathbb{L}\,\mathbb{Q} \qquad (30)$$

where $\mathbb{R}$ is the vector containing the q_i, $\mathbb{Q}$ contains the Q_i and $\mathbb{L}$ is the eigenvector matrix. Since, in the molecular vibration problem, the Q_i are subject to the relations

$$T = \tfrac{1}{2} \sum_{i=1}^{n} \dot{Q}_i^2 \qquad (31)$$

and

$$V = \tfrac{1}{2} \sum_{i=1}^{n} \lambda_i \, Q_i^2 \quad ,$$

the normal coordinates become

$$Q_i = (2/\lambda_i)^{1/2}\sqrt{\epsilon_i}\cos(\lambda_i^{1/2}t + \phi_i) \quad . \tag{32}$$

Thus, in general, a critical coordinate q_o may be related to the q_r as in equation 14 such that the α's become

$$\alpha_{oi} = \sum_r \gamma_r \alpha_{ri}(2/\lambda_i)^{1/2} \quad . \tag{33}$$

Thus in matrix notation one obtains

$$q_o = \Gamma \mathbb{L} \mathbb{Q} \tag{34}$$

where the elements $(2/\lambda_i)^{1/2}$ are contained in $\mathbb{Q}$, such that the Q_s of Slater is related to the Q of equation 34 by

$$Q = (2/\lambda\ )^{1/2} Q_s \quad . \tag{35}$$

In many cases it is more convenient to use symmetry coordinates in the vibrational problem, where the symmetry coordinate S_i may be written as a linear combination of the internal coordinates R_i:

$$\mathbb{S} = \mathbb{U}\mathbb{R} \quad . \tag{36}$$

In this case the elements of $\mathbb{L}$ in equation 34 must be replaced with the elements of the matrix product $\tilde{\mathbb{U}}\mathbb{L}$ where $\tilde{\mathbb{U}}$ is the transpose of the matrix $\mathbb{U}$ in equation 36.

C. The Marcus Theory

The RRKM theory[17,18] of unimolecular reactions attempts the quantum statistical description of a reacting system using a somewhat more realistic model than that of previous workers. As in the Slater theory, the motions are assumed to be a collection of, now, quantized harmonic oscillators.

Th
an
fr
of
qua
tat
sum
conf
acti
ener
so-ca
befor
thus

Where
of the
greate
critic
molecu

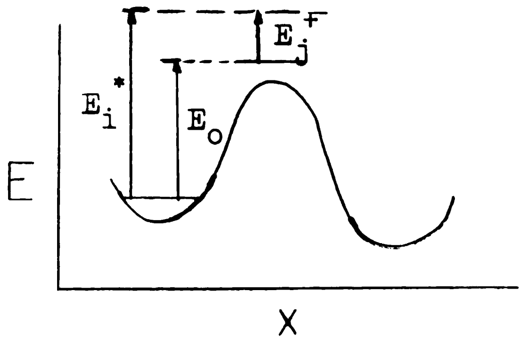
The theory allows for distinct frequencies of the oscillators and also for free energy transfer among any or all normal frequencies and internal rotations. The overall rotations of the molecule are generally assumed <u>not</u> to change their quantum state during the time of the reaction (adiabatic rotations) and the configuration of the active molecule is assumed to be randomly distributed among the possible favorable configurations. In addition, it is also assumed that the active molecule, having attained some minimum or critical energy, must also assume some critical configuration, the so-called "activated complex" of transition state theory, before reaction is possible. The Lindemannn mechanism is thus modified to become

$$A + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_i^* + M \qquad (37)$$

$$A_i^* \xrightarrow{k_i} A_j^+ \xrightarrow{\text{rapid}} \text{Products}$$

where A_j^+ is the activated complex with energy E_j^+ in excess of the zero point energy of the complex and the $E(A_i^*)$ is greater than E_o for all levels i. The relationship of the critical energy E_o to E_j^+ and E_i^*, the energy of the active molecule above its zero point energy, is given by

$$E_i^* = E_o + E_j^+ \quad . \qquad (38)$$



Application of the steady state approximation to A_i^* and A_j^+ yields for f_i, the fraction of molecules in level i,

$$f_i = \frac{A_i^*}{A} = \frac{k_1 M}{k_2 M + k_i} = \frac{(k_1/k_2)}{1 + k_i/(k_2 M)} \quad . \tag{39}$$

Thus the overall rate constant is given by

$$k = \sum_i k_i \, f_i \tag{40}$$

where the summation is over all levels i with energy greater than the critical energy. The sum over the levels may be replaced by an integral (for the active molecule)[40] such that

$$k = \int_{E_c}^{\infty} k_E \, f_E \, dE \tag{41}$$

where, as before, the deactivation rate is equated to the collision frequency (strong collision assumption), so that

$$f_E = \frac{F(E)}{1 + k_E/\omega} \quad , \tag{42}$$

and k_E is the probability of finding a high energy molecule in unit length δx of the reaction coordinate in the transition state times the mean velocity $\bar{v}_x$ of the complexes as they are crossing the barrier in the direction of the formation of products per unit energy δE^+, and F(E) is the equilibrium fraction of active molecules. In the complex, one vibrational mode will correspond to an imaginary or zero frequency for internal translation along the reaction coordinate. Thus, the probability of finding a high energy molecule in unit length δx is the fraction of active molecules that have made the transition to activated complex, and this number times the velocity across the barrier gives the rate:

$$k_E = \frac{\left(\dfrac{N^+(E_n)}{\delta x\ \delta E^+}\right)}{N^*(E^*)} \cdot \bar{v}_x \qquad (43)$$

where the numerator is the number of energy states per unit length per unit energy in the activated complex and the denominator is the number of energy states per unit energy in the active molecule. E_n is the non-fixed energy of the complex available for transfer to internal translation and is given by[40]

$$E_n = E^+ - \frac{p_x^2}{2M} \qquad (44)$$

where $p_x^2/(2M)$ is the momentum conjugate to the velocity along x. To obtain all possible transitions, a sum is taken over all possible distributions of E^+ into $E_n + (p_x^2/(2M))$,

$$k_E = \frac{\bar{v}_x}{\delta E^+\ \delta x\ N^*(E^*)} \sum_{E_n \leq E^+} \int_{\frac{p_x^2}{2M} = E^+ - E_n}^{\frac{p_x^2}{2M} = E^+ + \delta E^+ - E_n} N^+(E_n)\ \frac{\delta x \delta p}{h} \qquad (45)$$

where $N^+(E_n)$ is the total number of available internal energy states in the range δE^+, $\delta x \delta p/h$ is the number of translational states in unit volume (here one-dimensional) of phase space ($\delta x \delta p$ being the number of levels in 1/h unit area) and the integral gives the number of translational levels in an interval δE^+ for some energy E_n.

The mean velocity, $\bar{v}_x$, weighted according to the probability distribution law, is given by

$$\bar{v}_x = \frac{\displaystyle\sum_{E_n \leq E^+} \int_{\frac{p_x^2}{2M} = E^+ - E_n}^{\frac{p_x^2}{2M} = E^+ + \delta E^+ - E_n} N^+(E_n) v_x \frac{\delta x \delta p}{h}}{\displaystyle\sum_{E_n \leq E^+} \int_{\frac{p_x^2}{2M} = E^+ - E_n}^{\frac{p_x^2}{2M} = E^+ + \delta E^+ - E_n} N^+(E_n) \frac{\delta x \delta p}{h}} \quad (46)$$

where $v_x = \frac{p_x}{M}$. Substituting equation 46 in equation 45 leads to cancellation of the normalizing term, leaving

$$k_E = \frac{1}{\delta x \delta E^+ N^*(E^*)} \sum_{E_n \leq E^+} \int_{\frac{p_x^2}{2M} = E^+ - E_n}^{\frac{p_x^2}{2M} = E^+ + \delta E^+ - E_n} N^+(E_n) \frac{p_x}{M} \frac{\delta x \delta p}{h} \quad (47)$$

$$= \frac{1}{\delta x \delta E^+ N^*(E^*)} \frac{\delta x}{h} \sum_{E_n \leq E^+} N^+(E_n) \int_{\frac{p_x^2}{2M} = E^+ - E_n}^{\frac{p_x^2}{2M} = E^+ + \delta E^+ - E_n} \frac{p}{M} dp$$

$$= \frac{\dfrac{\delta x \delta E^{+}}{h} \displaystyle\sum_{E_n \leq E^{+}} N^{+}(E_n)}{\delta x \delta E^{+} \quad N^{*}(E^{*})} \quad .$$

And, finally,

$$k_E = \frac{\dfrac{1}{h} \displaystyle\sum_{E_n \leq E^{+}} N^{+}(E_n)}{N^{*}(E^{*})} \quad . \tag{48}$$

Since k_E does not take into account the effect of the centrifugal energy associated with the adiabatic rotations, a correction factor, I_r, the inertial ratio, must be added, where

$$I_r = \frac{Q_r^{+}}{Q_r^{*}} \tag{49}$$

and Q_r is the rotational partition function

$$Q_r = (\pi)^{\frac{n-2}{2}} \prod_{i=1}^{n} \left[\frac{8\pi^2 I_i k_b T}{h^2}\right]^{1/2} \tag{50}$$

and n is the number of rotational degrees of freedom and I_i the moment of inertia.

The equilibrium fraction of active molecules F(E)dE is given by

$$F(E^*)dE^* = \frac{n_E}{n_{tot.}}\,dE^* = \frac{n_o(g/E^*)\,\exp(-E^*/kT)}{n_o\,Q_v^*}\,dE^* \qquad (51)$$

where (g/E^*) is the degeneracy per unit energy and corresponds to the previously defined $N^*(E^*)$ and Q_v^* is the vibrational partition function for the active molecule

$$Q_v = \prod_{i=1}^{3N-6}\Big(1 - \exp(-h\nu_i/k_bT)\Big)^{-1} \quad . \qquad (52)$$

ν_i are the frequencies associated with the 3N-6 normal modes of vibration for a molecule of N atoms. Recalling equations 41 and 42 and substituting for k_E and F(E)dE, one obtains an expression for k

$$k = \int_{E_o}^{\infty} \frac{\dfrac{I_r}{h}\displaystyle\sum_{E_v^+ \leq E^+} P(E_v^+)N^*(E^*)\,\exp(-E^*/k_bT)}{Q_v^*\cdot N^*(E^*)\left[1 + \dfrac{I_r}{\omega h}\,\dfrac{\sum_{E_v^+\leq E^+} P(E_v^+)}{N^*(E^*)}\right]}\,dE^* \qquad (53)$$

or, finally,

$$k = \frac{k_bT}{h}\,\frac{I_r}{Q_v^*}\,\exp(-E_o/k_bT)\int_{o}^{\infty} \frac{\displaystyle\sum_{E_v^+ \leq E^+} P(E_v^+)\,\exp(-E^+/kT)}{1 + \dfrac{I_r}{\omega h}\,\dfrac{\sum_{E_v^+\leq E^+} P(E_v^+)}{N^*(E_o + E_v^+)}}\,\frac{dE^+}{k_bT} \qquad (54)$$

where $P(E_v^+)$ is the vibrational degeneracy at energy E^+ (equal to $N^+(E_n)$ when there are no internal rotations) and, as before, $E_o = E^* - E^+$ and $dE^* = dE^+$. At high pressures it can be seen that the denominator approaches unity and the limiting high-pressure rate constant is given by

$$k_\infty = \frac{k_bT}{h}\frac{I_r}{Q_v^*}\exp(-E_o/k_bT)\int_o^\infty \sum_{E_v^+ \leq E^+} P(E_v^+)\exp(-E^+/k_bT)\frac{dE^+}{k_bT}$$

$$= \frac{k_bT}{h} I_r \frac{Q_v^+}{Q_v^*}\exp(-E_o/kT) \quad . \qquad (55)$$

At low pressures the limiting form of the rate constant is proportional to the pressure and is given by

$$k_o = \frac{\omega\exp(-E_o/k_bT)}{Q_v^*}\int_o^\infty N^*(E^*)\exp(-E^+/k_bT)\,dE^+ \qquad (56)$$

$$= \frac{\omega}{Q_v^*}\int_o^\infty N^*(E^*)\exp(-E^*/k_bT)\,dE^*$$

If, however, there is more than one isomerically equivalent coordinate, then k_E must be multiplied by a statistical factor, the quantity α, to compensate for the additional number of equivalent reaction paths.

It should also be noted here that this development is for reactions which require a rigid activated complex, since it does not allow for the presence of any internal rotation in the activated complex. The equations, however, comprise a limiting case of the general expression developed by Marcus and Wieder.[41]

The critical energy, E_o, is evaluated by requiring k_∞ to have an Arrhenius temperature dependence. Comparing equation 55 to equation 1 and performing a logarithmic differentiation with respect to (1/T), one obtains

$$E_o = E_a + \langle E_v^* \rangle - \langle E_v^+ \rangle - RT \tag{57}$$

where

$$\langle E_v \rangle = k_b T^2 \frac{\partial(\ln Q_v)}{\partial T} = \sum_i \frac{h\nu_i \exp(-h\nu_i/k_b T)}{1 - \exp(-h\nu_i/k_b T)} \tag{58}$$

D. Effect of Isotopic Substitution

Kinetic isotope effects arise from the fact that isotopically substituted molecules react at different rates. This arises mainly as a result of the effect of the differing masses on the vibrational frequency pattern in the various isotopic molecules. From transition state theory, the high pressure rate constant can be shown to be proportional to the mean velocity v in the reaction coordinate and hence inversely proportional to the square root of the effective mass m, since

$$v = (2k_b T/\pi m)^{1/2} \tag{59}$$

Thus, the ratio of rate constants of isotopic molecules is inversely proportional to the effective masses of the atoms related by the reaction coordinate:

$$r_\infty = \frac{k_\infty}{k_\infty'} = \frac{v}{v'} = \left(\frac{m'}{m}\right)^{1/2} \qquad (60)$$

where the prime refers to the heavier isotopic molecule, and r_∞ will always be greater than unity (termed a "normal" isotopic effect) if the coordinate involves the substituted atom. If the atom substituted is not directly involved in the reaction coordinate, there will still be a small effect, since the reaction coordinate involves a linear combination of all the normal coordinates. At low pressures, where collisional activation is the rate-determining step, only a very small, but normal, isotope effect is expected because of the relative insensitivity of the collision process to isotopic substitution. Thus classical theory predicts a decrease in the isotope effect with decreasing pressure.

The non-classical RRKM theory, on the other hand, also allows for quantum statistical effects of isotopic substitution. Considering equation 55, in which the integral term has been equated with Q_v^+, the vibrational partition function of the activated complex, the ratio of the high-pressure limiting rate constants becomes

$$\frac{k_\infty}{k_\infty'} = \frac{I_r}{I_r'} \frac{Q_v^{*\prime}}{Q_v^*} \frac{Q_v^+}{Q_v^{+\prime}} \exp((E_o' - E_o)/k_bT) . \qquad (61)$$

The $I_rQ^*Q^+$ product term is usually slightly less than unity, but the exponential term is large enough to produce a large normal isotope effect at ordinary temperatures. At the low pressure limit, the ratio of rate constants becomes, recalling equation 56,

$$r_o = \frac{k_o}{k_o'} = \left[\frac{Z}{Z'} \, \frac{Q_v^{*'}}{Q_v^{*}} \, \exp((E_o' - E_o)/k_b T) \right] \cdot S \quad . \qquad (62)$$

Note that all dependence on properties of the activated complex have disappeared in the low-pressure region. S is the ratio of integrals of $N^*(E^*)$. S may be very small because at any given energy the density of energy levels in the active molecules is greater for the heavier isotopic molecules, the effect increasing with energy. Thus, the theory predicts that the isotope effect will decrease with decreasing pressure and invert at very low pressures. It should be noted that this effect arises from the quantized nature of the oscillators, and should be observed for all unimolecular reactions at sufficiently low pressures.

III. APPLICATION OF THE SLATER AND RRKM THEORIES TO THE ISOMERIZATION OF ISOTOPIC CYCLOPROPANES

A. Introduction

The theoretical formulations of the reaction rate constants for thermal unimolecular gaseous reactions given by Slater and by Marcus are based on a model in which the vibrations of the molecule are described by a set of harmonic oscillators. The application of the theories requires a vibrational analysis of the reacting molecule; the high-pressure experimental activation energy is used to fix the temperature dependence of the high pressure rate constant; the kinetic theory collision diameter is used in calculation of the rate of collisional deactivation.

B. The Vibrational Problem

The Wilson GF matrix technique[43] was employed in the vibrational analyses of the molecules. The vibrational problem is expressed in the internal valence coordinates of Decius[10] who has shown that a set of four types--namely bond stretching, valence angle bending, out-of-plane wag and torsion--is sufficient to describe the most general vibrational displacement of any molecule.

For a set of R_i internal valence coordinates, the potential energy, V, and the kinetic energy, T, for a vibrating molecule may be written as

$$2V = \tilde{\mathbb{R}} \mathbb{F} \mathbb{R} \tag{63}$$

and

$$2T = \tilde{\dot{\mathbb{R}}} \mathbb{G}^{-1} \dot{\mathbb{R}}$$

where $\mathbb{F}$ is the force constant matrix, $\mathbb{G}$ is the inverse kinetic energy matrix, the $\dot{\mathbb{R}}$ are the time derivatives of the internal coordinates and $\sim$ implies a transpose matrix. Through the equations of Lagrange, the vibrational problem leads to a secular equation of the form

$$(\mathbb{G}\mathbb{F} - \lambda\mathbb{E})\mathbb{L} = \mathbb{O} \tag{64}$$

where $\lambda = 4\pi^2\nu^2$ and $\mathbb{L}$ is the eigenvector matrix (i.e., the normalized amplitude matrix) which also describes the transformation from internal coordinates, R_i, to the normal coordinates, Q_i:

$$\mathbb{R} = \mathbb{L}\mathbb{Q} \tag{65}$$

As was noted earlier, it is often more convenient to use some linear combination S of the internal valence coordinates R_i. This simplifies the secular equation by reducing many off-diagonal elements to zero on the basis of the symmetry of the molecule. An orthogonal matrix $\mathbb{U}$ is constructed such that

$$\mathbb{S} = \mathbb{U}\mathbb{R}\,, \tag{66}$$

from which the expression for S in terms of the normal coordinates Q follows:

$$\mathcal{S} = \mathbb{U}\mathbb{L}\mathbb{Q} = \mathcal{L}\mathbb{Q} \ . \tag{67}$$

A "symmetrized" $\mathcal{G}$ and $\mathcal{F}$ may be defined by

$$\mathcal{G} = \mathbb{U}\mathbb{G}\tilde{\mathbb{U}} \tag{68}$$

and

$$\mathcal{F} = \mathbb{U}\mathbb{F}\tilde{\mathbb{U}} \tag{69}$$

which lead to a symmetrized vibrational secular equation

$$(\mathcal{G}\mathcal{F} - \Lambda)\mathcal{L} = 0 \tag{70}$$

where $\Lambda = \lambda\mathbb{E}$.

A useful description of the normal coordinates, Q, is the transformation $\mathbb{T}$ from normal coordinate space to Cartesian space:

$$X = \mathbb{T}\mathbb{Q} \ . \tag{71}$$

$\mathbb{T}$ is a 3N by 3N-6 matrix, N being the number of atoms in the molecule, corresponding to 3N-6 normal coordinates and 3N Cartesian displacement coordinates. If the Cartesian coordinates are taken three at a time, corresponding to the x_{ia}, y_{ia} and z_{ia} displacements of atom a in the i^{th} normal mode, these triples define a set of s-vectors,[43] which can be used to construct the transformation, $\mathbb{B}$, from internal coordinates to Cartesian displacement coordinates:

$$\mathbb{R} = \mathbb{B}X \ . \tag{72}$$

The reverse transformation is given by

$$\mathbb{X} = \mathbb{A}\mathbb{R} \tag{73}$$

where $\mathbb{A}$ is not simply the inverse of $\mathbb{B}$, since $\mathbb{B}$ is not square, but is defined by[7,8]

$$\mathbb{B}\mathbb{A} = \mathbb{E} \; . \tag{74}$$

The inverse kinetic energy matrix is related simply to $\mathbb{B}$ by[42]

$$\mathbb{B}\mathbb{M}^{-1}\tilde{\mathbb{B}} = \mathbb{G} \; , \tag{75}$$

where $\mathbb{M}$ is the matrix of reciprocal masses. It follows that

$$\mathbb{A} = \mathbb{M}^{-1}\tilde{\mathbb{B}}\mathbb{G}^{-1} \; . \tag{76}$$

Then, since $\mathbb{R} = \mathbb{L}\mathbb{Q}$, the transformation from $\mathbb{X}$ to $\mathbb{Q}$ is given by

$$\mathbb{X} = \mathbb{A}\mathbb{L}\mathbb{Q} = \mathbb{M}^{-1}\tilde{\mathbb{B}}\mathbb{G}^{-1}\mathbb{L}\mathbb{Q} \; ; \tag{77}$$

or, recalling equation 64 and comparing equation 77 with equation 71, it follows that

$$\mathbb{T} = \mathbb{M}^{-1}\tilde{\mathbb{B}}\mathbb{F}\mathbb{L}\Lambda^{-1} = \mathbb{A}\mathbb{L} \tag{78}$$

which removes the necessity for calculating the inverse of $\mathbb{G}$.

At this point it will be of interest to note that once the transformation $\mathbb{T}$ has been found, the calculation of the Slater α's can follow immediately. Recall that the critical coordinate, q_0, could be expressed as a linear combination of the internal coordinates and was related to the normal coordinates by equation 34. It is necessary to obtain an expression for Γ. Since the transformation $\mathbb{B}$, relating internal coordinates to Cartesian displacement coordinates, is known, it follows that any internal valence coordinate chosen as the critical coordinate may initially be described by

$$q_0 = \mathbb{B}'\mathbb{X} \tag{79}$$

where $\mathbb{B}'$ is a row vector for the coordinate q_0 ; and, further, if q_0 is to be a linear combination of contributing reaction coordinates, then $\mathbb{B}'$ is a row vector containing the algebraic column by column sum of the $\mathbb{B}'$ vectors of the contributing coordinates (equation 79 is formally the same for both cases). In light of equations 73 and 65 one can relate q_0 first to the complete set of internal valence coordinates R by

$$q_0 = \mathbb{B}'\mathbb{A}\mathbb{R} \tag{80}$$

and then to the normal coordinates, Q, by

$$q_0 = \mathbb{B}'\mathbb{A}\,\mathbb{L}\mathbb{Q} \tag{81}$$

and, finally, Γ may be identified as

$$\Gamma = \mathbb{B}'\mathbb{A} = \mathbb{B}'(\mathbb{M}^{-1}\mathbb{B}\mathbb{G}^{-1}) \ . \tag{82}$$

Finally, the Slater expression for the α's may be obtained by comparing equation 81 with equations 34 and 35, and

$$\alpha_{0i} = \mathbb{B}'\mathbb{A}\mathbb{L}(2/\lambda_i)^{1/2} = \mathbb{B}'\mathbb{T}(2/\lambda_i)^{1/2} \ . \tag{83}$$

The calculation of the normal frequencies of the various molecules was carried out using a modification of a program developed by J. H. Schachtschneider[26] employing the Wilson GF method. The structural parameters for cyclopropane were taken from a paper by Cyvin,[9] as were the symmetry coordinates and valence force constants. The high-frequency carbon-hydrogen stretching motions were separated in the usual manner[43] in each symmetry group. The potential constants of Cyvin were evaluated from data for cyclo-C_3H_6 and cyclo-C_3D_6, and give excellent fit to experiment for these isotopic molecules.* The frequencies of cyclo-$C_3^{13}H_6$ and cyclo-$C_2^{12}C^{13}H_6$ were calculated using the same potential constants. The calculated frequencies are compared in Table 1.

During the course of the investigation of the vibration problem, a curious anomaly was encountered in the literature. Earlier workers Ananthakrishnan,[1] Saksena[25] and Herzberg[13] all assigned the normal frequency at 884 cm^{-1} to a vibration of the ring and the 1051 cm^{-1} band to a CH_2 wagging mode. Later workers, Baker and Lord,[3] Günthard <u>et al</u>.[12] and Cyvin,[9] with no explanation, have described the 1051 cm^{-1} band as a ring mode. An examination of the symmetrized eigenvectors found in this study (Table 2) shows that the 884 cm^{-1} frequency is best described as a ring deformation. A correlation of the

---

*It was necessary to change the signs of some of the interaction constants in Cyvin's published work on cyclopropane in order for the calculated frequencies to agree with experiment. The absolute magnitudes of the constants were correct, however.

Table 1. Observed and Calculated Frequencies and Principal Moments of Inertia of Isotopic Cyclopropane Molecules

C_3H_6		C_3D_6		$C^{13}_3H_6$	$C^{12}_2C^{13}H_6$	
Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Calcd.	Assignment
3312	3301	2408	2375	3306	3310	C-H stretch, $Q_1(A_1')$
3234	3221	2439	2407	3218	3234	C-H stretch, $Q_1(E')$
3234	3221	2439	2407	3218	3225	C-H stretch, $Q_1(E')$
3200	3196	2310	2300	3195	3200	C-H stretch, $Q_1(E")$
3200	3196	2310	2300	3195	3197	C-H stretch, $Q_1(E")$
3196	3194	2390	2387	3182	3190	C-H stretch, $Q_1(A_2")$
1478	1479	1262	1278	1466	1471	CH_2 deform., $Q_2(A_1')$
1478	1478	1092	1094	1474	1478	CH_2 deform., $Q_2(E')$
1478	1478	1092	1094	1474	1478	CH_2 deform., $Q_2(E')$
1186	1188	955	956	1150	1175	ring deform., $Q_3(A_1')$
884	884	731	731	854	875	ring deform., $Q_4(E')$
884	884	731	731	854	873	ring deform., $Q_4(E')$
1156	1156	818	818	1156	1156	CH_2 twist., $Q(A_1")$
1208	1212	960	973	1193	1208	CH_2 twist., $Q_2(E")$
1208	1212	960	973	1193	1198	CH_2 twist., $Q_2(E")$
981	981	789	789	970	977	CH_2 wagging, $Q(A_2')$
1051	1051	902	903	1044	1051	CH_2 wagging, $Q_3(E')$
1051	1051	902	903	1044	1046	CH_2 wagging, $Q_3(E')$
867	867	620	621	866	867	CH_2 rocking, $Q_2(A_2")$
750	750	534	534	749	750	CH_2 rocking, $Q_3(E")$
750	750	534	534	749	750	CH_2 rocking, $Q_3(E")$
I_A = 64.342		83.301		68.135	65.577	
I_B = 41.523		60.339		43.419	42.757	
I_C = 41.523		60.339		43.419	41.523	

Units: frequencies, cm^{-1}; moments of inertia, amu·$Å^2$

Table 2. Symmetrized Eigenvectors for Cyclopropane.

		$Q_1(A_1')$	$Q_2(A_1')$	$Q_3(A_1')$	$Q(A_2')$
A_1' :	$S_1(A_1')$	1.01389	0	0	
	$S_2(A_1')$	0	0.25627	0.41909	
	$S_3(A_1')$	0	-1.44791	0.28316	
A_2' :	$S(A_2')$				1.07800
		$Q_1(E')$	$Q_2(E')$	$Q_3(E')$	$Q_4(E')$
E' :	$S_1(E')$	1.01389	0	0	0
	$S_2(E')$	0	-0.06155	0.12475	0.32168
	$S_3(E')$	0	-1.44867	-0.06588	-0.00385
	$S_4(E')$	0	0.03344	-1.00029	0.02264
		$Q(A_1'')$	$Q_1(A_2'')$	$Q_2(A_2'')$	
A_1'' :	$S(A_1'')$	0.90507			
A_2'' :	$S_1(A_2'')$		1.05980	0	
	$S_2(A_2'')$		0	1.41142	
		$Q_1(E'')$	$Q_2(E'')$	$Q_3(E'')$	
E'' :	$S_1(E'')$	1.05980	0	0	
	$S_2(E'')$	0	0.79724	-0.576853	
	$S_3(E'')$	0	1.27625	1.06888	

calculated cyclopropane on cyclo-C_3H_6 frequencies shows less than one percent lowering of the 1051 cm^{-1} frequency (to 1044 cm^{-1}), whereas the 884 cm^{-1}frequency is shifted by 3.5 percent upon substitution of carbon-13. Further confirmation of the present assignment comes from a simple three-center, equilateral triangular, molecular model used for calculation of the ring vibration modes. The "atoms" at the corners of the model were given an effective mass equal to the CH_2 subgroup, 14 a.m.u. Force constants for stretching were estimated by Badgers' Rule and modified slightly to account for the ring structure. The calculated frequencies, 1194, 890 (2), were in good agreement with the experimental frequencies, 1186, 884(2). This identification of the ring modes will have an important effect on the application of the RRKM theory, since the frequencies of the vibrational modes active in the reaction coordinate in the activated complex must be shifted toward the propylene frequencies to simulate the movement along the reaction coordinate. The ring deformation modes of cyclopropane become a C—C stretch, a $C\overset{\cdots}{-}C$ stretch and a C—C—C angle bend in the complex, and, thus, considerable changes in the ring frequencies occur in going to the complex.

C. The Slater Theory

The kinetic isotope effect observed in the isomerization of cyclopropane and cyclopropane-d_6 was used as a test of the ability of the Slater theory to predict the characteristics of deuterium isotope effect.

The evaluation of the Slater integral was fairly straightforward. It was necessary to be able to evaluate the Gamma function for non-integral, specifically half-integral, arguments. An expression developed by Artin[2] giving twelve decimal-place accuracy was used. The integral itself was evaluated by 32-point Gaussian quadrature using Laguerre polynomials which are orthogonal on the semi-infinite interval $(0, \infty)$.[15] The integration routine was checked by evaluating the integral for given values of $\log_{10} \theta$ and comparing them with those given by Slater.[36] The method was also used to evaluate the Gamma function and was found to have an error of one part in one hundred thousand for non-integral values of the argument greater than two and no error for integral values of the argument.

The initial single isotope calculations of the rate constant in the high-pressure limit and in the fall-off region yielded frequency factors that were too low by a factor of three or four. For the normal cyclopropane molecule it is found experimentally to be 1.5×10^{15} sec^{-1}, whereas a value of 5×10^{14} sec^{-1} was calculated. This is a definite failing of the theory, since the Slater frequency factor is a weighted average of the molecule frequencies, and the maximum limiting case is then always less than the highest molecular frequency.

The calculations revealed that the slope of the fall-off curve agrees fairly well with experiment,[6,20] although the absolute magnitudes of the rate constants were not correct, and the curves were shifted to higher pressures (0.77 and 0.22 log units for cyclo-C_3H_6 and cyclo-C_3D_6, respectively). Although this has been attributed in part to inefficient collisions,[35] it would seem unlikely that a molecule as complex as cyclopropane would exhibit the low collision efficiency necessary to account for such large shifts. Also, the large difference in the shift for the two isotopes was not expected. Finally, where full Slater calculations show a decrease in ν for a heavier isotope and thus a high-pressure frequency factor for k/k' that is greater than unity, Blades[5] has reported an experimental ratio of 0.82 for the k/k' frequency factor for deuterium substitution. Further, the fall-off of the isotopic k/k' with pressure does not have the correct shape.

D. The RRKM Theory

1. Introduction

The application of the RRKM theory requires that careful consideration be given the construction of a complex model, since the activated complex is critical to the description of the reaction.

The high frequency factor for the isomerization of cyclopropane (ca. 10^{15} sec^{-1}) implies a large positive entropy of activation. The observed entropy of activation (ΔS^{+}_{∞} = 7.35 e.u.[4] at 513.8°C, as compared to the standard entropy of reaction, ΔS^{o} = 8.0 e.u.) indicates that the activated complex has a structure rather close to propylene, i.e., the carbon ring has been deformed to a large extent and one hydrogen has undergone at least partial transfer to an adjacent carbon. Several models were considered and the isotope effects calculated according to this theory.

2. Calculation of the Rate Constant

The equation for the rate constant as a function of pressure has been described and the various terms defined in Chapter II, section C. Details of the calculation will be considered below:

The inertial ratio, I_r, is the ratio of the rotational partition function of the activated complex to that of the active molecule and is given by

$$I_r = \frac{Q_{rot.}}{Q_{rot.}^*} = \left(\frac{I_A I_B I_C}{I_A^* \, I_B^* I_C^*} \right)^{1/2} \qquad (84)$$

where I_A, I_B and I_C are the principal moments of inertia.

The vibrational partition function, Q_v, has already been described in equation 52.

The critical energy, E_o, is related to the high-pressure experimental activation energy, E_a, and the average vibrational energies of the complex (+) and active molecule (*) by equation 57. E_o has the significance of being the difference between the lowest energy atate of the complex and activate molecule. If equation 57 is used to calculate E_o, a small temperature dependence to E_o is introduced, contrary to the physical significance of E_o. This small error can be very important in isotope effects, where

$$\Delta E_o = E_o' - E_o \qquad (85)$$

appears in the exponential of equation 61 for the high pressure isotope effect, and considerable error in ΔE_o can result from small errors in E_o and E_o'. To insure that the isotopic rate constant ratio k/k' and the individual rate constants had an Arrhenius temperature dependence, E_o was evaluated from equation 57 for the lighter isotopic molecule at an intermediate temperature of the experimental range, and the quantity ΔE_o evaluated from the zero point energies of the active molecule and the activated complex of both isotopic species by

$$\Delta E_o = E_o' - E_o = (E_{zpt.} - E_{zpt.}')^{*} - (E_{zpt.} - E_{zpt.}')^{+} . \qquad (86)$$

ΔE_o calculated in this way is independent of temperature and has the correct physical significance. The critical energy of the heavier isotopic molecule was then determined as

$$E_o' = E_o + \Delta E_o$$

The collision frequency, $\omega = ZP$, is necessary, since the strong collision assumption was used in all calculations. Using a collision diameter, σ, of 5Å,[35] the kinetic theory collision frequency, Z, was calculated from

$$Z = 4\sigma^2 \left(\frac{\pi k_b T}{m}\right)^{1/2} \frac{N}{RT} \quad \mathrm{sec}^{-1}\ \mathrm{mm}^{-1} \qquad (87)$$

The quantity $\sum_{E_v \leq E} P(E_v)$ is the number of vibrational energy states for a molecule with a total energy, E, since it is assumed that the total energy can be distributed among the various degrees of freedom (vibrational, rotational, translational) in all possible combinations. If $P(E_v)$ is the number of ways of distributing the vibrational energy, E_v, among the vibrational degrees of freedom, then the sum of $P(E_v)$ over all $E_v \leq E$ will be the total number of vibrational energy states at a total energy E. A systematic counting procedure has been developed[40] and can be used to evaluate $\sum P(E_v)$. The direct count method for a molecule such as cyclopropane, however, is extremely time-consuming, even on a computer, so that good approximate expressions are desirable.

The approximation to $\sum P(E_v)$ developed by Whitten and Rabinovitch[39] was used exclusively for evaluation of both $\sum P(E_v^+)$ and $N^*(E^*)$, since the expression is simple and accurate. The expression is

$$\sum_{E_v \leq E} P(E_v) = \left[E_z(E'+1-\beta\omega)\right]^s \Big/ \left(\Gamma(s+1) \prod_{i=1}^{s} h\nu_i \right) \qquad (88)$$

where s is the number of active vibrational modes, E_z is the zero point energy,

$$E' = E/E_z$$

$$\beta = \frac{(s-1)}{s} \frac{\langle \nu^2 \rangle}{\langle \nu \rangle^2}$$, a frequency dispersion parameter,

$$\omega = \exp\left[-1.0506(E')^{0.25}\right] \qquad (1.0 \le E' \le 8.0)$$

and

$$\omega = \left[5.0(E') + 2.73(E')^{0.5} + 3.51\right]^{-1} . \qquad (0.1 \le E' \le 1.0)$$

The approximation is good to about one percent for $E \ge 0.5E_z$ and is valid at energies as low as $0.1E_z$.

Since the complex for the cyclopropane isomerization is assumed to be "rigid," only the vibrational degrees of freedom contribute to the reaction, but the total energy of the complex, E^+, can be distributed in any manner between the vibrational degrees of freedom and the internal translational degree of freedom. Equation 88 was then used for evaluating $\sum P(E_v^+)$ for each complex.

The density of energy states of the active molecule at energy E^*, $N^*(E^*)$, is related to $\sum P(E_v^*)$ by

$$N^*(E^*) = \frac{\partial \sum_{E_v^* \le E^*} P(E_v^*)}{\partial E^*} \qquad (89)$$

Equation 88 can be differentiated directly with respect to E to obtain an expression for $N^*(E^*)$,

$$N^*(E^*) = s\left[E_z(E' + 1 - \beta\omega)\right]^{s-1} \Big/ \left(\Gamma(s+1) \prod_{i=1}^{s} h\nu_i\right) \qquad (90)$$

The reaction path multiplicity, α, is defined as the number of equivalent but distinguishable reaction paths from a given molecule to products. For normal cyclopropane this number is twelve, since there are twelve equivalent non-bonded carbon-hydrogen distances that can be considered as reaction coordinates.

3: Construction of the Complex Models

The vibration frequencies of the molecule were calculated as described above, using the Wilson GF matrix method. The vibration frequencies of the activated complex were determined by an empirical method, although one detailed calculation was attempted. The complex was treated as "rigid", admitting no internal rotations. For the calculation, the complex was treated as a normal molecule, except that one frequency was considered an internal translation along the reactant coordinate, and hence one molecule frequency was deleted in going to the complex. For this calculation, the complex was constructed such that it had C_{2v} symmetry, in order to simplify the assignment of force constants. It was assumed that the ring was opened and that no interaction existed between the end CH_2 groups. The CH_2 groups were considered to be almost in the CCC plane, and the CH_2 group on the central atom was taken as perpendicular to the carbon plane. Force constants were assigned from those for cyclopropane and propylene, adjusting the values to correspond with any loosening or tightening of bonding in going from cyclopropane to the complex: the torsional force constants were reduced for the hindered-rotation in the complex, the

C—C and C═C bond force constants were altered to fit the partial bond characteristics of the complex, and the central carbon CH_2 group was treated as in cyclopropane, except that the force constants were made to reflect the relaxation of the constrained ring. Calculations made with this model returned frequencies which were not in good agreement with the expected shifts from cyclopropane. This is attributed to the absence of important interaction elements from the force constant matrix for the complex which are difficult to estimate. Further attempts to calculate the complex frequencies were not made.

For the isotope effect calculations, the models were constructed using an empirical method of fixing the vibrational frequency pattern of the complex, and the final frequencies were grouped[21] to facilitate calculation. The complex geometry of Setser[30] was used in all of the calculations. This model consists of a CCC angle of 109°, with one hydrogen bridged in the CCC plane.

IV. DISCUSSION

A. Nature of the Comparison Between Theory and Experiment

The kinetic isotope effect in the structural isomerization of carbon-13 labelled cyclopropane (natural abundance), cyclo-$C_2^{12}C^{13}H_6$, to propylene-C^{13} was calculated using both the Slater and RRKM theories of unimolecular reactions. The isomerization can be written:

$$\text{cyclo-}C_3^{12}H_6 \longrightarrow CH_3CH{=}CH_2 \qquad 12k_1$$

$$\text{cyclo-}C_2^{12}C^{13}H_6 \longrightarrow C^{13}H_3CH{=}CH_2 \qquad 4k_2$$

$$\longrightarrow CH_3C^{13}H{=}CH_2 \qquad 4k_3$$

$$\longrightarrow CH_3CH{=}C^{13}H_2 \qquad 4k_4$$

where k_1, k_2, k_3 and k_4 are the respective unimolecular first-order rate constants, and the factors 12 and 4 arise from the reaction path multiplicity for the reactions. The kinetic isotope effect has been investigated in detail by Sims and Yankwich[32], but the analysis used by these workers allowed determination only of the intermolecular isotope effect k/k' related to the individual isotopic rate constants k_i $(i=1,\ldots,4)$ by[38]

$$\frac{k}{k'} = \frac{12k_1}{4k_2 + 4k_3 + 4k_4} \quad . \qquad (91)$$

Comparison of theory with experiment should properly be made between the calculated rate constants k_i (i=1,...,4) and the experimental average isotope effect k/k' by means of equation 91. This was done in the case of the Slater theory, and it was found that within the calculation error $k_2=k_3=k_4$. For calculations using the RRKM theory, a specification of the vibrational frequency pattern of the complex is required; the empirical method described below for fixing the complex frequencies and the numerical integration necessary for evaluation of the RRKM rate integral prevent any real distinction between k_2, k_3 and k_4. Therefore, a complex frequency pattern representing the "average" effect of carbon-13 labelling was employed in all the RRKM calculations, and the calculated results compared directly with k/k'.

For all of the complex models considered, the isomerization rate constant k (k_1 above) was calculated in both the high pressure (k_∞) and fall-off regions (k/k_∞), and the deuterium isotope effect k_H/k_D for the structural isomerization of cyclo-C_3D_6 was also calculated as a function of pressure, and comparisons made between the calculated and corresponding experimental quantities.

B. Slater Calculations

The rate constants for isomerization of unlabelled cyclopropane (C_3H_6), perdeuterated cyclopropane (C_3D_6) and carbon-13 labelled cyclopropane ($C_2^{12}C^{13}H_6$) were calculated from the amplitude factors resulting from a vibrational analysis of each molecule (see Chapter III). The critical coordinate was chosen as a non-bonded C—H distance in each case, which was found by Slater[35] to give the best agreement with the structural isomerization rate constant at all pressures. Some calculations involving a C—C critical coordinate were also carried out. However, only the trends of the calculations using Slater theory were of interest, and a thorough investigation was not undertaken, since the main interest in this work centered on the RRKM calculations. Other workers[11,37,28] have shown that the basic assumptions of the Slater theory are incorrect.

C. RRKM Calculation

The calculation of the various quantities entering the RRKM rate expression are discussed in detail in chapter III. The evaluation of the rate integral must be done by numerical integration at all pressures except the high-pressure limit, for which the RRKM integral reduces to the vibrational partition function of the complex and hence an analytical formula can be used. It follows that in the high-pressure limit, errors due to integration disappear, and the calculated results reflect only errors in the theory or in the characterization of the complex. In the high-pressure limit, the properties of the complex determine the calculated result to a large degree; as the pressure is decreased, the properties of the complex become less important, and in the low-pressure limit, the rate expression becomes independent of the complex and depends only upon the properties of the active molecules, which are known quite acurately and cannot be adjusted. It follows that the calculated isotope effect will be dependent on the properties of the complex only at high pressures, and because of the reasons given above, comparison of the high-pressure isotope effect $(k/k')_\infty$ will be considered separately from the isotope fall-off curve, k/k' versus pressure. For all of the calculations, the numerical integration was chosen so that at high pressures the RRKM integral evaluated by integration agreed with the complex vibrational partition function to better than 0.1 percent.

The complex vibrational frequency pattern was determined by changing frequencies of the molecule systematically in going to the complex so that: (1) one frequency was removed as representing the reaction coordinate motion (In all cases, a C—H stretching frequency was chosen, as indicated by the deuterium isotope effect results[24], even though the carbon-13 kinetic isotope effect results indicate that the reaction coordinate must contain appreciable loosening of the ring and C—C motion in addition.[32]); (2) the twisting frequencies of cyclopropane were lowered to simulate torsion of the end CH_2 groups in a trimethylene-like complex structure, as suggested by the cis-trans geometrical isomerization of 1,2-cyclopropane-d_2; (3) the ring frequencies of cyclopropane (now assigned as 1186(1) A_1' and 884(2) E' rather than 1050(2) E' in earlier work) were changed to represent C—C stretching, C$\underset{\cdots}{\text{—}}$C stretching and CCC bending of the complex; (4) other frequencies were either unchanged or changed so as to correlate closely with corresponding frequencies in propylene (these other frequency changes had little effect upon the calculated isotope effect since they are not C-13 sensitive frequencies.); (5) the magnitude of the changes were such that the final complex frequencies were closer to the corresponding propylene frequencies than to the cyclopropane frequencies, since the large entropy of activation[4] (i.e., large preexponential factor) for the structural isomerization suggests considerable loosening of the cyclopropane ring structure in the complex; (6) the resulting complex frequencies of the isotopic molecule were in each case slightly adjusted in order that the Teller-Redlich product rule was closely satisfied (within 1% generally), and that the high-pressure isotope effect had the correct experimental temperature dependence.

The RRKM high-pressure isotope effect is given by

$$\frac{k}{k'} = \frac{I_r}{I_r'}\left(\frac{Q_v'}{Q_v}\right)^{*}\left(\frac{Q_v}{Q_v'}\right)^{+}\exp(\Delta E_o/RT) \qquad (61)$$

where * and + refer, as before, to active molecule and activated complex, respectively. The temperature dependence is determined almost exclusively by the exponential term, so that the requirement on the complex frequency patterns of the isotopic molecules was that

$$\Delta E_o \equiv (E_z - E_z')^{*} - (E_z - E_z)^{+} = \Delta E_a \qquad (92)$$

where E_z refers to zero-point energy, and ΔE_a to the experimental Arrhenius exponential term for the high-pressure isotope effect.

D. Results and Comparison with Experiment

1. Slater Theory

The Slater theory results indicated that fairly good agreement can be obtained with the isomerization rate constant (k_∞ and k/k_∞ vs. P) at all pressures using a C—H critical coordinate, the only discrepancy with experiment being a small shift (~0.5 log P units) along the pressure axis, which is not considered serious. The assumption of strong collisions and the harmonic approximation are expected to affect the results in this direction. The same trends were noted by Slater[35] using a slightly different vibrational analysis. Poorer agreement is obtained using a C—C critical coordinate.

The Slater theory has not been used to calculate isotope effects as a function of temperature and pressure, even though some simple comparisons have been made[33,38]. The calculated Slater deuterium isotope effect was found to be much too large at high pressures, and to encompass a much larger range of values of k_H/k_D over the experimental interval than observed experimentally; the same general trend was found for the carbon-13 isotope effect. Furthermore, the low-pressure limit of both the calculated deuterium and carbon-13 kinetic isotope effects was slightly greater than unity, whereas the deuterium isotope effect has been observed to invert at low pressures[22]; the inversion has been shown to be a consequence of the quantized nature of molecular vibrations[31], and thus should be of general occurrence, and the C-13 isotope effect should also invert at low pressures.

It appears that the Slater theory of unimolecular reactions fails to give even qualitative agreement for isotope effects in unimolecular reactions, even in cases where the agreement with the overall rate constant is very good. Isotope effects seem to be a better test of the details of the theory than the overall kinetic rate constant.

2. RRKM Theory

Many variations of the complex model were considered for both assignments fo the degenerate ring modes: 1050(2) cm^{-1} and 884(2) cm^{-1}. In every case it was found that the high-pressure calculated carbon-13 isotope effect was too large if the 1050(2) cm^{-1} frequencies were assigned to the ring modes. If, on the other hand, the 884(2) cm^{-1} modes were assigned as ring modes, the above prescription for frequency changes in going to the conplex led to a calculated high-pressure isotope effect in good agreement with experiment if ΔE_0 were fixed equal to ΔE_a as discussed above. Actually, the high-pressure isotope effect may be varied over a rather wide range of values (1.004 to 1.012 for example) by small changes of one or two cm^{-1} in one or two of the frequencies of the isotopic molecule. The empirical method of fixing the complex frequencies is certainly no better than a few cm^{-1} at best, so that a difference of one or two cm^{-1} between the isotopic molecules is allowed. The real test of the complex frequency model is the pressure dependence of the isotope effect. None of the models tested gave good results for the pressure fall-off of the rate constant. The 1050(2) cm^{-1} models all produced isotope effects which fell off at much lower pressures than observed, and spanned a range of values of k/k' much larger than observed over the experimental pressure interval. The same general trend was found for those models in which the 884(2) cm^{-1} frequencies were assigned as ring modes, but in these cases the effects were less pronounced.

In order to assess the sensitivity of the calculated results to changes in the frequency patterns of the isotopic complexes, ΔE_0 was fixed in a systematic manner to a given value using different relative changes for the complex frequencies of the isotopic molecule relative to the normal (unlabeled) molecule. In no case did these changes amount to more than 1 or 2 cm^{-1} in any frequency, and two or three frequencies at most were affected. Changes of this order of magnitude are entirely within reason and possibility, so that the method seems to test the isotope-sensitivity of the empirical method of fixing the complex frequency pattern. The results showed that even these small changes affected very drastically the calculated isotope effect fall-off curve, even though the shapes of the fall-off curves for either molecule were but little affected. The isotope effect is simply a ratio of the rate constants at any pressure, so that changing even slightly the prescription for the complex frequency pattern of the isotopic complex relative to the unlabeled complex will change the value of k' slightly at high pressures, but will have substantially less effect at low pressures; hence, the shape of the fall-off of the

Table 3. The Calculated Carbon-13 Isotope Effect, k/k', as Compared with Experiment

a) At the High-Pressure Limit

Model	$(k/k')_\infty$
Exp	1.008
1	1.007_2
2	1.008_1
3	1.008_9
4	1.007_0

b) As a Function of Pressure

$\frac{(k/k')}{(k/k')_\infty}$	log P_{calc}	log P_{exp}	log $\frac{P_{calc}}{P_{exp}}$
1.0000	∞	∞	--
0.9995	0.25	2.54	-2.29
0.9990	-0.24	2.18	-2.42
0.9985	-0.62	1.87	-2.49
0.9980	-0.87	1.61	-2.48
0.9975	-1.05	1.48	-2.53
0.9970	-1.24	1.16	-2.40
0.9965	-1.41	0.97	-2.38
0.9960	-1.56	0.75	-2.31
0.9955	-1.70	0.54	-2.24
0.9950	-1.84	0.36	-2.20
0.9945	-1.98	0.18	-2.16

isotope effect versus pressure curve can be quite seriously affected by such small changes. It was not possible for any of the models to make changes in the frequencies of the isotopic complex sufficient to obtain agreement with the experimental fall-off behavior of the isotope effect, and still retain a physically reasonable vibration pattern. (See Table 3.)

The extreme sensitivity of the calculated results to such small changes in frequency patterns indicates that the empirical method which has been used very successfully for fixing the complex frequencies in analyzing the isomerization rate constant results[41,31] and the deuterium isotope effect results[24] cannot be used for such small effects as the carbon-13 kinetic isotope effect. Rather, a more direct approach of calculating the complex frequencies by a vibrational analysis of the proposed complex structure seems a better method of proceeding. A few attempts at such a vibrational analysis were made, but the problem is onerous because the complex structure (the geometrical parameters of the complex were taken from Setser[30]; a slightly different choice of complex structure would not seriously affect the results since the calculated quantities are fairly insensitive to the geometry but are more sensitive to the force constants) lacks symmetry and because a large number of interaction potential constants are expected in the force field. Using only a few interaction constants taken over from cyclopropane, the complex frequency patterns calculated were not reasonable; in particular, frequencies very much higher than those for either cyclopropane or propylene resulted for some of the CH_2 group motions, which is unreasonable.

A more complete vibrational analysis will have to be carried out before the analysis of the carbon-13 isotope effect in the thermal isomerization of cyclopropane can be completed.

BIBLIOGRAPHY

1. Ananthakrishnan, R., Proc. Ind. Acad. Sci., 4A, 82 (1936).
2. Artin, Emil, Einführung in die Theorie der Gammafunktion. Leipzig, B. G. Teubner, 1931.
3. Baker, A. W., and R. C. Lord, J. Chem. Phys., 23, 1636 (1955).
4. Benson, S. W., and P. S. Nangia, J. Chem. Phys., 38, 18 (1963).
5. Blades, A. T., Can. J. Chem., 39, 1401 (1961).
6. Chambers, T. S., and G. B. Kistiakowsky, J. Amer. Chem. Soc., 86, 399 (1934).
7. Crawford, B. L., Jr., J. Chem. Phys., 20, 977 (1952).
8. Crawford, B. L., Jr., and W. H. Fletcher, J. Chem. Phys., 19, 141 (1951).
9. Cyvin, S. J., Spectrochimica Acta, 16, 1022 (1960).
10. Decius, J. C., J. Chem. Phys., 17, 1315 (1949).
11. Gill, E. K., and K. J. Laidler, Proc. Roy. Soc. (London), A250, 121 (1959).
12. Günthard, H. H., R. C. Lord and T. K. McCubbin, Jr., J. Chem. Phys., 25, 768 (1956).
13. Herzberg, G., Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra ... Princeton, N. J., D. Van Nostrand Co., Inc., 1945.
14. Johnston, H. S., and R. L. Perrine, J. Am. Chem. Soc., 73, 4782 (1951).
15. Krylov, V. I., Approximate Calculation of Integrals. New York, Macmillan Co., 1962.
16. Lindemann, F. A., Trans. Faraday Soc., 17, 598 (1922).
17. Marcus, R. A., J. Chem. Phys., 20, 359 (1952).

18. Marcus, R. A., and O, K. Rice, J. Phys. and Colloid Chem., 55, 894 (1951).

19. Mills, R. L., and H. S. Johnston, J. Am. Chem. Soc., 73, 938 (1951).

20. Pritchard, H. O., R. G. Snowden and A. F. Trotman-Dickenson, Proc. Roy. Soc. (London), A217, 563 (1953).

21. Rabinovitch, B. S., and T. H. Current, J. Chem. Phys., 35, 2250 (1961).

22. Rabinovitch, B. S., P. W. Gilderson and A. T. Blades, J. Am. Chem. Soc., 86, 2994 (1964).

23. Rabinovitch, B. S., E. W. Schlag and K. B. Wiberg, J. Chem. Phys., 28, 504 (1958).

24. Rabinovitch, B. S., D. W. Setser and F. W. Schneider, Can. J. Chem., 39, 2609 (1961).

25. Saksena, B. D., Proc. Ind. Acad. Sci., 10A, 449 (1939).

26. Schachtschneider, J. H., Tech. Rept. No. 263-63, Shell Development Co., Emeryville, California.

27. Schlag, E. W., and B. S. Rabinovitch, J. Am. Chem. Soc., 82, 5996 (1960).

28. Schneider, F. W., and B. S. Rabinovitch, J. Am. Chem. Soc., 84, 4215 (1962).

29. Schneider, F. W., and B. S. Rabinovitch, J. Am. Chem. Soc., 85, 2365 (1963).

30. Setzer, D. W., Ph.D. Thesis, Univ. of Washington, 1961.

31. Sims, L. B., Ph.D. Thesis, University of Illinois, 1967.

32. Sims, L. B., and P. E. Yankwich, J. Phys. Chem., 71, 3459-63 (1967).

33. Slater, N. B., Phil. Trans. Roy. Soc. (London), A246, 57 (1953).

34. Slater, N. B., Proc. Roy. Soc. (London), A194, 112 (1948).

35. Slater, N. B., Proc. Roy. Soc. (London), A218, 224 (1953).

36. Slater, N. B., Theory of Unimolecular Reactions. Ithaca, N. Y., Cornell Univ. Press, 1959.

37. Thiele, E., and D. J. Wilson, Jr., J. Chem. Phys., 35, 1256 (1961).

38. Weston, R. E., Jr., J. Chem. Phys., 26, 975 (1957).

39. Whitten, G. Z., and B. S. Rabinovitch, J. Chem. Phys., 38, 2466 (1963).

40. Wieder, G. M. Ph.D. Thesis, Brooklyn Polytechnic Institute, 1961.

41. Wieder, G. M., and R. A. Marcus, J. Chem. Phys., 37, 1835 (1962).

42. Wilson, E. B., Jr., J. Chem. Phys., 9, 76 (1941).

43. Wilson, E. B., Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*. New York, McGraw-Hill Book Co., 1955.