Dissociation and Isomerization of Vibrationally Excited Species. II. Unimolecular Reaction Rate Theory and Its Application*

GRACE M. WIEDER† AND R. A. MARCUS‡

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York

(Received May 31, 1962)

Data on quasi-unimolecular reactions have usually been compared with theoretical equations based on classical treatments, because the expressions are simpler than those obtained on the basis of a quantum model. The quantum reformulation of the RRK theory in Part I is used to compute the pressure dependence of the rate constants and the limiting low-pressure rates for a variety of unimolecular reactions without employing adjustable parameters. An asymptotic expansion of the integral for the limiting low-pressure second-order rate constant provides a very simple expression for this quantity.

The errors inherent in corresponding classical calculations are estimated by comparing these results with those obtained from the theory in its classical limit. The error is temperature dependent and at low pressures increases from a factor of about three (under typical experimental conditions) for small reactants such as O_3 and N_2O to 10^5 or more for large molecules such as cyclopropane, C_2H_6, and N_2O_5. In most cases the rates calculated from the quantum form are in reasonable agreement with those obtained experimentally when all of the reactant oscillators are assumed effective in intramolecular energy transfer.

INTRODUCTION

THE increasing availability of reliable gas kinetic data has stimulated renewed interest in the application of theories of quasi-unimolecular reaction rates (e.g., references 1–9). Slater and RRK theories in

¹ (a) N. B. Slater, Proc. Roy. Soc. (London) **A218**, 224 (1953); *Theory of Unimolecular Reactions* (Cornell University Press, Ithaca, New York, 1959); (b) E. K. Gill and K. J. Laidler, Proc. Roy. Soc. (London) **A250**, 121 (1959); (c) E. Thiele and D. J. Wilson, Can. J. Chem. **37**, 1035 (1959); J. Phys. Chem. **64**, 473 (1960); (d) R. E. Powell, J. Chem. Phys. **30**, 724 (1959).

² (a) R. A. Marcus, J. Chem. Phys. **20**, 359 (1952); (b) R. A. Marcus and O. K. Rice, J. Phys. & Colloid Chem. **55**, 894 (1951).

³ B. S. Rabinovitch and R. W. Diesen, J. Chem. Phys. **30**, 735 (1959); B. S. Rabinovitch, D. H. Dills, W. H. McLain, and J. H. Current, *ibid.* **32**, 493 (1960); R. E. Harrington, B. S. Rabinovitch, and R. W. Diesen, *ibid.* **32**, 1245 (1960); B. S. Rabinovitch and J. H. Current, *ibid.* **35**, 2250 (1961); E. W. Schlag, *ibid.* **35**, 2117 (1961); B. S. Rabinovitch, Can. J. Chem. (to be published); R. A. Marcus, J. Chem. Phys. **20**, 355 (1952).

⁴ H. M. Rosenstock, J. Chem. Phys. **34**, 2182 (1961); M. Wolfsberg, *ibid.* **36**, 1072 (1962); B. S. Rabinovitch (private communication).

⁵ R. E. Harrington, B. S. Rabinovitch, and H. M. Frey, J. Chem. Phys. **33**, 1271 (1960); J. N. Butler and G. B. Kistiakowsky, J. Am. Chem. Soc. **82**, 759 (1960).

⁶ O. K. Rice, J. Phys. Chem. **65**, 1588 (1961).

⁷ R. A. Marcus, J. Chem. Phys. **20**, 364 (1952); cf. data of R. E. Dodd and E. W. R. Steacie, Proc. Roy. Soc. (London) **A223**, 283 (1954).

⁸ (a) B. S. Rabinovitch, paper presented at the Symposium on Experimental and Theoretical Advances in Elementary Gas Reactions, A. C. S. Meeting, St. Louis, Missouri, 1961, describing behavior of CH_3NC. F. W. Schneider and B. S. Rabinovitch, American Chemical Society Meeting, Washington, D. C., 1962. (b) B. S. Rabinovitch, D. W. Setser, and F. W. Schneider, Can. J. Chem. **39**, 2609 (1961); B. S. Rabinovitch and J. H. Current, *ibid.* **40**, 557 (1962).

⁹ E. Thiele and D. J. Wilson, J. Chem. Phys. **35**, 1256 (1961).

their classical mechanical forms have been frequently used to interpret experimental data[1] partly because of the relative simplicity of the classical equations.[10]

There has been in recent years an increasing awareness of the magnitude of the errors inherent in treating vibrations as classical (cf. references 2–4) and of the importance of anharmonicity in intramolecular coupling of molecular vibrations in energetic molecules.[2–9,11] Only by neglecting these factors, however, was Slater[1] able to develop his strikingly elegant and stimulating theory of pressure effects on unimolecular reaction rates.

To include both quantum and anharmonic effects, a quantum mechanical transition state reformulation of the RRK theory was developed.[2] It was used to predict[7] the pressure dependence of methyl radical recombination and has been employed to explain data on the life-times of energetic molecules[3] and on unimolecular reactions,[8] and to interpret isotope effects at low pressures.[8b] Attempts are in progress to apply it to the interpretation of mass spectra.[4]

Some advantages of this formulation are (1) an absence of the curve-fitting parameter appearing in the generally used RRK formulation, and (2) applicability under conditions where the assumptions inherent in the

Slater theory are not justified, e.g., when anharmonicity or quantum effects are important, or when the molecule near configurations of the activated complex has vibration frequencies which differ from those of the initial state.

In spite of the uncertainty that still exists in regard to the proper characterization of many gaseous reactions, there are a number of decompositions and isomerizations of polyatomic molecules which are believed to proceed according to unimolecular mechanisms.[12] These kinetic data are used in the present paper to test the quantum formulation mentioned earlier and to estimate the magnitude of the errors involved in calculations where the corresponding classical theory is employed.

Reduced quasi-unimolecular rate constants as a function of pressure p are computed from the quantum form of the theory for (a) cyclopropane→propylene, (b) cyclobutane→ethylene, (c) methylcyclopropane→butene-1+butene-2 isomers, (d) N_2O→N_2+O, (e) cis butene-2→trans butene-2, (f) C_2H_5Cl→HCl+C_2H_4, and (g) N_2O_5→NO_2+NO_3. Results on the effect of temperature on shifting the logarithmic plots of the reduced-rate constant vs p curves are calculated for reactions (a) and (c) and compared with the experimentally observed shifts.

Second-order rate constants are computed from the limit as p→0 of the theoretical expression for reactions (a), (d), and (g), and for (h) O_3→O_2+O, (i) F_2O→OF+F, (j) NO_2Cl→NO_2+Cl, (k) H_2O_2→2OH, (l) N_2O_4→2NO_2, and (m) C_2H_6→2CH_3.

The error in classical calculations is estimated for very low and very high pressures by comparing the quantum expressions and their classical limit. Specific calculations are made for each of the above reactions.

As discussed in more detail later, there is some uncertainty in several of the reactions just cited, both with respect to the accuracy of the results and the correction for heterogeneity. In such cases, the estimates made in this paper on the errors of classical theory will still be substantially unaffected. Moreover, an approximate correction factor, to amend the calculated logarithmic plots of reduced rate constant vs

pressure in case of subsequent corrections to the experimental high-pressure Arrhenius frequency factors, is given in Appendix IV.

THEORY

Quantum Form

The derivation of an expression for the quasi-unimolecular rate constant as a function of p in Part I was based on the reaction sequence

$$A+M\underset{k_2}{\rightleftharpoons}A^*+M,$$

$$A^*\overset{k_a}{\rightarrow}A^+\rightarrow\text{products},$$
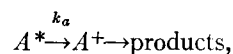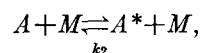
where A^* and A^+ denote the active molecule (characterized by internal energy greater than some critical minimum) and activated complex, respectively. M is any third body capable of deactivating A^*.

In the theory it was assumed[2] that each active molecule was randomly distributed among all configurations, those favorable to reaction and those which are not, subject to energy and angular-momentum conservation. The chance that an active molecule of any given energy is in some critical configuration characterizing the activated complex was then calculated by statistical mechanical arguments, due account being taken of the quantized nature of the vibrations. By multiplication of this probability with a suitably weighted frequency factor (describing passage through the potential energy surface characterizing the activated complex in many-dimensional configuration space), the specific reaction rate constant k_a was calculated as a function of the energy of the "active" molecule.

Steady-state considerations were applied to (A^*) and it was assumed (as one usually assumes in unimolecular reactions of polyatomic molecules) that the fraction of energetic molecules having insufficient energy to react has essentially its equilibrium value at all pressures.[13] By integrating over all energies of the active molecule, the unimolecular rate constant was computed as a function of pressure. The result was given by Eq. (1).[14]

$$k=\alpha\frac{kT}{h}\frac{P_1{}^+P_R{}^+}{P_1P_2}\frac{\exp(-E_a/RT)}{(r/2)!}\int_0^\infty\sum_{E_v{}^+\le E^+}\frac{[(E^+-E_v{}^+)/RT]^{r/2}P(E_v{}^+)\exp(-E^+/RT)}{1+k_a/k_2p}d(E^+/RT),\qquad(1)$$

where

$$k_a=\alpha\frac{\sigma_1}{\sigma_1{}^+}\frac{P_R{}^+}{h}\frac{1}{(r/2)!}\sum_{E_v{}^+\le E^+}\frac{[(E^+-E_v{}^+)/RT]^{r/2}P(E_v{}^+)}{N^*(E_a+E^++E_0)}.\qquad(2)$$

---

[12] A. F. Trotman-Dickenson, *Gas Kinetics* (Butterworths Scientific Publications, Ltd., London, 1955).

[13] In the case of the dissociation of diatomic molecules, however, it appears that depletion of the upper vibrational levels may occur. Compare E. E. Nikitin and N. D. Sokolov, J. Chem. Phys. **31**, 1371 (1959); J. C. Polanyi, *ibid.* **31**, 1338 (1959); B. Widom, *ibid.* **34**, 2050 (1961); H. O. Pritchard, J. Phys. Chem. **65**, 504 (1961).

[14] Comparison to Part I shows that a factor close to $\sigma_1/\sigma_1{}^+$, namely $P_1{}^+/P_1$, has been replaced by $\sigma_1/\sigma_1{}^+$ in the equation for k_a in Eq. (2) and that the definition given below for E_a differs very slightly from that given in Part I, a change of definition which, however, has no effect on application of Eq. (1). Justification for these minor changes will be given in Part III. In many applications, $\sigma_1/\sigma_1{}^+=P_1{}^+/P_1$ essentially (e.g., rigid complexes of this paper). In other cases, the ratios differ by at most a factor of 2 or 3.

Using the classification of the degrees of freedom (called "modes" for brevity) as being either active or adiabatic,[15] the principal symbols used in Eq. (1) and elsewhere are as follows:

$(r/2)! = \Gamma(1+r/2)$, the gamma function.

α = number of equivalent optical or geometric isomeric forms in which the activated complex may exist.[16]

s^+, s = number of active vibrations of A^+, A^*, respectively.

r, t = number of active rotations of A^+, A^*, respectively.

P_1^+, P_1 = partition function of the adiabatic rotations of A^+, A, respectively.

σ_1/σ_1^+ = ratio of symmetry numbers in P_1^+/P_1.

P_R^+, P_R = partition function of the r (the t) active rotations on A^+ (of A^*), respectively.

P_2^+, P_2 = partition function of all active modes of A^+, A, respectively.

E_0^+, E_0 = ground-state vibrational energy of A^+, A, respectively.

Q_2^+, Q_2 = the partition functions corresponding to P_2^+, P_2 but measured from the vibrational potential energy minimum of A^+, A, rather than from the ground vibrational state. Hence

$Q_2^+ = P_2^+ \exp(-E_0^+/RT)$,

$Q_2 = P_2 \exp(-E_0/RT)$.   (3)

U = potential energy of the least unstable configuration of the atoms of A^+ minus that of most stable configuration of A.

E_a = energy of A^+ in its lowest vibrational rotational translational state minus that of A in its lowest state.

---

[15] An adiabatic mode is defined[2] as one which is largely restricted to stay in the same quantum state when A^+ is formed from A^* because, for example, of momentum conservation. The three translations and the two rotations of A^* associated with the largest moments of inertia are adiabatic[2]. The third rotation has also been assumed to be adiabatic in applications.[2,3,7,8] The active modes are those which are active in intramolecular energy transfer. All vibrations are assumed active.[2,3,7,8]

[16] The original equation[2] did not contain α. It applied to conditions where the activated complex could be represented by a unique structural configuration. If, however, the postulated complex exists in α isomeric forms, as is the case in some reactions discussed in this paper, k and k_α must be multiplied by α to account for the full degeneracy of the quantum states.

E^+ = energy of the active modes of A^+ in any of the allowed states of A^+ minus E_0^+. E^+ was called[2] the "nonfixed energy" of the activated complex. (It does not contain energy "fixed" as zero-point energy.) It has contributions from the vibrations, nonadiabatic rotations, and internal translation of A^+.

$E_v^+, P(E_v^+)$ = energy of the vth vibrational level of A^+ minus the zero-point energy of A^+, and degeneracy of this level, respectively. (E_v^+ was denoted by E_v in Part I.)

$N^*(w+E_0)$ = number of energy states per unit energy of the active modes of A^* when they contain a total energy $w+E_0$ and hence a "nonfixed" energy w. In Part I, $N^*(w+E_0)$ was denoted by $N^*(w)$.

$y^+ = E^+ + E_0^+$, the total energy in the active modes of A^+.

k_2 = collisional deactivation rate constant, i.e., the collision frequency multiplied by some deactivation factor λ usually taken to be ~ 1.

h, R, T have their usual significance.

Some of the above terms are related

$$s^+ + r + 1 = s + t,$$ (4)

$$E_a = U + E_0^+ - E_0.$$ (5)

It has been shown[2] that when $p \rightarrow \infty$ in Eq. (1), the limiting high-pressure first-order constant k^∞ is given by an expression equivalent to that derived previously by Eyring[17]:

$$k^\infty = \alpha(kT/h)(P_1^+ P_2^+/P_1 P_2) \exp(-E_a/RT).$$ (6)

The pressure dependence of the reduced rate constant k/k^∞ is obtained with the aid of Eqs. (1) and (6) from a knowledge of the molecular properties of the active molecule, which is assumed to have the same properties as the reactant, and from the properties of a postulated rigid or loose activated complex.

In deriving Eqs. (1) and (6), the vibrational energy levels of A^+ and (other than those of A^*) of A were treated quantum mechanically. This quantum treatment manifests itself in the appearance in these equations of the quantum mechanical partition function P_2 of A, and in the degeneracy factor $P(E_v^+)$ and quantum mechanical partition function P_2^+ of A^+.

---

[17] See S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

A different treatment was employed for the high energy levels of A, i.e., for the levels of A^*. Since the energy of the active modes in the critically energized molecule must be greater than E_a, a quantity usually much larger than skT, a classical treatment was used to compute $N^*(w+E_0)$ for a given energy range rather than the laborious quantum mechanical calculations.

When, in addition to vibrations of A^*, some of its rotations are active, N^* becomes (using the results of Appendix I)

$$N^*(w+E_0) = \int_0^{w+E_0} N_v^*(w+x+E_0)N_r^*(x)dx, \qquad (7)$$

where $N_r^*(x)$ is the number of active rotational states per unit energy with rotational energy x, and $N_v^*(w-x+E_0)$ is the number of classical vibrational states per unit energy with nonfixed vibrational energy $w-x$. It has been shown in Part I that for t active rotations

$$N_r^*(x) = (x/RT)^{\frac{1}{2}t-1}P_R/\Gamma(t/2)RT. \qquad (8)$$

The expression for $N_v^*(w-x+E_0)$ for a system of s oscillators, of which the ith has a frequency ν_i^*, is given by Eq. (9)[2,18]

$$N_v^*(w-x+E_0) = (w-x+E_0)^{s-1}/\Gamma(s)\prod_{i=1}^{s}h\nu_i^*. \qquad (9)$$

It may be shown from Eqs. (7) to (9) that

$N^*(w+E_0)$

$$= P_R(w+E_0)^{s+(\frac{1}{2}t)-1}/(RT)^{\frac{1}{2}t}\Gamma(s+\tfrac{1}{2}t)\prod_{i=1}^{s}h\nu_i^*. \qquad (10)$$

When no rotations are assumed active, i.e., when $t=0$, $N^*(w+E_0)$ equals $N_v^*(w+E_0)$, which is given by Eq. (9) with $x=0$. Equation (10) reduces to Eq. (9) for this case, as indeed it should.

When some of the vibration frequencies of the active molecule are very high relative to the rest, a better approximation than the above for the number of vibrational states per unit energy is obtained by

separating the frequencies into two classes and computing the degeneracies of the high frequency group by a quantum mechanical treatment. These degeneracies become weighting factors for a series of terms, each of the form of Eq. (9), involving the lower frequency group. In the present work, this was done in reactions (a) to (c) where the high-frequency C—H stretching modes are treated in a quantized manner. For example, if a molecule contains m C—H frequencies, for which the geometric mean is b kcal/mole, and if

$$\tfrac{1}{2}\sum_{i=1}^{m}h\nu_i^* \quad \text{is} \quad E_0'$$

for these frequencies, the modified $N_v^*(w+E_0)$ is given by

$$N_v^*(w+E_0) = \sum_{n=0}^{n\leq \epsilon b^{-1}} c_n(\epsilon-nb)^{s-m-1}/\Gamma(s-m)\prod_{i=1}^{s-m}h\nu_i^*,$$
$$\qquad (11)$$

where $\epsilon = w+E_0-E_0'$. The coefficients c_n denote the number of ways in which n quanta can be distributed among m degenerate oscillators $(n+m-1)!/n!(m-1)!$.

Since the oscillators associated with the activated complex, on the other hand, are likely to be in energy states corresponding to low quantum numbers, a strictly quantum mechanical summation was used to determine the number of vibrational energy states for a particular value of E^+. The procedure used to evaluate $\sum[(E^+-E_v^+)/RT]^{r/2}P(E_v^+)$ as a function of E^+ involved merely a systematic method for enumerating the number of energy levels. In the present work, the frequencies of each activated complex were grouped in integral multiples of the lowest frequency in order to simplify the otherwise exceedingly laborious computations. The numerical values of these stepwise density functions for the quasi-unimolecular reactions in this paper are given elsewhere.[19]

The quantum second-order rate constant for energization of the reactant, k_0^q, is estimated from the limit of Eq. (1) as $p\rightarrow 0$

$$k_0^q = k_2\frac{\sigma_1^+P_1^+}{\sigma_1 P_1 P_2}\exp(-E_a/RT)\int_0^{\infty}N^*(E_a+E^++E_0)$$
$$\times\exp(-E^+/RT)dE^+. \qquad (12)$$

Using Eq. (10), Eq. (12) becomes:

$$k_0^q = k_2\frac{\sigma_1^+P_1^+}{\sigma_1 P_1}\frac{P_2^c}{P_2^q}\frac{\exp(-E_a/RT)}{\Gamma[s+(\tfrac{1}{2}t)]}$$
$$\times\int_{x=0}^{\infty}\left[\left(\frac{E_a+E_0}{RT}\right)+x\right]^{s+(\frac{1}{2}t)-1}e^{-x}dx, \qquad (13)$$

---

[18] The appearance of the quantum-mechanical vibrational ground-state energy E_0 in Eq. (9) resulted from its exclusion in the original definition of the nonfixed energy of A^*. Since the classical treatment of harmonic oscillators considers the former quantity distributable, it must be added to the nonfixed energy $w-x$ to obtain the total vibrational energy. A detailed mathematical justification of this intuitively reasonable statement will be given in Part III. Equation (9) was termed in reference 2 a semiclassical expression because of the appearance there of h. Some detailed comparison of the semiclassical expression with the exact expression may be found in the paper by Rabinovitch and Current[3]. See also E. W. Schlag and R. A. Sandsmark, J. Chem. Phys. **37**, 168 (1962). A preliminary comparison for cyclopropane indicates that at $E_a+E^+=70$ kcal mole^{-1}, a typical value of interest, their exact

$$\int_0^{E_a+E^+}N^*dE$$

is 2.5-fold and 1.4-fold less than that computed from Eqs. (9) and (11), respectively.

[19] G. M. Wieder, Ph.D. thesis, Polytechnic Institute of Brooklyn, June 1961.

TABLE I. Experimental data for pressure-dependent calculations.

Reactant	T °K	Kinetic data A^{∞} (sec^{-1})	E^{∞} (kcal)	Ref.	Spectral data Point group	Vibrational frequencies, reference
(a) Cyclo-C$_3$H$_6$	765	$10^{15.17}$	65.0	a	D_{3h}	(App. III)[b,i]
(b) Cyclo-C$_4$H$_8$	722	$10^{15.6}$	62.5	b	D_{4h}	j
(c) CH$_3$-cyclo-C$_3$H$_5$	763.5	$10^{15.45}$	65.0	c	C_s	App. III
(d) N$_2$O	888	$10^{11.9}$	61.1	d	$C_{\infty v}$	k
(e) cis-butene-2	742	$10^{13.6}$	62.8	e	C_{2v}	l
(f) C$_2$H$_5$Cl	729	$10^{14.6}$	60.8	f	C_s	m
(g) N$_2$O$_5$	300	$10^{14.76}$	21	g	C_{2v}	App. III

[a] See reference 33.
[b] See reference 37.
[c] See reference 38.
[d] See reference 39.
[e] See reference 40.
[f] See reference 43.
[g] See reference 35.
[h] See reference 54.
[i] See reference 55.
[j] (1) G. N. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, J. Am. Chem. Soc. 75, 5634 (1953); (2) T. P. Wilson, J. Chem. Phys. 11, 369 (1943).
[k] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand and Company, Inc., Princeton, New Jersey, 1945).
[l] C. M. Richards and J. R. Nielsen, J. Opt. Soc. Am. 40, 442 (1950).
[m] L. W. Daasch, C. Y. Liang, and J. R. Nielsen, J. Chem. Phys. 22, 1293 (1954).

where c and q denote classical and quantum properties, respectively. An asymptotic estimate of the above integral is given in Appendix II, where it is shown that when $E_a + E_0$ is (as usual) large compared with $[s+(\tfrac{1}{2}t)-1]RT$, the expression simplifies considerably

$$k_0{}^q \cong k_2 \frac{\sigma_1{}^+ P_1{}^+}{\sigma_1 P_1} \frac{P_2{}^c}{P_2{}^q} \frac{\exp(-E_a/RT)}{\Gamma(s+(\tfrac{1}{2}t))} \left(\frac{E_a+E_0}{RT}\right)^{s+(\tfrac{1}{2}t)-1}. \quad (14)$$

The fractional error in going from Eq. (13) to Eq. (14) is shown in Appendix II to be less than

$$[s+(\tfrac{1}{2}t)-1]RT/(E_a+E_0).$$

The error can be further reduced by retaining additional terms of the asymptotic expansion of (13) given in Appendix II. In the reactions discussed in this paper, two terms of the expansion sufficed to reduce the error to 5% or less.

It may be seen from Eq. (13) that the limiting low-pressure second-order rate constants from the theory may be calculated from the activation energy at low pressures and the vibration frequencies of the molecule. Essentially no knowledge of the quantitative properties of the activated complex is needed.

On the other hand, to calculate the k/k^{∞} vs p plot from the theory, it is necessary to know the properties of the activated complex as well. These properties are deduced from a knowledge of the high-pressure frequency factor, guided by certain considerations described later.

Classical Form

In comparing the quantum form of the theory with its classical limit, it is convenient to introduce into Eqs. (1), (2), (6), and (13) quantities which change less on proceeding to the classical limit, namely U, Q's, and y^+. Q differs from its classical limit in second-order quantities, while P differs in first quantities.[20] U does not change at all, since it is a potential energy term.

With the aid of Eqs. (3) and (5), Eqs. (1), (2), and (6) become:

$$k = \alpha \frac{kT}{h} \frac{P_1{}^+ P_R{}^+}{P_1 P_2} \frac{\exp(-U/RT)}{(r/2)!}$$

$$\times \int_{y^+=0}^{\infty} \frac{\left[\int_{y=0}^{y^+} \left(\frac{y^+-y}{RT}\right)^{r/2} p(y)\,dy\right]}{1+k_a/k_2 p} \exp(-y^+/RT)\,d(y^+/RT) \quad (15a)$$

$$k_a = \alpha \frac{\sigma_1}{\sigma_1{}^+} \frac{P_R{}^+}{h} \frac{1}{(r/2)!} \frac{\int_{y=0}^{y^+} \left(\frac{y^+-y}{RT}\right)^{r/2} p(y)\,dy}{N^*(U+y^+)}, \quad (15b)$$

$$k^{\infty} = \alpha \frac{kT}{h} \frac{P_1{}^+ Q_2{}^+}{P_1 Q_2} \exp\left(\frac{-U}{RT}\right). \quad (16)$$

---

[20] For example, cf. expansion of a vibrational $Q = \Pi_i [\exp(\theta_i/2T) - \exp(-\theta_i/2T)]^{-1}$ in powers of θ, where $\theta_i = h\nu_i/k$ with the expansion of the corresponding $P = \Pi_i [1 - \exp(-\theta_i/T)]^{-1}$.

In Eq. (15) $p(y)$ denotes a sequence of δ functions, peaked at the energy levels $y_v^+(y_v^+=E_v^++E_0^+)$ and such that in the immediate neighborhood τ_v of any energy level y_v^+,

$$\int_{\tau_v} p(y)dy = P(E_v^+).$$

The y integral in Eq. (15) equals zero until y^+ exceeds E_0^+.

Proceeding now to the classical limit, Eqs. (15) and (16) remain unchanged, except that now the Q's and $p(y)$ denote the corresponding classical partition functions and the classical density of vibrational energy levels, respectively. Since the latter equals

$$(y^+)^{s^+-1}/\prod_{i=1}^{s^+} h_i v^+ \Gamma(s^+),$$

the y integral in Eq. (15) then becomes a beta function:

$$\int_{y=0}^{y^+} (y^+-y)^{\frac{1}{2}r}(y^+)^{s^+-1}dy = (y^+)^{s^++\frac{1}{2}}B[s^+, (\tfrac{1}{2}r)+1], \quad (17)$$

where $B[s^+, (\tfrac{1}{2}r)+1]$ equals

$$\Gamma(s^+)\Gamma[(\tfrac{1}{2}r)+1]/\Gamma[s^++(\tfrac{1}{2}r)+1].$$

The classical form of Eqs. (15) and (16) reduces to the classical Kassel equations[21] when $r=t=0$, the pre-exponential factor in (13) is replaced by A^∞ (it proves to be temperature independent for this case), P_1^+/P_1 is set equal to unity, and the effective number of Kassel oscillators is taken to be s.

The ratio of limiting high-pressure rate constants for classical and quantum theories is seen from Eq. (16) to be

$$\frac{k_\infty^c}{k_\infty^q} = \left(\frac{Q_2^+}{Q_2}\right)^c \Big/ \left(\frac{Q_2^+}{Q_2}\right)^q. \quad (18)$$

The classical analog of Eq. (13) for the same U is also obtained by introducing U and Q's [using Eqs. (3) and (5)], then setting $E_0^+=0$ and replacing Q_2^q by Q_2^c

$$k_0^c = k_2 \frac{\sigma_1^+ P_1^+}{\sigma_1 P_1} \frac{\exp(-U/RT)}{\Gamma[s+(\tfrac{1}{2}t)]} \int_{x=0}^\infty \left(\frac{U}{RT}+x\right)^{s+(\frac{1}{2}t)-1} e^{-x}dx. \quad (19)$$

Once again, the asymptotic expansion in Appendix II permits an estimate of the integral (with U replacing E_a+E_0 in the Appendix). The ratio of the leading terms in these expansions of the k_0^c and k_0^q is given by

$$\frac{k_0^c}{k_0^q} = \frac{Q_2^q}{Q_2^c} \frac{\exp(E_0^+/RT)}{(1+E_0^+/U)^{s+(\frac{1}{2}t)-1}}. \quad (20)$$

[21] L. S. Kassel, *The Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Company, Inc., New York, 1932).

ACTIVATED COMPLEXES AND THEIR PROPERTIES—GENERAL REMARKS

Activated complexes in unimolecular reactions have been classified[2] as "rigid" or "loose." A rigid complex has all the attributes of the decomposing or isomerizing molecule, except that one of the degrees of freedom is an internal translation (the reaction coordinate) which has replaced a vibrational or internal rotational mode of the reactant. A loose activated complex, unlike the rigid model, possesses one or more rotations in addition to those of the original molecule. For example, the most common loose complex, the one with which we shall be concerned in this work, occurs in some dissociations in which a molecule ruptures into two fragments for which the activation energy for recombination is close to zero. In this loose complex, all rotations which the fragments have in their free state are present. The stretching frequency of the ruptured bond becomes the internal translation in this case. A complex of this type was used[7] to predict approximately the pressure dependence of the rate constant for the dissociation of ethane to form methyl radicals from the high-pressure rate constant.

It is a rather curious fact that low activation energy bimolecular associations of polyatomic species, such as recombination of methyls,[22] of ethyls,[23] of propyls[24] or of perfluoromethyls,[25] or association of BF_3 with $P(CH_3)_3$ or with amines,[26] appear to have rather high pre-exponential factors, corresponding to an over-all collision efficiency of the order of 1 to 0.1. Evidently, in such reactions the two fragments rotate in a relatively unrestricted fashion in the activated complex, which is therefore a "loose" complex. Higher activation energy bimolecular associations, such as dimerization of two unsaturated molecules,[27] appear to have low Arrhenius frequency factors, i.e., to possess rigid activated complexes.

Possible explanations of this apparent difference between high and low activation energy bimolecular associations could be offered, though further data supporting it would be desirable.[28] In the present work, we merely content ourselves with using this apparent result and assume accordingly that only the low

[22] R. Gomer and G. B. Kistiakowsky, J. Chem. Phys. **19**, 85 (1951); G. B. Kistiakowsky and E. K. Roberts, *ibid.* **21**, 1637 (1953).

[23] K. J. Ivin and E. W. R. Steacie, Proc. Roy. Soc. (London) **A208**, 25 (1951).

[24] S. G. Whiteway and C. R. Masson, J. Chem. Phys. **25**, 233 (1956).

[25] P. B. Ayscough, J. Chem. Phys. **24**, 944 (1956).

[26] G. B. Kistiakowsky and R. Williams, J. Chem. Phys. **23**, 334 (1955); G. B. Kistiakowsky and C. E. Klots, *ibid.* **34**, 715 (1961).

[27] G. B. Kistiakowsky and J. R. Lacher, J. Am. Chem. Soc. **58**, 123 (1936); cf. S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill Book Company Inc., New York, 1960). p. 302, for summary of data.

[28] Such apparent exceptions as CH_3+O_2 and CH_3+NO may be due to three-body effects, so that the reported rate constants would indeed be too low. See Benson, reference 27, p. 301, for survey of three-body effects.

activation energy bimolecular associations (and their inverse processes) have loose complexes.

In this study, computations of the dependence of the quasi-unimolecular rate constants on pressure were based on rigid activated complex models in reactions (a) to (f), because in each of these cases the activation energy of the reverse reaction, as estimated from the difference between the experimental activation energy and ΔH of the forward reaction, was greater than 20 kcal/mole.[29] A loose complex, consisting of freely rotating NO_2 and NO_3 radicals, was selected for (g), because of the high-frequency factor for recombination.[30]

In the cases for which rigid complexes were postulated, it was assumed that the product of the moments of inertia of the activated complex was effectively the same as that for the active molecule and that only the vibrational degrees of freedom in both species contribute their energy to the breaking bond. The ratio of partition functions of the adiabatic rotations P_1^+/P_1 then reduced to the ratio of symmetry numbers σ_1/σ_1^+. Since $r=t=0$ by the second assumption, P_R^+ equals unity and P_2 becomes the partition function of the vibrations of the active molecule.

In the vibrational assignment to each rigid complex, those frequencies of the reactant that would appear to exert a relatively small contribution to the chosen reaction coordinate were retained. Of the remainder, one frequency was replaced by the internal translation, and the others (usually not more than two) were lowered to attain agreement with $\Delta S^{\ddagger}$, the experimental activation entropy. The latter quantity was determined for each reaction from Eq. (21), which is obtained by equating the experimental high-pressure frequency factor A^{∞} to that given by Eyring[17] (with whose formulation the present theory is identical at high pressures)

$$\Delta S^{\ddagger}=R[\ln(A^{\infty}h/kT)-1]. \quad (21)$$

This $\Delta S^{\ddagger}$ for rigid complexes is related to S_v and to $S_v^{\ddagger}$, the vibrational entropies of A and A^+, respectively,

$$\Delta S^{\ddagger}=S_v^+-S_v+R\ln(\alpha\sigma_1/\sigma_1^+). \quad (22)$$

QUASI-UNIMOLECULAR RATE CONSTANTS

Properties of A^+ and A

The assignments of vibration frequencies used for the parent molecule, A, were taken from the literature (Table I) except for the two cases where the latter was incomplete. For N_2O_5, the assignment was based on some of the known fundamentals of N_2O_5 and on estimates of characteristic group frequencies in related

[29] The activated complex for reaction (c), for which ΔH has not been measured, was assumed to be rigid in analogy to reaction (a).
[30] G. Schott and N. Davidson, J. Am. Chem. Soc. **80**, 1841 (1958).

TABLE II. Assumed parameters for pressure-dependent calculations.

Reactant	Type	Properties of activated complex			Properties of active molecule	
		σ_1^+	α	r	$\sigma_d(A)$	t
(a) Cyclo-C_3H_6 I.	Rigid	2	1	0	3.9	0
II.	Rigid	1	1	0	3.9	0
(b) Cyclo-C_4H_8	Rigid	4	1	0	5.5	0
(c) CH_3-cyclo-C_3H_5	Rigid	1	8	0	5.0	0
(d) N_2O	Rigid	1	1	0	3.3	0
(e) cis-butene-2	Rigid	1	2	0	5.0	0
(f) C_2H_5Cl	Rigid	1	1	0	5.5	0
(g) N_2O_5	Loose	4[a]	1	4	6.0	1

[a] Complex has an internal symmetry number of 12 due to free rotations of NO_2 and NO_3 groups. the σ_1^+ refers to the adiabatic rotations.

compounds. A similar procedure was used for methylcyclopropane, and subsequently compared with a recent assignment for that compound. In N_2O_5, the internal rotations were assumed to be unhindered, to obtain agreement with its approximately known entropy. These procedures and properties are described in Appendix III.

The frequencies of the activated complexes were estimated as described in the previous section. All three external rotations of A (and hence A^+) were taken to be adiabatic. As a compromise in the loose complex for N_2O_5, one of the two internal rotations was assumed adiabatic, i.e., $t=1$. Properties are given in Appendix III.

E_a for these reactions was determined from the limiting high pressure activation energy E^{∞} by equating Eq. (6) to the Arrhenius expression $[k^{\infty}=A^{\infty}\exp(-E^{\infty}/RT)]$ and logarithmically differentiating both sides with respect to $(1/RT)$

$$E_a=E^{\infty}-\tfrac{1}{2}(r-t+2)RT+\langle E_v^*\rangle-\langle E_v^+\rangle, \quad (23)$$

where $\langle E_v^*\rangle$ and $\langle E_v^+\rangle$ are the mean vibrational energies (in excess of the ground-state energies) of the active molecule and activated complex, respectively. Both $\langle E_v^*\rangle$ and $\langle E_v^+\rangle$ were determined from the properties of A and A^+.

The rate constant for collisional deactivation k_2 was determined from the usual kinetic theory collision frequency.

Tables I and II summarize, respectively, the experimental data and assumed parameters used in the pressure-dependent calculations. (The grouped activated complex frequencies are given in Appendix III.)

TABLE III. Experimental data for low-pressure calculations.

Reactant	$T°K$	E^0(kcal)	Kinetics ref.	Vibrational frequencies, ref.	E_0^+(kcal)
(h) O_3	373	24.0	a	l	2.50
(i) F_2O	533	39.0	b	m	1.85
(d) N_2O	888	59.2	c	n	3.36
(j) NO_2Cl	476	27.5	d	o	6.51
(k) H_2O_2	723	48	e–g	p	14.35
(l) N_2O_4	277	11.0	h	q (App. III)	13.9
(m) C_2H_6	473	...	i, j	n	37.6
(g) N_2O_5	300	19.3	k	App. III	14.1

ᵃ S. W. Benson and A. E. Axworthy, Jr., J. Chem. Phys. **26**, 1718 (1957).

ᵇ W. Koblitz and H. J. Schumacher, Z. physik. Chem. (Leipzig) **B25**, 283 (1934).

ᶜ See reference 39.

ᵈ H. F. Cordes and H. S. Johnston, J. Am. Chem. Soc. **76**, 4264 (1954).

ᵉ P. A. Giguère and I. D. Liu, Can. J. Chem. **35**, 283 (1957).

ᶠ D. E. Hoare, J. B. Protheroe, and A. D. Walsh, Nature **182**, 6541 (1958).

ᵍ W. Forst, Can. J. Chem. **36**, 1308 (1958).

ʰ T. Carrington and N. Davidson, J. Phys. Chem. **57**, 418 (1953).

ⁱ Reference 22; R. E. Dodd and E. W. R. Steacie, Proc. Roy. Soc. (London) **A223**, 283 (1954).

ʲ E. W. R. Steacie, J. Chem. Soc. **1956**, 3986.

ᵏ Reference 35a.

ˡ M. K. Wilson and R. M. Badger, Jr., J. Chem. Phys. **16**, 741 (1948).

ᵐ H. J. Bernstein and J. Powling, J. Chem. Phys. **18**, 685 (1950).

ⁿ See Table I, reference k.

ᵒ R. Ryason and M. K. Wilson, J. Chem. Phys. **22**, 2000 (1954).

ᵖ R. L. Miller and D. F. Hornig, J. Chem. Phys. **34**, 265 (1961).

ᑫ See reference 58.

Integration

The integration region E^+ in Eq. (1) was divided into successive intervals, so chosen that $P(E_v^+)$, a piecewise constant function, had a constant value in each interval. $N^*(E_a+E_0+E^+)$ can also be treated as such a function (a good approximation since the interval size is so much less than $(E_a+E_0+E^+)$. In almost all cases of this paper the frequencies ν_i were grouped in multiples of the lowest frequency ν^+, for convenience. In each interval, $n h\nu^+$ to $(n+1)h\nu^+$, where $n=0, 1, 2, \cdots, P(E_v^+)$ had a constant value.

The integration was cut off at an upper limit for which the error of neglecting further terms is small. Since the error is a maximum[2] at $p=\infty$, and the value of the integral is known exactly at $p=\infty$, the cut-off could be chosen so that in no instance was the error greater than 4%, other than (e). In (e), $\sum P(E_v^+)$ rose very rapidly with E^+, and for large E^+ (greater than 21.1 kcal) the sum was converted approximately to an integral to keep the error below the 4% limit

$$\sum_{E_v^+ < E^+} P(E_v^+)$$

was replaced by $C(E^+)^n$ for $E^+ > 21.1$, and C and n were evaluated by fitting this function to the $\sum P(E_v)$'s from 18 to 21 kcal. n, incidentally, was about 10.

SECOND-ORDER LIMITING RATE CONSTANTS

Table III gives the experimental data employed in the low-pressure calculations. It was assumed that $t=0$ for each reaction except (g) and that $t=1$ for (g). Equation (13) was used to calculate the rate constants, with the aid of the approximation and error estimate of Appendix II [cf. Eqs. (A2) and (A3)]. To use Eq. (20) for k_0^c/k_0^q, estimates of E_0^+ were needed, and are given in Table III.

An additional calculation was also made for (m), the dissociation of ethane, upon the assumption that two rotations of the four in ethane are active, in order to compare with the results obtained when all rotations are considered adiabatic. The pertinent rotational partition functions are given in Appendix III.

In each reaction except (m), E_a was evaluated by differentiating the logarithm of the appropriate expression for the second-order constant with respect to T, multiplying by kT^2 and equating the result to E^0, the experimental low-pressure activation energy.

RESULTS AND COMPARISONS WITH EXPERIMENT

Pressure Dependence of the Rate Constants

a. Isomerization of Cyclopropane to Propylene

There has been some controversy regarding the choice between either a C–H migration or a C–C breaking reaction coordinate. Recent studies[31,32] favor the formation of a trimethylene intermediate followed by a CH migration in the latter to give propylene.

In model I of Table II, the frequency assignment of the activated complex based on a ring-rupture model results from the removal of one of the ring deformations of cyclopropane and the lowering of two other
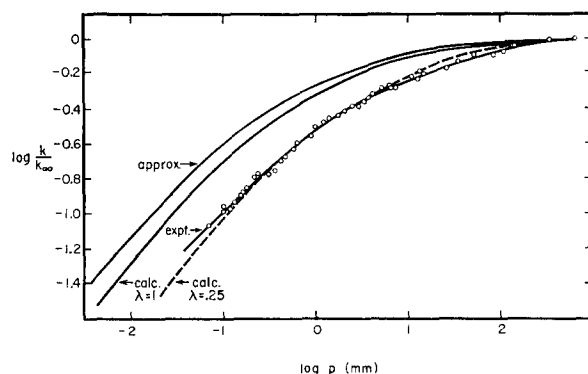
FIG. 1. Pressure dependence of the reduced-rate constant for the isomerization of the cyclopropane at 765°K.

[31] B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, J. Chem. Phys. **28**, 504 (1958); see also reference 8b. Since the rates of geometrical and structural isomerization do differ, the activated complex of the latter presumably involves more than a ring opening, namely some CH migration. Model II is presumably more appropriate than I which only has ring opening.

[32] S. W. Benson, J. Chem. Phys. **34**, 521 (1961).

frequencies to become torsional modes in the complex. Figure 1 shows the theoretical k/k^∞ vs p plots, where λ is the assumed collision efficiency, with the experimental curve obtained at 765°K, by Pritchard, et al.[33] The calculated curves were based on a quantum mechanical treatment of the C–H stretching frequencies in the active molecules involving Eq. (11), and the approximate curve was obtained from Eq. (9).

Alternate calculations (model II) based on an activated complex involving the elimination of a C–H stretch and the weakening of several others shifted the theoretical curves shown to lower pressures by only 0.06 log p units.[19] The p dependence of k was also determined at 710°K on the basis of the second model, and the temperature decrease of 55° shifted the calculated log$p$ by 0.25 units towards lower pressures. This result is in diasgreement with the experimental value of 0.53 units reported by Schlag and Rabinovitch[34] from their data at 718° and those of Pritchard et al., corrected to 773° by Johnston and White.[35c] However, the comparison may not be on a sound basis, since the experimental runs were performed in different laboratories and may have been subject to systematic errors which were not comparable. Incidentally, the maximum shift predicted by Slater's approximate expression[1a] for this T variation is 0.22 for $n=14$.

b. Decomposition of Cyclobutane to Ethylene

Recent deuterium isotope studies[36] suggest that reaction occurs via a C–C rupture rather than by a hydrogen migration mechanism. A plausible reaction coordinate, and the one assumed here, is the simultaneous expansion of two opposite C—C bonds in the

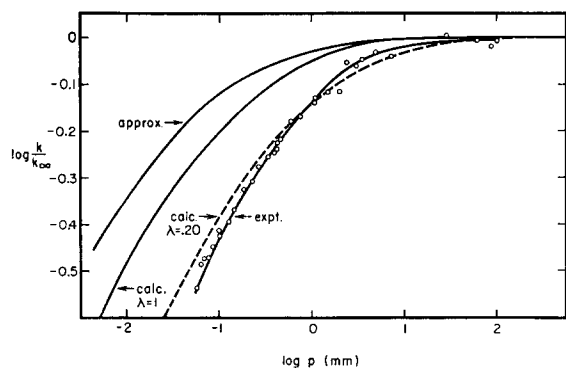FIG. 2. Pressure dependence of the reduced-rate constant for the decomposition of cyclobutane at 722°K.
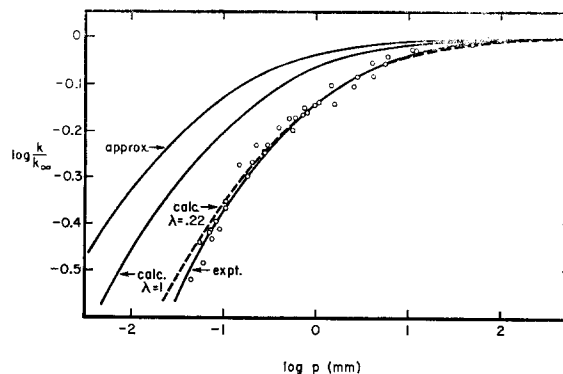
FIG. 3. Pressure dependence of the reduced-rate constant for the isomerization of methylcyclopropane at 763.5°K.

square ring formed by the four C atoms, leading to the separation of two C_2H_4 molecules. The frequencies of the resulting planar rectangular complex were obtained by the removal of a ring stretching frequency of the reactant and by substantially lowering the out-of-plane ring bend and two of the ring deformation frequencies chosen so as to fit $\Delta S^\ddagger$ at high pressures. The theoretical curves are shown in Fig. 2 with the experimental data of Pritchard et al.[37]

c. Isomerization of Methylcyclopropane to Butene-1 and cis and trans Butene-2

The kinetics were investigated by Chesick[38] in order to determine the effect of substituents on an activated cyclopropane molecule. He concluded that the isomerization is a truly homogeneous unimolecular reaction, and that, since the falloff in the rate occurred at $\sim 1/30$ the pressure at which the decrease was observed in the cyclopropane rearrangement, the addition of the methyl substituent increased the lifetime of the active molecule.

The products found were four isomeric butenes: butene-1, cis and trans butene-2, and isobutene. Formation of the last product was accompanied by an activation energy that was about 2.3 kcal higher than that for any of the processes yielding the nonbranched butenes. In order to simplify the calculations in the present work, the isobutene reaction was neglected, since the rate of its production contributed only about 8% to the total decomposition rate at 763.5°K. The pre-exponential factors and activation energies of the rearrangements producing butene-1 and butene-2 are approximately equal.

The reaction coordinate was chosen to be a partial H migration combined with an unsymmetrical ring deformation resulting in an activated complex with eight optical isomeric forms.[19] One C–H stretching frequency

[33] H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, Proc. Roy. Soc. (London) A217, 563 (1953).
[34] E. W. Schlag and B. S. Rabinovitch, J. Am. Chem. Soc. 82, 5996 (1960).
[35] (a) R. L. Mills and H. S. Johnston, J. Am. Chem. Soc. 73, 938 (1951); (b) H. S. Johnston and R. L. Perrine, ibid. 73, 4782 (1951); (c) H. S. Johnston and J. R. White, J. Chem. Phys. 22, 1969 (1954).
[36] R. Srinivasan and S. M. B. Kellner, J. Am. Chem. Soc. 81, 5891 (1959).

[37] (a) H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, Proc. Roy. Soc. (London) A218, 416 (1953); (b) C. T. Genaux, F. Kern, and W. D. Walters, J. Am. Chem. Soc. 75, 6196 (1953).
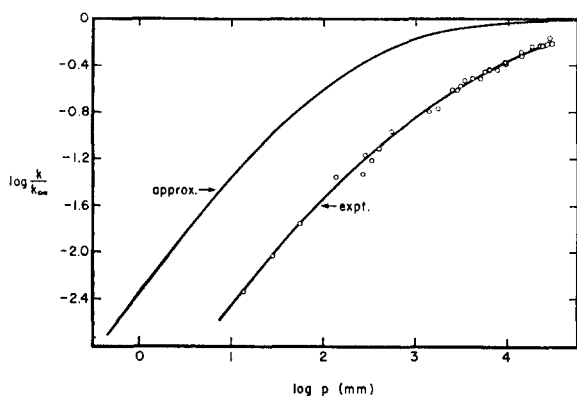[38] J. P. Chesick, J. Am. Chem. Soc. 82, 3277 (1960).

FIG. 4. Pressure dependence of the reduced-rate constant for the dissociation of nitrous oxide at 888°K.

of the reactant was removed and three of the skeletals were lowered in the complex to fit the experimental $\Delta S^{\ddagger}$. The theoretical curves are shown in Fig. 3 along with experimental curve obtained by Chesick at 763.5°.

The experimental kinetics at 710.1°K show a $\log p$ shift towards lower pressures of 0.3_0 units relative to the curve at 763.5°. The theoretical displacement based on detailed calculations at these two temperatures is 0.30 units, in excellent agreement with experiment.

d. Dissociation of N_2O to N_2 and O

N_2O is one of the few small polyatomic molecules for which the decomposition kinetics have been studied over the broad pressure range required for the observance of quasi-unimolecular behavior. In this detailed analysis Johnston has expressed doubt, however, both as to interpretation of mechanism and role of concommitant heterogeneous reactions.[39] Currently, the reaction has a rather low A^{∞}, a result consistent with the fact that the dissociation involves a violation of the spin conservation rule.[13] (More precisely, the *ground*
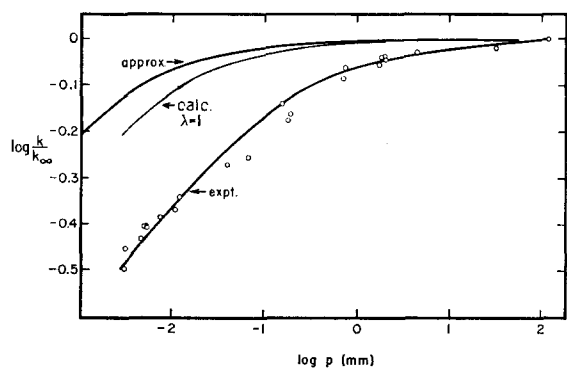

FIG. 5. Pressure dependence of the reduced-rate constant for the isomerization of *cis* butene-2 at 742°K.

[39] H. S. Johnston, J. Chem. Phys. **19**, 663 (1951). [For recent references on complications, cf. C. P. Fenimore, *ibid.* **35**, 2243 (1961).]
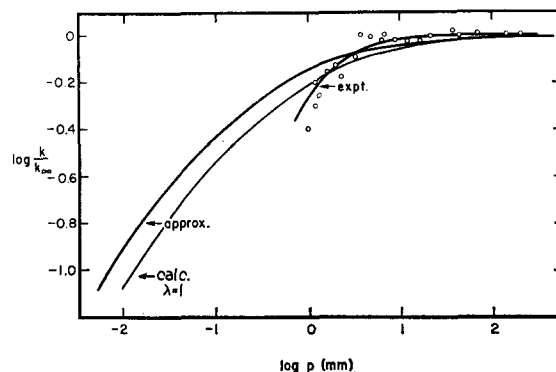
FIG. 6. Pressure dependence of the reduced-rate constant for the decomposition of ethyl chloride at 729°K.

state of N_2O is a singlet while those of N_2 and O are singlets and triplets, respectively.)

The reaction coordinate was taken to be the antisymmetric stretching vibration (of the O away from the N_2). The theoretical curve in Fig. 4 is based on a transmission coefficient κ of 0.018, to get agreement with A^{∞} [κ is to be introduced into the numerator of both Eqs. (1) and (2)].

e. Isomerization of cis butene-2 to trans butene-2

Rabinovitch and Michel[40] have recently studied the kinetics over a wide pressure range. They suggested that the considerable lack of agreement between the high-pressure Arrhenius factors previously obtained by Kistiakowsky and Smith[41] and by Anderson *et al.*[42] was due to the presence of side reactions which strongly affect the observed kinetics above 10-mm butene-2 pressure. However, Rabinovitch and Michel have cited evidence that the reaction is a simple elementary
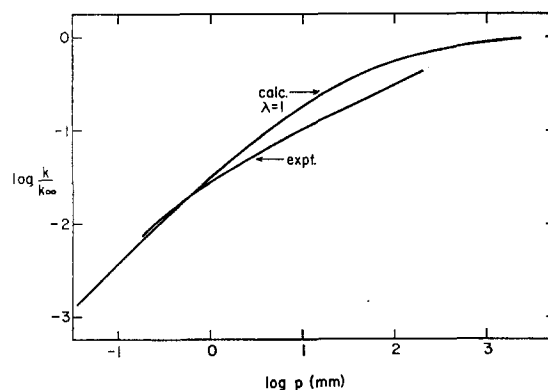

FIG. 7. Pressure dependence of the reduced-rate constant for the dissociation of nitrogen pentoxide at 300°K.

[40] B. S. Rabinovitch and K. W. Michel, J. Am. Chem. Soc. **81**, 5065 (1959).

[41] G. B. Kistiakowsky and W. R. Smith, J. Am. Chem. Soc. **58**, 766 (1936).

[42] W. F. Anderson, J. A. Bell, J. M. Diamond, and K. R. Wilson, J. Am. Chem. Soc. **80**, 2384 (1958).

TABLE IV. Quasi-unimolecular rate constant behavior.

Reactant	$T°K$	$p_{\frac{1}{2}}$(expt) (mm)	Ref. (from Table I)	$p_{\frac{1}{2}}$(expt)$/p_{\frac{1}{2}}(q)$[a]	E_a (kcal mole^{-1})
(a) Cyclo-C_3H_6	765	4.6	a	3.6[b]	62.7
(b) Cyclo-C_4H_8	722	0.23	b	6.0	59.8
(c) CH_3-cyclo-C_3H_5	763.5	0.17	c	4.6	62.2
(d) N_2O	888	1.3×10^4	d	36	59.5
(e) cis-butene-2	742	0.019	e	~24	61.7
(f) C_2H_5Cl	729	0.90	f	~2.0	57.5
(g) N_2O_5	300	290	g(3)	2.0	20.1

[a] All collision efficiencies assumed unity.

[b] When H migration is used as reaction coordinate, this value becomes 4.0 (cf. text). The 4.6 in (c) is also based on an H migration.

process below 2–5 mm, and from an extrapolation plot determined the value of the limiting high pressure rate used in the present work. Any such uncertainties are of course multiplied in the determination of A^∞. There is now believed to be considerable doubt about the validity of this A^∞ [B. S. Rabinovitch (private communication)].

A torsional skeletal motion was assumed for the reaction coordinate, and the activated complex frequencies were obtained by the removal of one of the skeletal modes of the reactant and lowering the methyl torsional frequencies slightly. The approximate theoretical curve [from Eq. (9)] is shown in Fig. 5 with the experimental plot.

Quantization of the C–H frequencies would be expected to have approximately the same effect for C_4H_8 as for cases (b) and (c). In the latter cases, the more accurate curve was shifted about 0.43 log$p$ units to the right along the abscissa, and the same shift was assumed for C_4H_8 to obtain the calc $\lambda=1$ curve of Fig. 5. The uncertainty in the data did not warrant a separate and perhaps more accurate calculation of this curve.

f. Decomposition of C_2H_5Cl to C_2H_4 and HCl

This reaction was included in an investigation of the kinetics of a series of HCl elimination reactions by Howlett.[43] Since the reported A^∞ values for those reactions believed to be unimolecular were somewhat scattered, an approximate weighted geometric mean value of 10^{14} was used in the present work to minimize the experimental error. E^∞ was lowered by about 2 kcal to obtain agreement with the reported rate constant using the mean frequency factor above.

It was assumed (cf. reference 12 and others) that reaction takes place by way of a cyclic activated complex. The frequencies were obtained by the removal of a C–H stretching mode of C_2H_5Cl and by the adjustment of some of the other frequencies. Figure 6 shows the approximate theoretical pressure-dependence plot

with that from the experimental data. Quantization of the C–H frequencies was assumed to have approximately the same effect for C_2H_5Cl as they did for C_3H_6, namely a shift of 0.27 log$p$ units to the right. The resultant curve is given as calc $\lambda=1$ in Fig. 6.

g. Decomposition of N_2O_5 to NO_2 and NO_3

The complex decomposition of N_2O_5 has been quite thoroughly investigated,[44] and the Ogg mechanism is generally accepted. The thermal decomposition has been studied over a very broad pressure range in the presence of NO, under conditions in which the initial rate is that of the primary unimolecular step. Application of the consistency theorems deduced by Kassel[45] to the experimental data led both Kassel and Johnston and White[35c] to conclude that there was some systematic error in the high-pressure region. Rather than attempt to make some of the rotations in the loose activated complex hindered to account for the apparently low A^∞, (the data at present do not appear to warrant such refinements) a simple, less accurate, but self-consistent procedure was adopted. Both k and k_a were merely multiplied by a correction factor of 0.016 to equate the calculated A^∞ with that found experimentally. Figure 7 shows the theoretical curve with the plot given by Johnston and White summarizing the data.

h. Summary

As a summary of the isothermal pressure dependence calculations, the pressures at which the rate constants attain one-half their high-pressure values are given in Table IV, where $p_{\frac{1}{2}}$ (expt) and $p_{\frac{1}{2}}(q)$ denote the experimental and quantum mechanical results, respectively. All results are based on quantization of C–H frequencies in A^* as discussed previously.

Since the experimental values of A^∞ may subsequently be improved through further studies, an approximate estimate of the corresponding effect of such

[43] K. E. Howlett, J. Chem. Soc. 1952, 3695, 4487.

[44] See S. W. Benson, reference 27, for a review.
[45] L. S. Kassel, J. Chem. Phys. 21, 1093 (1953).

TABLE V. Limiting second-order frequency factors (mole^{-1}cm^3 sec^{-1}).

Molecule	T °K	A (expt)	Ref. (from Table III)	$A(q)/A$ (expt)	$\sigma_d(A)$	t	E_a	No. terms $(m+1)$[a]
(h) O_3	373	4.6×10^{15}	a	1.1	3.35	0	23.1	1
(i) F_2O	533	2.5×10^{17}	b	0.12	4.5	0	38.4	2
(d) N_2O	888	5.2×10^{15}	c	16	3.3	0	59.2	2
(j) NO_2Cl	476	6.3×10^{16}	d	11	6.7	0	27.6	2
(k) H_2O_2	723	4.6×10^{18}	e	0.07	3.5	0	48.0	2
(l) N_2O_4	277	2.0×10^{17}	h	2.2	5.3	0	11.8	2
(m) C_2H_6	473	5.5×10^{23} [b]	j	2.9	3.5	0	85.0	2
				7.6		2		
(g) N_2O_5	300	3.1×10^{19}	Ref. g(3) of Table I	0.19	6.0	1	19.5	2

[a] $m+1$ is the number of terms used in Eq. (A2) of Appendix II to reduce error of Eq. (13) to 5% or less.

[b] This value was obtained from a third-order rate constant for recombination of CH_3 radicals of 2.7×10^{20} mole^{-2} cm^6 sec^{-1} and a K_{diss} of 10^{-36} mole cm^{-3} (cf. Gill and Laidler in reference 1.)

a correction on the theoretical $\log k/k^\infty$ vs $\log p$ plots is of interest. In Appendix IV, it is shown that an error of a factor of γ in A^∞ approximately causes an error of a factor of $\gamma^{1-\theta}$ in $p_{\frac{1}{2}}$(calc) and roughly shifts the plot along the $\log p$ axis by an amount $(1-\theta)\log\gamma$, where $\theta=[s+(\frac{1}{2}t)-1]kT/(E_a+E^++E_0)$ and E^+ is a suitable average of E^+ (as described in Appendix IV). Typical values of θ for the various reactions in this paper are given in Appendix IV.

Second-Order Rate Constants

The results are reported in Table V, where A(expt) and $A(q)$ denote the experimental and quantum frequency factors, respectively. The corresponding activation energies are equal as a result of the procedure outlined earlier. Equation (13) and collision efficiencies of unity were applied in all cases.

Error Estimates of Classical Theory Calculations

The ratio of limiting high pressure-rate constants for classical and quantum theories is given by Eq. (18).

TABLE VI. Estimate of error in classical theory.

Reactant	k_0^c/k_0^q	k_∞^c/k_∞^q	Reactant	k_0^c/k_0^q
(a) Cyclo-C_3H_6	4.1×10^4	0.98	(h) O_3	5.0
(b) Cyclo-C_4H_8	3.1×10^4	0.53	(i) F_2O	3.1
(c) CH_3-cyclo-C_3H_5	4.5×10^3	0.14$_5$	(j) NO_2Cl	48.5
(d) N_2O	2.7	0.61	(k) H_2O_2	120
(e) cis-butene-2	2.8×10^4	0.75	(l) N_2O_4	1.1×10^3
(f) C_2H_5Cl	8.6×10^3	0.38	(m) C_2H_6	2.3×10^6 ($t=0$)
(g) N_2O_5	1.1×10^3	0.10		1.5×10^6 ($t=2$)

The ratio may be computed using the properties of A^+ and A found earlier.

The ratio of limiting low pressure rate constants for classical and quantum theories is given by Eq. (20) if one uses the leading term of the asymptotic expansion. By way of comparison, the ratios calculated from the "exact" Eq. (13) and (19) were 5.4×10^4 and 2.8 for cyclopropane and N_2O, respectively, compared with 4.1×10^4 and 2.7 calculated from Eq. (20). To calculate the ratio for systems (a) to (g), the properties found in the previous section were used. In the case of the reactions (h) to (l), it was necessary to estimate E_0^+ as well, for E_0^+ had not been previously determined. The results are tabulated in Table VI.

DISCUSSION

Estimates of Error in Classical Theory

The errors in the classical theory are seen from Table VI to be considerable in the low-pressure region, particularly in cases involving four or more atoms. At very high pressures, on the other hand, where the unimolecular rate constant is not pressure dependent, the ratio depends only on the ratios of the classical to quantum partition functions for A^+ and for A. These species differ only in one or two degrees of freedom and so k_∞^c/k_∞^q is not far from unity.

Results from the Quantum Form of the Theory

The $p_{\frac{1}{2}}$(expt)/$p_{\frac{1}{2}}(q)$ ratios in Table IV show that, with the exception of the cis butene-2 isomerization and the N_2O decomposition, the half-pressures predicted by theory are in agreement with experiment, within a factor of 6. As mentioned previously, there is some uncertainty about these two reactions, and about those

involving C_2H_5Cl and N_2O_5.[46] Adding to this list the systems studied by Rabinovitch and co-workers,[3,8] it may be concluded that the correspondence between theory and experiment is reasonable in view of the fact that Eq. (1), upon which the calculations are based, does not contain the arbitrary parameter for fitting the experimental pressure-dependence curves and in view of possible errors in A^∞. The results do not appear to be markedly sensitive to the choice of reaction coordinate as long as the selection is reasonable and the experimental entropy requirements are satisfied, as illustrated by the use of alternate activated complex models for the cyclopropane and[19] N_2O reactions.

It is seen in Figs. 1–7 that in every case, except for the decomposition of N_2O_5, the computed rate constants are too high at low pressures. It will be recalled that introduction of the C–H quantization in the active molecule lowered the rate at low pressures without, of course, affecting it at high pressures. Further refinement, by introducing a similar treatment for the moderately high frequencies of A^*, would continue this trend, and so tend to reduce still further the $p_{\frac{1}{2}}(\text{expt})/p_{\frac{1}{2}}(q)$ ratio.[47]

A portion of the discrepancy of the factor of 4 or 5 could be due to a deactivational collision efficiency less than unity. The effect of introducing collision efficiency parameters of 0.25, 0.20, and 0.22 for reactions (a), (b), and (c), respectively, is shown in Figs. 1–3. Since these λ values are still of a magnitude of the order of unity, this suggests that collisional deactivation is a relatively efficient process for large molecules in accord with the results of various kinetic studies in the presence of foreign gases.[33,37a,48]

In the case of very small molecules, such as N_2O the assumption that the population of molecules having energies just below the critical amount is the equilibrium one may be contributory to some additional

error, because of possible depletion effects (cf. dissociation of diatomic molecules.[13])

The tendency of the lifetime of the active molecule to increase with increasing molecular complexity, as illustrated, in general, experimentally [and particularly by the decreased falloff pressure for the rate of reaction (c) relative to (1)], seems to support the assumption that energy flows relatively freely among the vibrational degrees of freedom of the active molecule. When the vibrational modes of the methyl group in methylcyclopropane are at least weakly coupled to the reacting part of the molecule, they add to the number of energy sinks, and thus decrease the k_a/k_2 ratio. The theory predicts a $p_{\frac{1}{2}}$ lowering by a factor of 30 upon methyl side-group substitution of cyclopropane, as compared to the experimentally observed decrease by a factor of 27.

The kinetic study by Frey and Kistiakowsky of the isomerization of "hot" cyclopropane[49] (formed by the attack on ethylene by methylene generated from the 3130 A photolysis of ketene) showed that the lifetime of the energy-rich cyclopropane was much shorter than that observed in the thermal isomerization. It corresponds to a $k_a \sim 2.5 \times 10^9$ sec^{-1} for $\lambda = \frac{1}{4}$. Extrapolation of Table 12 of reference 19 gives for this k_a value an $E^+ \sim 33$ kcal, which when added to $E_a (=63)$ yields 96 kcal for the nonfixed energy of the photochemically produced cyclopropane molecules. This last quantity should be compared to the heat of the reaction, $CH_2 + CH_4 = \text{cyclo-}C_3H_6$, which although, unfortunately, uncertain appears to lie in the range 67–84 kcal mole^{-1}. If we take Benson's estimate[27] of $\Delta H = 78$ as reasonable, the nonfixed energy of the cyclopropane molecules would be about $(84 + \epsilon^*)$ kcal mole^{-1} (cf. Appendix V), where ϵ^* is the portion of the excess energy of CH_2 available for subsequent thermal excitation of the cyclopropane. Our results then suggest that ϵ^* is about 12 kcal mole^{-1}. This is consistent with what may be expected, since the photons by the ketene[49] have an excess over the dissociation energy of about 15 kcal, of which a fraction may be taken up by methylene. According to the basic assumption of this paper all excess vibrational energy of the CH_2 should be available for the reaction. At most $m_{C_2H_4}/m_{C_3H_8}$ of the excess translation energy of CH_2 would be available.[50]

The predicted influence of temperature on $\log k/k^\infty$ in the case of reaction (c) is in excellent agreement with the kinetic investigation by Chesick at two different temperatures. It would be desirable, in regard to cyclopropane, to be able to base the comparison on

[46] It is interesting to note that the calculated ratio, 50, of $p_{\frac{1}{2}}$'s for the cis-butene and cyclobutane isomerization is approximately equal to the corresponding ratio of the A^∞'s, 100. This result is not unexpected since rigid complexes were used for both, both reactants have the same number of active modes, and both reactions have the same E^∞. Raising the A^∞ factor for the cis-butene reaction would result in improved agreement between theory and experiment.

[47] Indeed, recently a more accurate calculation of N^* has been made using the nonclassical summation for all frequencies of the active molecule, not just for the C—H ones. A 709 computer was programmed for estimating these sums and excellent agreement with the experimental curve was obtained. These calculations and comparisons with the data have now been made for [8a] CH_3NC and for cyclopropane [(reference 8(b)]; D. W. Setser and B. S. Rabinovitch [Can. J. Chem. (to be published)]. These authors used a σ of 5.9 Å (we used 3.9) and an A^∞ of $10^{15.30}$ (we used $10^{15.17}$). Use of the former would have shifted our $\log k$ vs $\log p$ curve 0.10 units to the left along the p axis while use of the latter would have shifted it 0.05 units to the right [see Eq. (A11) and Table VII of Appendix IV]. The net shift due to these two sources is, therefore, negligible and the better agreement of S. and R. is presumably due to their accurate calculation of N^*. See also Schlag and Sandsmark.[8]

[48] D. J. Wilson and H. S. Johnston, J. Am. Chem. Soc. 75, 5763 (1953); H. S. Johnston ibid. 75, 1567 (1953); M. Volpe and H. S. Johnston ibid. 78, 3903 (1956); R. E. Harrington, B. S. Rabinovitch, and M. R. Hoare, J. Chem. Phys. 33, 744 (1960).

[49] H. M. Frey and G. B. Kistiakowsky, J. Am. Chem. Soc. 79, 6373 (1957).

[50] D. W. Setser and B. S. Rabinovitch [Can. J. Chem. (to be published)] have studied the behavior of hot cyclopropane using a variety of CH_2 sources and have made an extensive analysis of the energetics. Their Table II indicates that their estimate of E^+ from the k_a data of reference 49 is slightly higher than ours, perhaps due to a more accurate count[47] for N^*, obviating thereby the necessity of assuming $\lambda = \frac{1}{4}$.

accurate data collected under the same experimental conditions.

The results in Table V show that the calculated frequency factors for the energization rates are in moderate agreement with the observed parameters. The effects of anharmonicity on the density of energy states, a factor which we have not considered, would be greatest with small molecules, since then all the energy needed for reaction has to reside in only a few vibrations. For F_2O, Rice[6] suggests that anharmonicity might increase the calculated rate about threefold.

Concluding Remarks

The results of this paper, together with those of other workers,[3,8,34,38,47] support the assumption made here that *all* vibrational modes participate in energy exchange in the active molecule. Normally, when the Kassel classical theory is fitted to the data, one of the theoretical parameters thereby evaluated is the "effective" number of oscillators s, which usually proves to be substantially less than the number of molecular vibrations. Since these vibrations are actually quantized rather that classical, they are not fully excited in the sense of energy equipartition, and so from a classical viewpoint they appeared to behave, more or less, as a smaller number of oscillators. The estimates of classical error made in this paper show that, although classical mechanics may be used to a fair approximation when small reactants are involved, other things being equal, a quantum treatment should be employed for complex molecules, especially at low temperatures.

The results of this paper, together with those of other workers,[3,8,47] also indicate that the theory employed here has yielded approximate but encouraging results for quantitatively relating pressure effects in quasi-unimolecular reactions, as well as second-order energization rates and unimolecular reaction rates of hot species, to fundamental molecular properties, without having to invoke adjustable parameters. The theoretical expression for the Arrhenius frequency factor of the energization rate depended (with the exception of a minor factor close to unity) only on the activation energy and on the molecular properties of the parent molecule, A. The theoretical expression for pressure effects in quasi-unimolecular reactions depended also on some estimate of the properties of the activated complex, as inferred from the high-pressure Arrhenius frequency factor A^∞. Fortunately, where tested, the theoretical predictions were rather insensitive to the exact assumptions about this complex, as long as agreement with A^∞ was made.

The agreement between theoretical and experimental quasi-unimolecular behavior was least satisfactory for the N_2O and *cis*-butene reactions, in both of which competing heterogeneous processes occur, though they have been, at least in part, unraveled. At the present time, it is not clear, therefore, whether the disparity is due to shortcomings of theory or of experiment. Johnston, who analyzed the N_2O data, expressed considerable doubt of their validity[39] and Rabinovitch (private communication) has expressed a similar doubt concerning *cis*-butene results. When these results become freed of heterogeneous and other complications, the effect of these errors in experimental A^∞ on the $\log k / k^\infty$ vs p plot can be obtained from Appendix IV.

APPENDIX I. VALIDITY OF APPROXIMATION INVOLVING THE UPPER INTEGRATION LIMIT IN EQ. (7)[51]

In Part I, the upper integration limit in Eq. (7) corresponded to w instead of $w + E_0$. Introducing Eqs. (8) and (9) for N_r^* and N_s^* into Eq. (7), it is seen that the replacing of w by $w + E_0$ introduces negligible error when

$$\frac{\int_{x=w}^{w+E_0} (w + E_0 - x)^{s-1} x^{(\frac{1}{2}t)-1} dx}{\int_{x=0}^{w+E_0} (w + E_0 - x)^{s-1} x^{(\frac{1}{2}t)-1} dx} \ll 1. \quad (A1)$$

In the numerator of (A1), $x^{(\frac{1}{2}t)-1}$ does not exceed $(w + E_0)^{(\frac{1}{2}t)-1}$ if $(\frac{1}{2}t) - 1$ is positive or $w^{(\frac{1}{2}t)-1}$ if $(\frac{1}{2}t) - 1$ is negative. Hence, in either case $x^{(\frac{1}{2}t)-1} < m$, the maximum of these. Introducing this inequality, the numerator may be integrated at once and the left-hand side of (A1) becomes less than

$$\frac{m}{(w + E_0)^{\frac{1}{2}t-1}} \left(\frac{E_0}{w + E_0}\right)^s \frac{\Gamma[s + (\frac{1}{2}t)]}{\Gamma(s) \Gamma(\frac{1}{2}t)}.$$

Remembering that s is usually large and that $\frac{1}{2}t$ is normally small (e.g., 0, 1, or 2) the second factor proves to be overwhelmingly small when w is set equal to $E_a + E^+$, the value of interest. The third factor

$$\frac{(s + t/2 - 1)!}{(s - 1)!(\frac{1}{2}t - 1)!}$$

is of the order of unity. Even if t could be large (i.e., A^* would then have many free internal rotations), application of Stirling's formula for $x!$ shows that the

---

[51] In all of the small molecules in Table V, t was taken equal to zero (rigid activated complexes), so that Eq. (9) is used for N^*, rather than Eq. (7) and this discussion in Appendix I becomes irrelevant. We consider then the case $t \neq 0$, and note that part of the subsequent notation is ridiculous for $t = 0$.

third factor is either small or at most is of the order of unity, if $\frac{1}{2}l \ll s$.

If the lhs of Eq. (A1) had not been small in the systems of present interest, configurations in which x is of the order of $E_a + E^+$, i.e., in which the rotations have most of the energy leaving little for the vibrations, would make a significant contribution, and these are represented very poorly by the classical vibration distribution expression $(E_a + E^+ + E_0 - x)^{s + (\frac{1}{2}l) - 1}$ when vibrational quantum effects are important. Physically, this cannot occur when $\frac{1}{2}l \ll s$ and $E_a + E^+ + E_0$ is large relative to the zero-point energy E_0.

APPENDIX II. ASYMPTOTIC EXPANSION OF EQ. (13) AND ERROR ESTIMATE

Making the substitutions $W = (E_a + E_0)/RT$, $y = W + x$, the integral in (13) is

$$e^W \int_W^\infty y^n e^{-y} dy,$$

where $n = s + (\frac{1}{2}l) - 1$. Call it J. Successive $(m+1)$-fold integration by parts leads to a value for this term of

$$J = \sum_{k=0}^m \frac{n!}{(n-k)!} W^{n-k} + \frac{n! e^W}{(n-m-1)!} \int_W^\infty y^{n-m-1} e^{-y} dy. \quad (A2)$$

Only if n is an integer does the series terminate.

Let R_{m+1} denote the error which results in retaining only the first $m+1$ terms of Eq. (A2). The fractional error is

$$\frac{R_{m+1}}{J} = \frac{n!}{(n-m-1)!} \frac{\int_W^\infty y^{n-m-1} e^{-y} dy}{\int_W^\infty y^n e^{-y} dy}.$$

The integrand in the numerator is dominated by $y^{n-m-1}(y/W)^{m+1}$, since $y/W \geq 1$. Accordingly,

$$\frac{R_{m+1}}{J} \leq \frac{n!}{(n-m-1)!} W^{-m-1} \frac{\int_W^\infty y^n e^{-y} dy}{\int_W^\infty y^n e^{-y} dy}$$

$$= \frac{n!}{(n-m-1)!} W^{-m-1}. \quad (A3)$$

Thus, if only the first term is retained, as in Eq. (14) of the text, the fractional error does not exceed n/W, which was to be proved. Further reduction of the error can be made simply by retaining more terms than the first in Eq. (A2), the behavior of Eq. (A3) with increasing m for nonintegral m, being that characteristic of asymptotic expansion (i.e., for some m and W, the approximation eventually gets worse[52] with increasing m).

APPENDIX III. FREQUENCY ASSIGNMENTS, GROUPINGS, AND OTHER PROPERTIES

(a) *Cyclopropane.* Model I: The frequencies of the activated complex were grouped in multiples of 0.64 kcal, the number in each group being in parentheses. 0.64 (2), 1.92 (2), 2.56 (2), 3.20 (5), 4.48 (3), 8.96 (6). $P_2^+ = 57.0$. Model II: 1.80 (5), 3.60 (10). 9.00 (5).

(b) *Cyclobutane.* Frequencies of the activated complex grouped in multiples of 0.26 kcal, 0.26, 0.52 (3), 2.60 (5), 3.38 (8), 4.16 (4), 8.32 (8). $P_2^+ = 1490$.

(c) *Methylcyclopropane.* When this work was in progress, a complete vibrational analysis had not been performed on methylcyclopropane and approximate frequencies were assigned[53] with the aid of the cyclopropane frequencies[54,55] and the partial assignment to 1, 1-dimethylcyclopropane[56] as a guide. This assignment was: CH$_3$ torsion (350 cm^{-1}), skeletal (350, 400, 680), CH$_2$ twisting (739, 739), CH$_2$ rocking (854, 1188, 1188), CH$_2$ wagging (866, 866), CH$_2$ bending (963), CH$_3$ rocking (1000, 1050), ring deformation (1029, 1029, 1188), CH$_3$ deformation (1400, 1450, 1470), CH$_2$ deformation (1442, 1442) C–H stretch (methyl) (2870, 2933, 2954) C–H stretch (ring) (3020, 3020, 3038, 3082, 3102).

The frequencies of the activated complex were grouped in multiples of 1.03 kcal: 1.03 (5), 2.06 (5), 3.09 (7), 4.12 (5), 8.24 (7). $P_2^+ = 589$.

(d) *Nitrous oxide.* Frequencies used for the activated complex were 1.68 (2), 3.36. $P_2^+ = 3.12$.

(e) *cis butene-2.* Frequencies used for the activated complex were 0.66 (3), 1.98 (3), 2.64 (3), 3.30 (5), 3.96 (7), 8.58 (8). $P_2^+ = 2.71$. Because of an error these ν^+, in conjunction with $\alpha = 2$, fit an A^∞ one half that in Table I. With sufficient accuracy, this error was corrected simply by taking $\alpha = 1$.

(f) *Ethylchloride.* Frequencies used for the activated complex were 0.40 (2), 2.80 (4), 3.60 (2), 4.00 (5), 8.40 (4). $P_2^+ = 53.5$.

(g) *Nitrogen pentoxide.* The frequency assignment used for N$_2$O$_5$ was: middle bending (250 cm^{-1}), NO$_2$ wagging (500, 680), end (NO$_2$) bending (730,* 730*), out of plane bending (760, 760), middle sym. stretching

[52] For example, A. Erdelyi, *Asymptotic Expansions* (Dover Publications, Inc., New York, 1956).

[53] The vibrational partition function of P_2 based on the approximate assignment in the present work is in agreement to within 2% with that derived from the recent assignment to methylcyclopropane by L. M. Sverdlov and E. P. Krainov, Optics and Spectroscopy 7, 296 (1959).

[54] H. H. Günthard, R. C. Lord, and T. K. McCubbin, Jr., J. Chem. Phys. 25, 768 (1956).

[55] P. M. Mathai, G. G. Shepherd, and H. L. Welsh, Can. J. Phys. 34, 1448 (1956).

[56] F. F. Cleveland, M. J. Murray, and W. S. Galloway, J. Chem. Phys. 15, 742 (1947).

TABLE VII. Factor for correcting k/k^∞ vs p plots for errors in A^∞.

Reaction	$\theta(p=0)$	$\theta(p=\infty)$	Reaction	$\theta(p=0)$	$\theta(p=\infty)$
(a)	0.260	0.241	(e)	0.335	0.304
(b)	0.328	0.298	(f)	0.252	0.234
(c)	0.345	0.308	(g)	0.195	0.186 (from $E^\infty - E^0$, experimental)
(d)	0.141	0.127			0.182 (from postulated A^+)

(1030), middle asym. stretching (1335), NO_2 sym. stretching (1240,* 1240*), NO_2 asym. stretching (1720,* 1720*). The asterisk denotes spectroscopic assignment.[57] The remaining frequencies were estimated roughly from N_2O_4 fundamental frequencies,[58] Raman spectra of solutions of N_2O_5 in CCl_4 and $CHCl_3$,[59] and infrared studies of nitric acid and nitrate esters.[60]

Moments of inertia of N_2O_5 were calculated assuming N–O distances of 1.2 and 1.35 Å in the NO_2 end group and in the bridge, respectively, and ONO and NON bond angles of 125° and 110° in the NO_2 group and in the bridge, respectively. To obtain agreement with the value[61] of 85.0±3.5 eu for the standard entropy of gaseous N_2O_5 using the above properties, it was necessary to assume free internal rotation in N_2O_5. A symmetry number of 2 was used for each internal rotation. The value so obtained, neglecting coupling of internal rotations, was 82.0 eu.

Based on the assumed structures and properties of N_2O_5 and NO_3 (see below), the pre-exponential factor of the equilibrium constant at 300°K for the reaction, $N_2O_5 \rightleftharpoons NO_2 + NO_3$, was calculated to be 3.6×10^5 mole/liter, in very good agreement with the approximate experimental value of 3.3×10^5 estimated by Schott and Davidson.

Two of the rotations of the loose activated complex were taken to be those of a quasi-diatomic molecule with an internuclear separation of 3 Å and masses of NO_2 and NO_3. The remaining six rotations and the nine vibrations of the complex were taken to be those of NO_2[62,63] and NO_3. NO_3 was assumed to be planar and to have N—O bond distances of 1.33 Å (cf. 30). Its vibrational frequencies were taken to be those of the

NO_3^- ion.[64] The frequencies used for the activated complex were 2.06 (2), 2.15, 2.36, 3.00, 3.78, 4.04 (2), 4.62 kcal.

In Eq. (1) the rotational partition functions (p.f.) of A^+ and of A occur only as the product of all rotational contributions, and there is no need to decompose them into active and adiabatic parts. In Eq. (2), however, P_R^+ occurs alone and we estimate it by dividing the rotational p.f. of A^+ by its adiabatic part, P_1^+. To estimate P_1^+ for the loose complexes of N_2O and C_2H_6 ($P_R^+ = 1$ for rigid complexes) we note that NO_3, CH_3 and (approximately) NO_2 are symmetric tops with moments of inertia I_A, $I_B = I_C$. The I_A—p.f. of this top is $(8\pi^3 I_A kT)^{\frac{1}{2}}/\sigma_A h$. The $I_B I_C$ contribution is

$$8\pi^2 I_B kT/\sigma_B \sigma_C h^2,$$

so the effective I_B—p.f. is $(8\pi^2 I_B kT)^{\frac{1}{2}}/\sigma_B h$.

For N_2O_5 with $t=1$, two of the four adiabatic rotations are those of the diatomic rotor described above. The motion of the other two adiabatic rotations of A^+ approximates that of the remaining two assumed adiabatic rotations in A^*, which will be presumed for convenience to involve in some rough manner rotations of the two NO_2 groups in N_2O_5. Accordingly we treat as adiabatic the rotation of NO_3 about one of its NO bonds and the rotation of NO_2 about its symmetry axis. These contribute

$$(8\pi^2 I_B^{NO_3} kT)^{\frac{1}{2}}/2h \text{ and } (8\pi^2 I_B^{NO_2} kT)^{\frac{1}{2}}/2h,$$

respectively.

For C_2H_6 with $t=0$, two of the four adiabatic rotations involve the CH_3 groups, treated as a diatomic rotor, and two involve rotation of each CH_3 about its own symmetry axis. The latter two each contribute $(8\pi^3 I_A^{CH_3} kT)^{\frac{1}{2}}/3h$. When $t=2$, only the first two rotations are adiabatic. The properties assumed for C_2H_6 and CH_3 were those employed in reference 7.

APPENDIX IV. EFFECT OF ERROR IN FREQUENCY FACTOR ON THEORETICAL LOG k/k^∞ VS LOG p PLOTS

Let us suppose that for a given k^∞, an error δ in the high-pressure activation energy E^∞ causes an error of a factor of γ in the frequency factor A^∞.

$$k^\infty = \gamma A^\infty \exp[-(E^\infty + \delta)/RT], \qquad (A4)$$

where A^∞ and E^∞ are constants and where $\gamma = 1$ when $\delta = 0$. Then

$$\gamma = \exp(\delta/RT). \qquad (A5)$$

[57] W. G. Fately, H. A. Bent and B. Crawford, Jr., J. Chem. Phys. **31**, 204 (1959).
[58] R. N. Wiener and E. R. Nixon, J. Chem. Phys. **26**, 906 (1957).
[59] J. Chédin, Compt. rend. **201**, 552 (1935).
[60] J. F. Brown, J. Am. Chem. Soc. **77**, 6341 (1957).
[61] J. D. Ray and R. A. Ogg, Jr., J. Chem. Phys. **26**, 984 (1957).
[62] G. R. Bird, J. Chem. Phys. **25**, 1040 (1956).
[63] G. E. Moore, J. Opt. Soc. Am. **43**, 1045 (1953).
[64] R. Teranishi and J. C. Decius, J. Chem. Phys. **22**, 896 (1954).

We may investigate the effect of γ on the $\log k/k^\infty$ vs $\log p$ plot in an approximate way by keeping all vibration frequencies of A^+ fixed and merely introducing γ as a multiplicative factor into Eq. (2) for k_a. We also observe from Eq. (23) that an error of δ in E^∞ causes one of δ in E_a.

The value of p which corresponds to any given value of k/k^∞ depends on γ. We find from Eq. (1) that $p(\gamma)$ is the solution of Eq. (A6).

$$\int_0^\infty \frac{f(E^+)dE^+}{1+k_a(\gamma)/k_2 p(\gamma)} = \int_0^\infty \frac{f(E^+)dE^+}{1+k_a(1)/k_2 p(1)}, \quad \text{(A6)}$$

where $f(E^+)$ is the function obtained by equating either side of (A6) to k/k^∞. $k_a(\gamma)$ and $p(\gamma)$ denote the value of k_a and p at $\gamma=\gamma$, while $k_a(1)$ and $p(1)$ denote the values at $\gamma=1$.

$k_a(\gamma)$ depends on γ both directly through γ as a multiplicative factor and indirectly through $N^*(E_a+\delta+E^++E_a)$. From Eq. (2) we find

$$k_a(\gamma)/k_a(1)$$

$$= \gamma[(E_a+\delta+E^++E_0)/(E_a+E^++E_0)]^{-[s+(\frac{1}{2}t)-1]}.$$

Remembering that δ is very small, we may use the approximate formula $[1+(x/n)]^n \cong e^x$ to obtain

$$k_a(\gamma)/k_a(1) \cong \gamma \exp\{-[s+\tfrac{1}{2}t-1]\delta/(E_a+E^++E_0)\}$$

$$= \gamma^{(1-\theta)}, \quad \text{(A7)}$$

where we have used Eq. (A5) and introduced θ

$$\theta = [s+\tfrac{1}{2}t-1]RT/(E_a+E^++E_0). \quad \text{(A8)}$$

If θ were independent of E^+, the solution of Eqs. (A6) and (A7) would be

$$p(\gamma)/p(1) = \gamma^{1-\theta}. \quad \text{(A9)}$$

Since θ depends but slightly on E^+ (see Table VII), Eq. (A9) still provides a good first approximation, and for the E^+ in θ one then employs the average value $\langle E^+ \rangle$ at the given pressure p

$$\langle E^+ \rangle = \int_0^\infty E^+ g(E^+)dE^+ \Big/ \int_0^\infty g(E^+)dE^+, \quad \text{(A10)}$$

where $g(E^+)$ denotes the integrand of Eq. (1). A special case of (A9) is

$$p_{\frac{1}{2}}(\text{calc})(\gamma)/p_{\frac{1}{2}}(\text{calc})(1) = \gamma^{1-\theta_{\frac{1}{2}}}. \quad \text{(A11)}$$

For the reactions in this paper, the extreme values of θ are those given in Table VII for $p=0$ and $p=\infty$ -

(We note that $\langle E^+ \rangle = 0$, essentially, at $p=0$ and $\langle E^+ \rangle = E^\infty - E^0$ at $p=\infty$.) At $p=\infty$ $\langle E^+ \rangle$ was from its computed value

$$(1+\tfrac{1}{2}r)RT+\sum_{i=1}^{s+} h\nu_i^+[\exp(h\nu_i^+/kT)-1]^{-1}.$$

The latter, in turn, is derived from Eqs. (A10) and (1) at $p=\infty$, making use of the interchange of summation and integration described in Part I. Physically, the RT is contributed by the internal translation, the $rRT/2$ by the active rotations and the remainder by the vibrations of A^+.

In summary, we note that when $\theta \ll 1$, an increase in A^∞ of a factor of γ shifts the $\log k/k^\infty$ plot uniformly along the $\log p$ axis by an amount $\log\gamma$. When θ is not negligible, the shift is still approximately uniform, since θ varies but slowly with E^+, and the shift amounts to $(1-\theta)\log\gamma$, with θ given by (A8). The corresponding change in $p_{\frac{1}{2}}(\text{calc})$ is given by (A11).

APPENDIX V. INFERENCE OF AMOUNT OF ENERGY OF A HOT SPECIES

The nonfixed energy E^* of a hot species (e.g., hot molecule or hot radical) whose k_a corresponds to some E^+ is E_a+E^+.[65] This E^*, about $63+33=96$ kcal mole^{-1} for the cyclopropane reaction, is to be compared with the one estimated from the following thermochemical and kinetic arguments.

Consider a hot molecule D which is the sole product of an exothermic elementary step, be it uni- or bimolecular.

$$B \rightarrow D, \quad \text{(A12)}$$

$$B+C \rightarrow D. \quad \text{(A13)}$$
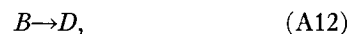
The "standard" energy reaction of either step ΔE^0 at the given temperature is

$$\Delta E^0 = \Delta U + \Delta E_0 + \langle \Delta E_v \rangle + \langle \Delta E_{\text{rot}} \rangle + \langle \Delta E_{\text{trans}} \rangle, \quad \text{(A14)}$$

where the terms on the rhs are, successively the change of potential energy, zero-point, thermally averaged nonfixed vibrational, rotational, and translational energies, respectively, accompanying the elementary step.

In the unimolecular case (A12) any excess translational and (neglecting centrifugal potential) rotational energy of B can't add to E^*, the nonfixed energy of D, because of momentum conservation. In the bimolecular

---

[65] As will be discussed in Part III, one should also include an average difference in centrifugal "potential" energy of the adiabatic rotations, a term which, however, is normally less than or about equal to RT. In the cyclopropane isomerization where we assumed $P_1^+/P_1 = \sigma_1/\sigma_1^+$, this extra term is zero.

case (A13), any excess translational energy of the center of mass and much of any excess in the two relative translations which contribute to the rotation of D can also not add to E^*, for the same reason.

Let ϵ be that portion of excess energy of the reactants in (A12) or (A13) (in excess of the thermal averages of the various degrees of freedom) which can contribute to E^*. E^* then becomes

Case (A12)

$$E^* = (-\Delta U + E_0{}^B + \langle E_v{}^B \rangle + \epsilon^*) - E_0{}^D, \quad (A15)$$

Case (A13)

$$E^* = (-\Delta U + E_0{}^{B,C} + \langle E_v{}^{B,C} \rangle + \langle E_{\text{rot}}{}^{B,C} \rangle$$
$$+ \tfrac{1}{2}(RT) + \epsilon^*) - E_0{}^D, \quad (A16)$$

where $RT/2$ arises from the sixth translation of B and C. Combining these results with Eq. (A14), the non-fixed energy of D, in each case, becomes essentially

$$E^* = -\Delta E^0 + \langle E_v{}^D \rangle + \epsilon^* \quad (A17)$$

upon introducing the typical values for the thermal averages. For example $\langle \Delta E_{\text{trans}} \rangle = \langle \Delta E_{\text{rot}} \rangle = 0$ for case (A12), etc.

Equation (A17) may also be expressed in terms of the heat of reaction $\Delta H^0 = (\Delta E^0 + \Delta n RT)$, where $\Delta n = 0$, -1 for case (A12), (A13). In the reaction cited in the text, Δn is -1, $\langle E_v \rangle$ for cyclopropane is about 8 kcal mole^{-1}. Using Benson's rough estimate of ΔH, -78 kcal mole^{-1}, we find $E^* \cong 84 + \epsilon^*$, so $\epsilon^* \cong 12$ kcal mole^{-1}.