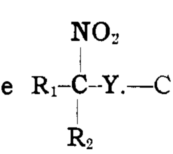
$R{-}\overset{NO_2}{\overset{|}{CH}}{-}R'$

**(b) Compounds of the Type R–CH–R'.**—Figure 3 shows the spectrum of 2-nitropropane which is representative of this group of compounds. The $N^{14}$ triplet is split into a doublet from the single proton on the carbon containing the nitro group. The additional but much smaller splittings are due to the adjacent methyl (or, in other compounds, methylene) protons. Again, interaction with protons on carbons more than two removed from the nitro group are not observed.

In nitro cyclohexane one finds the dominant $N^{14}$ coupling, a rather strong doublet splitting from the single hydrogen and a further quintet which must be interpreted as derived from two pairs of *approximately* equivalent protons. No assignment of the latter can be made at present. Nitro cyclopentane yielded only a very weak and unresolved e.p.r. spectrum.



$R_1{-}\underset{R_2}{\overset{NO_2}{C}}{-}Y$

**(c) Compounds of the Type $R_1$–C–Y.**—Compounds of this type, as exemplified by the last three alcohols in Table II show only a $N^{14}$ coupling. This is true whether $R_1$ is $CH_3$ or a second alcohol group as in the diols. The spectra resemble the peroxylamine disulfonate spectrum- the only essential difference is $|a_N|$ is about twice as large as that of the peroxylamine.

Other compounds with Y = Cl, $NO_2$ show no evidence of anion radical formation. Compounds from which no spectra were obtained include 1-chloro-1-nitro propane, 2-chloro-1-nitro propane, 1-chloro-1-nitro ethane, and 2,2-dinitropropane. It is surprising that the last named compound gave no signal since tetranitromethane as well as dinitro methane gave well resolved spectra. In the latter two cases, the radical ions are quite unstable (as well as the starting materials) and the spectra may be composed of several structures.

Finally, the $N^{14}$ coupling constants in aliphatic compounds (*ca.* 25 gauss) is much larger than in the corresponding aromatic nitro anions. Contrary to the results with aromatics practically no solvent effect on the $N^{14}$ coupling could be found with the aliphatic anions. It has been pointed out by Geske and Ragle[7] that the value of $|a_N|$ in an aromatic nitro anion approaches that of the aliphatic counterpart when the nitro group is twisted out of the plane of the benzene ring by steric effects of bulky substituents. In the present study one notes this "aliphatic behavior" for nitromesitylene reflected in the magnitude of $|a_N|$.

**Acknowledgments.**—This work was supported by the Air Force through the Air Force Office of Scientific Research and by the Atomic Energy Commission through contract AT(11-1)-686. This support is gratefully acknowledged.

(7) D. H. Geske and J. L. Ragle, *J. Am. Chem. Soc.*, **83**, 3532 (1961).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

# The Thermal Unimolecular Isomerization of Methyl Isocyanide. Fall-off Behavior[1]

BY F. W. SCHNEIDER AND B. S. RABINOVITCH

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The thermal unimolecular isomerization of methyl isocyanide to acetonitrile has been investigated as part of a continuing thorough investigation of this reaction type. Fall-off has been studied at three temperatures, and in one case (230°) extends over the range of $k/k_\infty$ from 1.00 down to 0.0016. Activation energies have also been determined over a wide range of fall-off ($A_\infty = 10^{13.6}$, $E_a(\infty) = 38.4$ kcal./mole). The data has been treated on the basis of RRKM theory; results which justify the assumptions made in the theory with regard to intramolecular and intermolecular energy exchange are summarized. Accurate evaluation of the quantum statistical summation of the harmonic vibrational energy levels involved in the theory is made. Additional values of the semi-classical approximation correction factor $a$ are given. The vibrational patterns employed are essentially the full set for the molecule and activated complex, rather than the empirical approximation of a single degenerate oscillator model or similar elaborations not directly related to the actual vibrational patterns. The agreement of theory with experiment is very satisfactory. Some further comparisons and assessment of the quantum statistical formulation of unimolecular reactions are given. The calculations are extended to the quantitative inclusion of anharmonicity effects, and evaluation of the role and importance of such factors. Governed by the uncertainty of the correction, anharmonicity effects appear to raise the low pressure rate by 25–40%. An overall figure axis rotation is also taken as active and its effect on the calculated behavior determined.

In the forty years since the formulation of the Lindemann–Christiansen–Hinshelwood mechanism of unimolecular reactions, much experimental work has been done to test this scheme and alternative assumptions and approximations regarding each step. It is remarkable, however, that with the possible exception of $N_2O_5$[2] there is still no example of a reaction system whose study approaches completeness. Such a study ideally should include fall-off data from the high to low pressure limits at several temperatures, and determination of the activation energy variation over this range; the study of various inert gas efficiencies in activation–deactivation over the fall-off region, and especially at the low pressure end; the study of the effect of variation of molecular parameters, as by variation of molecule chain

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[1] Presented at the Symposium on Elementary Reactions, Am. Chem. Soc., St. Louis, Mo., March, 1960, and Washington Meeting, March, 1962, Am. Chem. Soc. Abstracted in part from the Ph.D. Thesis of F. W. S., University of Washington, 1962. This work was supported by the National Science Foundation.

[2] R. L. Mills and H. S. Johnston, *J. Am. Chem. Soc.*, **73**, 938 (1951), and a number of succeeding papers; references to the older literature on this reaction are given.

length in a homologous series; and, with the developments of the past 10–12 years in mind, study of effects due to isotopic substitution; and so on. The amount of relevant data that exists concerning some of these aspects is amazingly sparse.

This present state of experimental thermal unimolecular reaction kinetics may not be greatly modified in the near future, since many aspects of interest concerning the behavior of molecules, implicit in the study of unimolecular reactions, are now very effectively approached by relatively new techniques. Paradoxical as it seems, conclusions derived from this simple, long-used method for the study of molecules have not, in fact, contributed very effectively toward the interpretation of more recent data obtained by the newer methods —flash and ultraviolet photolysis, shock waves, electron impact, chemical activation, etc. On the contrary, the latter have provided much of the best evidence now available regarding intermolecular and intramolecular transfer of energy in both simple and complex molecule systems, at high levels of vibrational excitation. The experimental inaccuracies which have attended the ostensibly simple thermal technique are largely responsible for this situation; but, in significant part, it has its origin also in the comparative insensitivity of some aspects of the thermal behavior to various alternative assumptions, particularly regarding intermolecular energy transfer[3] above the low pressure region.

The above resume has virtually omitted specific reference since it is not intended as a review, but is given to clarify the context of the present study. Despite some defects of thermal studies as a source of fundamental information on some aspects of energy transfer, it seemed to us on the whole very worthwhile, in view of the paucity of data, to attempt the documentation of a system in the complete manner described at the outset; and to couple such study with further assessment of the improvement in theoretical treatment afforded by accurate quantum statistical evaluation of rate in the non-equilibrium regions; and to give attention to the effect of vibrational anharmonicity on energy level spacings.

A system which seemed amenable for these purposes was the isocyanide–nitrile isomerization. Quantitative study of these was once mentioned by Ogg,[4] while Kohlmaier and Rabinovitch[5] have recently described exploratory kinetic data for tolyl isocyanide. Isomerization reactions have experimental advantages in that they are not attended by production, usually, of highly reactive products or chain carriers; nor are they accompanied by pressure change (change in number of "inert" molecules), while at the same time the product species may be expected to have activation efficiency similar to the parent molecule. Methyl isocyanide, the first known member of the family, is a simple molecule, but not too small, and is a symmetric top of $C_{3v}$ symmetry.[6] These properties gave promise of experimental accessibility of both high and low pressure limits, of simple vibrational analysis, and of easy experimental decrease of the symmetry of the molecule by deuterium substitution, with splitting of the four doubly degenerate vibrations, and leading back to the original higher symmetry on perdeuteration. Carbon chain lengthening and introduction of internal rotational degrees of freedom may also be readily accomplished. Finally, the reaction temperatures are comparatively low; this is advantageous experimentally, and also emphasizes the test of the quantum statistical treatment.

The present paper reports a study of methyl isocyanide which apparently confirms this reaction as one of the best known prototypes of a unimolecular reaction.

## Experimental[7]

**Materials and Apparatus.**—Methyl isocyanide was prepared by a modified method of Gautier, and was purified by G.L.P.C. Its purity, as determined by infrared, mass spectrometric and gas chromatographic analyses, was better than 99.9%.

The static method has been used for the rate determinations. A conventional vacuum apparatus served for gas handling, volume and pressure measurement. Several Pyrex vessels of different volume were used as reactors. A 500-ml. bulb, heated in an air furnace, was used mainly in the earlier work. All other vessels, ranging from 1-ml. to 3-l., were heated in an oil-bath. Temperature constancy was maintained to 0.1° and the temperature gradient was ±0.2° over the 510-ml. reactor in the air furnace; in the oil-bath the gradient over the 3-l. reactor was less than ±0.1°, and was less than ±0.05° for the other reactors; temperature constancy over long periods of time was better than 0.1°. Temperature was measured with mercury thermometers, checked frequently against a standard thermometer (and calibrated to 0.1° against a standard N.B.S. platinum resistance thermometer), which was itself checked on occasion.

**Procedure.**—Depending on the pressure and vessel, the isocyanide sample was either frozen into a finger of the reactor or was expanded into it. During a run, four aliquot samples of nearly constant volume were usually taken at specific time intervals. The sampling volume could be varied to allow for resulting cumulative pressure drop during the run which in the worst case was not bigger than 10%. At very low pressures the whole sample was used for analysis. The isomerization was usually carried out between 5 to 35% reaction. Mercury vapor did not affect the rate of reaction; nevertheless mercury was particularly excluded at low pressures. Runs made in different vessels, especially with reference to the 500-ml. vessel for which temperature averaging is the most empirical, were always checked for consistency by use of overlapping pressure regions. An absolute discrepancy between the 500-ml. vessel and the others amounted to a temperature correction of only 0.3°.

**Analysis.**—Methyl isocyanide and acetonitrile mixtures were analyzed by G.L.P.C. with Tetraglyme (dimethyl ether of tetraethylene glycol) as liquid phase on a 1.8-meter Fluoropak 80 column. The column was recalibrated before and after each series of analyses with known calibration mixtures in order to obtain a calibration curve at nearly constant sample volume, usually ~0.04 cc. (S.T.P.). Reasonable reproducibility of analysis was achieved, within an absolute value of ±0.5% usually.

## Results

**Treatment of the Data.**—Corrections were applied to the data for: (a) effective time required to heat the sample to reaction temperature (at very high pressures only; generally not more than 4 seconds); (b) dead space (from 0.2 to 1% de-

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[3] F. P. Buff and D. J. Wilson, *J. Chem. Phys.*, **32**, 677 (1960).

[4] R. A. Ogg, *ibid.*, **7**, 753 (1939).

[5] G. H. Kohlmaier and B. S. Rabinovitch, *J. Phys. Chem.*, **63**, 1793 (1959).

[6] M. E. K. Pillai and F. F. Cleveland, *J. Mol. Spect.*, **5**, 212 (1960), and references cited.

[7] See F. W. Schneider, Ph.D. Thesis, University of Washington, 1962, for further details.

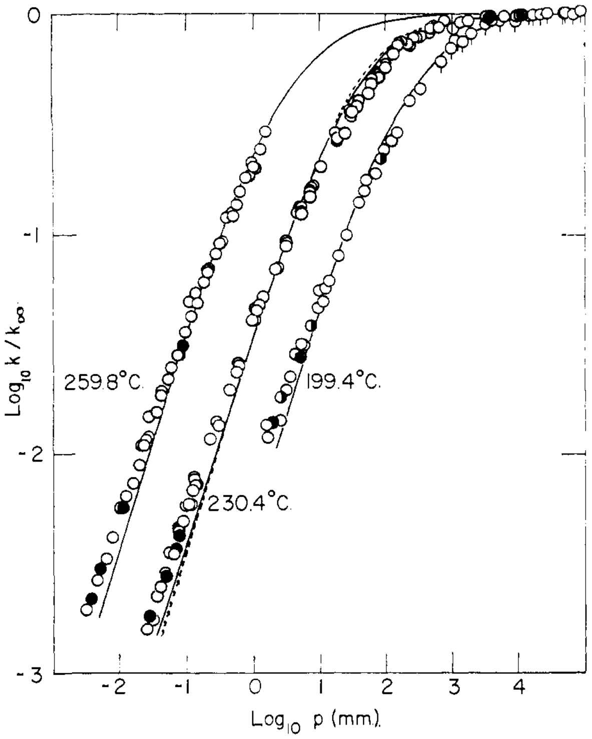

Fig. 1.—Pressure dependence of unimolecular rate constants for $CH_3NC$: log $k/k_\infty$ *versus* log $p$ at 199.4°, 230.4°, 259.8°. For clarity the 260° curve is arbitrarily displaced by one log $k$ unit to the left in the figure while the 200° curve is displaced the same distance to the right; actually, both of these curves would almost coincide with the 230° curve. Vertical marks have been placed under the 200° high pressure points to assist in distinguishing these from the 230° data. The solid curves represent the calculated results for the 300 harmonic model, adjusted on the pressure axis to coincide with the experimental points at log $k/k_\infty = -1$ (Table VIII). The dotted curve at 230° is for the 600 harmonic model, similarly adjusted.

pending on the vessel); (c) decrease of pressure through sampling (never more than a total of 10%); (d) gas imperfection, particularly dipolar association at the highest pressures (about 1% at 1000 mm. and 6% at 14.4 atmospheres, Appendix 1); (e) change in collision number at high pressures (<2%); (f) self-heating at the higher pressures and temperatures (generally less than 5%, Appendix 1).

Somes ample runs are shown in Table I, Appendix 2.

**Heterogeneity. Side Reactions.**—No effect on the rate over the whole pressure range given was found upon increasing the surface–volume ratio tenfold, beyond an indication of some heterogeneity at the lowest pressures. In a few runs near 0.01 mm. pressure, greater scatter was found which rendered them unreliable as an indication of increasing heterogeneity; one in ~200 are wall collisions. Identical rates were obtained in a fused quartz reactor and in Pyrex vessels of different volume. Reactors were first seasoned briefly with $CH_3NC$. The seasoning procedure had no effect on the rate constants. Autocatalysis and side reactions were shown to be absent. No polymer or side products were produced when the reaction was carried through five half-lives.

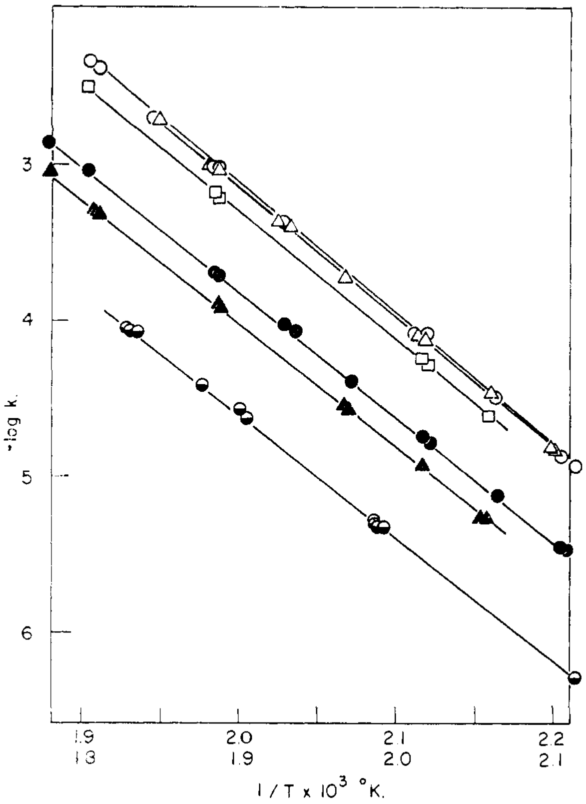

Fig. 2.—Arrhenius plots for methyl isocyanide data: ○, 8 atmospheres; △, 1500 mm.; □, 150 mm.; ●, 10 mm.; ▲, 5 mm.; ◒, 0.1 mm. Lines were fitted by least squares; the lower range of abscissa values is for 0.1 mm. and the higher range for all other pressures.

**Oxygen.**—Up to 5% of dry, $CO_2$-free air produced no change in rate, except for the inert gas effect.

**Influence of Radicals.**—Bigger amounts than 0.15% *tert*-butyl peroxide (*e.g.*, 0.012 mm. peroxide and 7.8 mm. isocyanide) had an accelerating effect on the rate. In a typical run with 1% addend (8.33 mm. reactant and 0.085 mm. peroxide) the rate was accelerated by 50%. Sensitized reaction is being investigated further.

**Kinetic Data.**—Pressure fall-off was studied at 199.4°, 230.4° and 259.8°. Log $k$ *vs.* log $p$ curves are given in Fig. 1. The data are tabulated in Table II, Appendix 2. Extrapolation of $k^{-1}$ *vs.* $p^{-1/2}$ plots[8,9] gave $k_\infty$ as $7.50 \times 10^{-5}$ sec.$^{-1}$ at 199.4°, and $92.5 \times 10^{-5}$ sec.$^{-1}$ at 230.4°. The curve at 259.8° could be studied with the present technique only in the fall-off and near second-order regions, and $k_\infty$ was not determined experimentally; in anticipation of later calculations, a value of $k_\infty = 76.7 \times 10^{-4}$ sec.$^{-1}$ may be assigned. The classical empirical Kassel fit parameter $s$ was determined from the *shape* of the fall-off by superposition with calculated fall-off curves[10]; $s \simeq 3.0$

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[8] E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).

[9] B. S. Rabinovitch and K.-W. Michel, *ibid.*, **81**, 5065 (1959).

[10] E. W. Schlag, B. S. Rabinovitch and F. W. Schneider, *J. Chem. Phys.*, **32**, 1599 (1960).

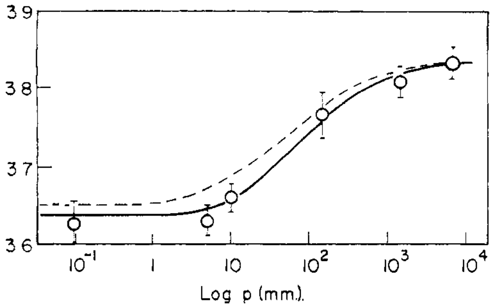

Fig. 3.—"Continuous" Arrhenius activation energies obtained from fall-off curves *versus* log *p*, given by solid curve. Separate determinations, from the data of Fig. 2, shown for comparison, O, with indication of standard deviation; calculated values from the 300 model given by the dashed line.

at 199.4°, and ≃ 3.1 at 230.4°; *i.e.*, a very slight increase with temperature was noticeable (the decimals have only qualitative significance).

**The Arrhenius Activation Energy.**—Activation energy determinations over ~80° ranges were made at six pressures (Fig. 2). Table III summarizes the Arrhenius parameters obtained by least square calculations. Activation energies were also determined as a "continuous" function of pressure between $10^4$ and 15 mm. from the two fall-off curves at 199.4° and 230.4°; all three curves were used down to 0.03 mm. The continuous values are in good agreement with the separate activation energy determinations (Fig. 3). The activation energy spread between low and high pressures is 2.0 kcal./mole.

**Inert Gas Runs.**—Inert gas efficiencies have been determined for $N_2$ and $C_2H_6$ at various regions of the fall-off, on a collision to collision basis. The variation with pressure seems negligible; $C_2H_6$ was found to have a higher efficiency (~0.6) than $N_2$ (~0.25), based on using $\sigma(CH_3NC) = 4.5$ Å.,[11] and arbitrarily putting $\sigma(C_2H_6)$ at the same value and setting $\sigma(N_2) = 3.7$ Å. Inert gas studies will not be discussed further at this time.

## Discussion

**Suitable Models for Energy Transfer.**—We may clarify the selection of suitable models by considering a particular expression for the rate of production and removal of molecules having energy $E$ (*i.e.*, in the range d$E$ near $E$)

$$\mathrm{d}n_\mathrm{E}/\mathrm{d}t = R(E) - k_\mathrm{E}n_\mathrm{E} - \int_0^\infty \{P(E,\epsilon)n_\mathrm{E} - P(\epsilon,E)n_\epsilon\}\mathrm{d}\epsilon \quad (1)$$

Equation 1 actually involves some implicit simplifying assumptions that are clarified below. $n_\mathrm{E}$ is the concentration of molecules of energy $E$. $R(E)$ refers to some special process for direct formation of molecules at energy $E$: $R(E) > 0$ for activation by chemical reaction, irradiation, electron impact, etc., but $R(E) \equiv 0$ for unimolecular thermal reactions; the identity may be considered responsible for the relative weakness of the thermal method as a tool for tests of energy exchange. $k_\mathrm{E}$ is the average specific reaction probability of molecules at total relevant energy $E$; it is implicit here that only the total energy need be specified; the relevant energy is that which is in active, nonadiabatic degrees of freedom.[12] $P(E,\epsilon)$ is the probability per second for transfer of energy by collision from the molecule at $E$, so that it assumes the energy $\epsilon$; $P(\epsilon,E)$ refers to the reverse process.

**Intramolecular Energy Transfer.**—The important differences in unimolecular rate theories of Rice–Ramsperger–Kassel[13] and of Slater[14] have concerned the extent of intramolecular interchange of energy between the normal vibration modes during the lifetime of the molecule, *i.e.*, the magnitude of the internal relaxation time $\tau_\mathrm{int}$; this determines the form of the specific reaction probability. The RRK theory postulates that in general $\tau_\mathrm{int} << \tau_\mathrm{react}$, where the latter refers to the relaxation time for the disruptive reaction process; the theory of Slater is identified with the contrary assertion $\tau_\mathrm{int} >> \tau_\mathrm{react}$, *i.e.*, orthogonality of the normal mode motions as the extreme statement. In the RRK theory, randomization of internal energy distributions is assumed[15] and obviates the need of explicit terms for internal energy transfer in eq. 1; the internal relaxation process leading to reaction is a function only of the total active energy $E$, and the specific reaction probability is appropriately given as in eq. 1. On the extreme contrary assertion, internal energy transfer terms are identically zero ($\tau_\mathrm{int} = \infty$) and the specific reaction probability is then to be given for each detailed energy distribution at energy $E$. For intermediate rates of internal energy transfer, specific terms for this process may be included.[3,16]

At the time when this isocyanide work was initiated, the correct assessment of the orthogonality assumption was an active matter. Very recently, several pieces of evidence have indicated the general correctness of the RRK assumption: (1) evidence which is primarily of an experimental nature and which contravenes the predictions that stem from the orthogonality postulate; (2) evidence of an experimental and theoretical nature which more directly assesses the importance of intramolecular energy relaxation, at the high energy levels involved in reaction.

In the former category belongs the examination of the data on the cyclobutene, cyclobutane and nitrogen pentoxide decompositions by Thiele and Wilson[17] who pointed out, on the basis of symmetry arguments, an incompatibility between the predicted fall-off (allowed number of effective vibration modes) and the observed behavior. At the same time, Rabinovitch and Michel[9] independently gave a similar argument for the isomerization of olefins, ethylene-$d_2$ and butene-*2*. With regard to an effect of a different kind, Schlag and Rabinovitch have shown that reduction of sym-

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(11) P. M. Craven and J. D. Lambert, *Proc. Roy. Soc.* (*London*), **A205**, 439 (1951).

(12) R. A. Marcus and O. K. Rice, *J. Phys. Coll. Chem.*, **55**, 894 (1951); R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952).

(13) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1932.

(14) N. B. Slater, *Phil. Trans. Roy. Soc.* (*London*), **A246**, 57 (1953); "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

(15) N. B. Slater, *J Chem. Phys.*, **24**, 1256 (1956).

(16) D. J. Wilson, *J. Phys. Chem.*, **64**, 323 (1960).

(17) E. Thiele and D. J. Wilson, *Can. J. Chem.*, **37**, 1035 (1959); *cf.* K. A. Holbrook, *Trans. Faraday Soc.*, **57**, 2151 (1961).

metry and splitting of the vibrational degeneracy in cyclopropane-$d_2$, as compared with cyclopropane, scarcely alters the observed Slater $n$-value for propylene formation, although a marked increase in $n$ is predicted on the basis of the orthogonality assumption.[8] In fact, the latter reaction has been shown[18] to obey very well a quantum statistical, transition state modification of RRK theory given by Marcus and Rice,[12] while a reasonable account of a number of thermal unimolecular reactions has been given by Marcus and Wieder[19]; good obedience to the Rice – Ramsperger – Kassel – Marcus (RRKM) theory has also been found for the rates of decomposition of radicals and molecules produced by chemical activation.[20] Into the second category of evidence falls the demonstration by Butler and Kistiakowsky[21] that production of excited methylcyclopropane moledules by different chemical reactions, leading therefore to different states of excitation of the normal mode vibrations, does not thereby give rise to a variation in the rate of decomposition. Their findings were confirmed by similar experiments for butyl radicals and other systems,[22] and the short memory of species excited in different ways, with resulting random incidence of decomposition events, has been demonstrated at life-times, $\tau_{\text{react}}$, as low as $10^{-8}$–$10^{-10}$ sec. On the theoretical side, the magnitudes of vibrational anharmonicity constants derived from infrared studies have long suggested the implausibility of effective orthogonality assumptions.[23] Very recently, Thiele and Wilson[24] have considered energy flow between the vibrational stretching motions for an excited linear triatomic model obeying a Morse potential function, and find such rapid interchange as to indicate the unsuitability of the normal mode concept in this case.

This RRK assumption appears to be well supported, and for large molecules as well as small ones.

**Intermolecular Energy Transfer.**—Both contending theories have made the strong collision assumption

$$\int_0^{E_0} P(E,\epsilon)d\epsilon = \omega$$

where $\omega$ is the collision frequency, and deactivation probability is equated with collision probability. The close similarity of relative inert gas efficiencies in many unimolecular thermal studies, which usually bunch within a factor of ten, has tended to support this assumption.[25] However, even if the collision efficiency were unity for the parent gas, Wilson and Johnston[25b] have shown that it cannot be uniquely unity for all inert gases; that such is true is almost axiomatic for the collisions of a rare gas atom with a large complex polyatomic molecule. Also, theoretical models from the low vibrational energy domain have been applied to support the conclusion that vibrational energy may be transferred on virtually every collision only by multiquantum processes, in which the energy transferred is so small (less than 50 cal./mole, say) as to cause the conventional collisional assumption to fail.[26]

We leave consideration of diatomic or very small molecules in abeyance and summarize some recent evidence concerning intermolecular energy transfer for highly vibrationally excited polyatomic molecules as follows: Studies of gas phase fluorescence quenching of vibrationally excited $\beta$-naphthylamine, and other emitters, by both simple and complex, non-polar and polar, inert molecules have been made by Neporent,[27] Boudart and Dubois[28] and Stevens.[29] Their findings, for the vibrational energy region up to 25 kcal./mole mainly, may be described as showing that polyatomic inert molecules may remove vibrational energy in average amounts up to several kcal. per mole, per collision; the average amount of energy transferred rising with increase of vibrational energy of the excited species, and being larger for large or polar inert gases. In recent studies in this Laboratory of excited butyl radicals, produced with vibrational energy of ~45 kcal./mole by chemical activation, butene molecules have been shown[30] to remove in excess of 10 kcal./mole per collision, on the average; in this system, also, $P(E,\epsilon)$ was found to be larger when $(E-\epsilon)$ is $>>RT$, than when $(E-\epsilon)$ is $<< RT$. Other polyatomics such as methyl chloride[31a] seem to behave similarly, while even rare gas atoms may on the average remove up to several kcal./mole of energy on each collision with hot butyl. The deactivation by ethylene and butene of vibrationally excited cyclopropane and dimethylcyclopropane, respectively, which were produced at ~100 kcal. level by chemical activation, again indicate transfer of energy in large amounts, in some cases as high as 15 kcal./mole per collision, on the average.[18b,31b]

This evidence supports the validity of the application of the strong collision assumption to the highly polar methyl isocyanide molecule, and avoids

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(18) (a) B. S. Rabinovitch, D. W. Setser and F. W. Schneider, *Can. J. Chem.*, **39**, 2609 (1961); (b) see D. W. Setser, Ph.D. Thesis, University of Washington, 1961, for details; D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

(19) R. A. Marcus and G. M. Wieder; see G. M. Wieder, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1961, and *J. Chem. Phys.*, in press.

(20) Data summarized by B. S. Rabinovitch and J. H. Current, *ibid.*, **35**, 2250 (1961).

(21) J. N. Butler and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **82**, 759 (1960).

(22) R. E. Harrington, B. S. Rabinovitch and H. M. Frey, *J. Chem. Phys.*, **33**, 1271 (1960). The very fact that *C-H bond formation is* the activation process for butyl radicals, while it is *C-C bond rupture* that occurs, itself demonstrates the non-orthogonality of the vibrations; *cf.* H. M. Frey, *Trans. Faraday Soc.*, **57**, 951 (1961). D. W. Setser and B. S. Rabinovitch, reference 18(c), give further evidence for dimethylcyclopropane.

(23) E. E. Nikitin, *Proc. Acad. Sci.* (*U.S.S.R.*), *Phys. Chem.*, **129**, 921 (1959) (Engl. transl.)

(24) E. Thiele and D. J. Wilson, *J. Chem. Phys.*, **34**, 1256 (1961); *cf.* abstract by A. Kuppermann, Am. Chem. Soc. National Meeting, March, 1962).

(25) (a) M. Volpe and H. S. Johnston, *J. Am. Chem. Soc.*, **78**, 3903 (1956); (b) D. J. Wilson and H. S. Johnston, *ibid.*, **75**, 5764 (1953).

(26) B. H. Mahan, *J. Phys. Chem.*, **62**, 100 (1958).

(27) B. S. Neporent and S. O. Mirumyants, *Opt. i Spektr.*, **8**, 336 (1960) (Engl. transl.), and other papers in this series by Neporent.

(28) M. Boudart and J. T. Dubois, *J. Chem. Phys.*, **23**, 223 (1955).

(29) B. Stevens, *Mol. Phys.*, **3**, 589 (1960).

(30) R. E. Harrington, B. S. Rabinovitch and M. R. Hoare, *J. Chem. Phys.*, **33**, 744 (1960).

(31) (a) G. Kohlmaier, B. S. Rabinovitch and M. R. Hoare, *J Chem. Phys.*, submitted. (b) D. W. Setser, J. W. Simons and B. S. Rabinovitch, Sixth Photochemistry Conference, Brussels, June, 1962. (c) Compare the very recent paper by G. A. Taylor and G. B. Porter, *J. Chem. Phys.*, **36**, 1353 (1962), on deactivation of ketene.

the complexity of stochastic methods.[32] Correctness of this assumption, which is most likely for the present case of identical molecules, may be assessed by the comparison of experimental and calculated values in the low pressure region to be given below.

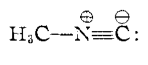
**Quantum Statistical Considerations.**—The form of the theory which is considered appropriate in view of the above evidence is that of RRK. However, as is well known,[12,13] and as was recently illustrated explicitly for typical molecular frequencies,[20] the classical statistics are an approximation of such gross nature as to be suitable mainly as an empirical curve-fitting technique; this approximation in some instances fails even qualitatively to reveal the correct behavior[33] as for the unimolecular inverse isotope effect.[18]

We employ here the quantum statistical RRKM theory in the form appropriate when no internal rotational degrees of freedom exist; $I_r$ is the ratio of

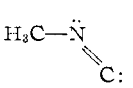
$$k_{\text{uni}} = \frac{I_r e^{-E_0/kT}}{Q_v h} \sum_{\epsilon^+ = 0}^{\infty} \frac{\sum\limits_{\epsilon_v^+ < \epsilon^+} P(\epsilon_v^+) e^{-\epsilon^+/kT}}{1 + \frac{I_r}{\omega h} \frac{\sum\limits_{\epsilon_v^+ < \epsilon^+} P(\epsilon_v^+)}{N(E_0 + \epsilon^+)}} \qquad (2)$$

symmetry numbers and of over-all moments of inertia of the molecule and activated complex, $Q_v$ is the molecule vibrational partition function, $P(\epsilon_v^+)$ is the vibrational degeneracy at the vibrational energy $\epsilon_v^+$ of the activated complex of total energy $\epsilon^+$, and $N(E_0 + \epsilon^+)$ is the density of vibrational energy levels of the molecule at this energy where $E_0$ is the critical energy. In the evaluation of eq. 2, accurate summations[20,34] of the vibrational energy levels, which have been a stumbling block to realistic calculations, have been made. The molecular and activated complex frequencies as known from vibrational analysis are used, as distinct from an empirically selected, singly degenerate oscillator model. The latter procedure is somewhat in the nature of a more sophisticated method of curve fitting. Good, and extensive, data make the more exact calculational models necessary.

**Mechanism of the Isomerization. The Activated Complex.**—For the evaluation of eq. 2, the vibrational analysis and frequencies for the molecule are known[6] (Table IV), but a model for the transition state must be obtained. The principal resonance form of methyl isocyanide is a, since various struc-

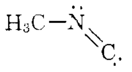

$H_3C{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}{:}$

a

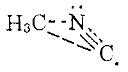


b

ture determinations confirm the symmetric top configuration[35]; however, it is of interest that in some metal complexes of isocyanides infrared evidence for bending of the RNC chain has been found.[36] The methyl isocyanide rearrangement is a Wagner–Meerwein 1,2-shift,[37] and there is no reaction path degeneracy. The activated complex may be represented as a cyclic species of $C_1$ or $C_s$ symmetry having resonance structures which may include



a



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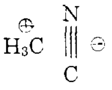
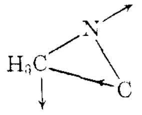


c

**Vibration Frequency Assignment.**—There are several ways of arriving at the structure and frequencies of the complex.[38] Some plausible bond orders and corresponding bond distances are given in Table V, along with other molecule parameters. The frequency assignments for stretching modes of the activated complex were made with the aid of Badger's rule,[39a] and of frequencies for cyclopropene[39b] and related structures (Table IV); two of the ring deformations of the complex have the nature of N≡C and C—N stretches and it was simply assumed that such a rule applies roughly. A twisting vibration cannot be similarly treated and its assignment is more arbitrary. Structure a and the cylindrical symmetry of structure c lend themselves to a low frequency here. The reaction coördinate is closely related to an asymmetric ring deformation, *e.g.*



and it is arbitrarily designated as such. More sophisticated consideration would relate the reaction coördinate to other of the normal vibrations.

The RRKM theory is comparatively insensitive to selection of the reaction coördinate and to moderate variations in structure and frequency of the activated complex,[18,19] where these give adequate correspondence with the observed high pressure frequency factor $A_\infty$, *i.e.*, the activation entropy. The only significantly arbitrary variable above is the single twist frequency which has been set down in the "300 model" as coincident with the degenerate molecule bending modes. But even a variation up to 600 cm.$^{-1}$ for this one frequency is scarcely disastrous, as is shown later in an illustrative comparison.

All vibrational modes of the molecule and complex are here taken as active and the over-all rotations as adiabatic.

**The Inertial Ratio.**—The ratio $I_r$ is

$$I_r = \frac{\sigma}{\sigma^+}\left(\frac{I_A^+ I_B^+ I_C^+}{I_A I_B I_C}\right)^{1/2} \qquad (3)$$

where the symmetry number $\sigma$ is 3 for the molecule, and $\sigma^+ = 1$ for an activated complex of $C_1$ or $C_s$ symmetry. The moments of inertia of the

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(32) E. W. Montroll and K. E. Shuler, *Adv. Chem. Phys.*, **1**, 361 (1958).

(33) J. Bigeleisen and M. Goeppert-Mayer, *J. Chem. Phys.*, **15**, 261 (1947).

(34) R. E. Harrington, B. S. Rabinovitch and R. W. Diesen, *ibid.*, **32**, 1245 (1960).

(35) M. Kessler, H. Ring, R. Trambarulo and W. Gordy, *Phys. Revs.*, **79**, 54 (1950); C. C. Costain, *J. Chem. Phys.*, **29**, 872 (1958).

(36) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

(37) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Ch. 9.

(38) H. S. Johnston, *Ann. Rev. Phys. Chem.*, **8**, 249 (1958); *Adv. Chem. Phys.*, **3**, 131 (1961).

(39) (a) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **35**, 458 (1961); (b) D. F. Eggers, private communication. We thank Dr. Eggers for this information and for discussion of it.

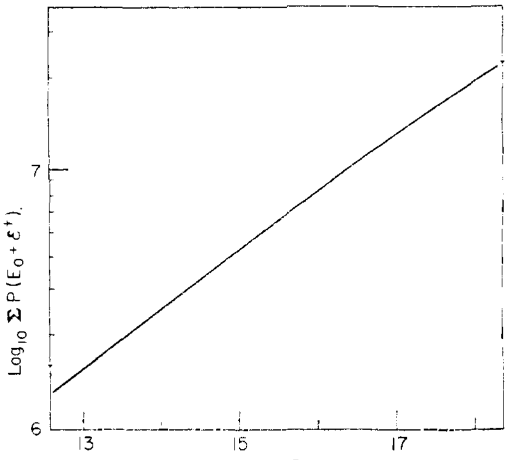

Fig. 4.—Log $\Sigma P(E_0 + \epsilon^+)$ *versus* $E_0 + \epsilon^+$(cm.$^{-1}$) for $CH_3NC$.

molecule, $I_A$, $I_B = I_C$, of the activated complex, $I_A{}^+$, $I_B{}^+$ and $I_C{}^+$, and the ratio $I_r$ were calculated for several C—C bond orders including the 300 and 600 models. It is evident from Table VI that the uncertainty in the C—C bond distance and CNC angle affect $I_r$ (and hence the absolute calculation of $k_\infty$) by less than 15%.

**E₀.**—The relation between $E_0$, the critical energy, and the experimental high pressure activation energy $E_a$ is given by[40]

$$E_0 = E_a - N\left[\sum_i^{11} \frac{h\nu_i{}^+}{\exp(h\nu_i{}^+/kT) - 1} - \sum_i^{12} \frac{h\nu_i}{\exp(h\nu_i/kT) - 1} + kT\right] \quad (4)$$

where $\nu_i{}^+$ and $\nu_i$ are the frequencies of the activated complex and the molecule, respectively. Then

300 model: $E_0 = E_a - 0.50$ kcal. = 37.85 kcal./mole
600 model: $E_0 = E_a - 0.24$ kcal. = 38.11 kcal./mole

**Collision Frequency.**—At high pressures nonideality corrections[41] apply to the collision frequency $\omega$. Two effects arise: The excluded volume increases $\omega$ by a factor of $1/(1 - 2nb)$, where $n$ is in molecules per cc. and $b$ is van der Waals constant; also, molecular shielding lowers $\omega$ by a factor of $[1 - (11/8)nb]$. The total correction amounts to a factor of $(1 + 0.625b)$. At $10^4$ mm., $\omega$ is raised by 2.3%; this is insignificant.

**Accurate Harmonic Energy Level Count.**—The accurate quantum statistical energy level count includes all possible frequency combinations up to high energies and is a formidable task[34] by other than computer methods,[20] although easier here at the comparatively low energies involved. The problem was simplified, and the final result scarcely affected, by using six groups for the fundamental frequencies (Table IV), where each group is represented by its geometric mean.[34] $N(\epsilon) = \partial\Sigma P(\epsilon_v)/\partial\epsilon_v$ was evaluated from 12,000 to 18,500 cm.$^{-1}$ (Fig. 4); $\Sigma P(\epsilon_v{}^+)$ for the activated complex was obtained for both the 300 and 600 models (Fig. 5).

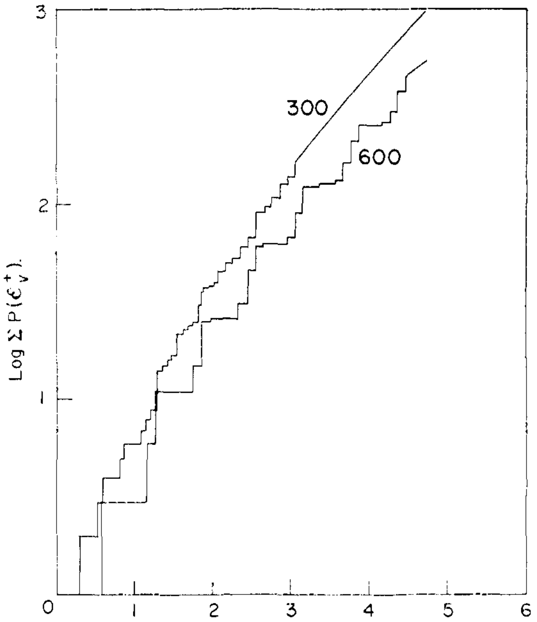

Fig. 5.—Log $\Sigma P(\epsilon_v{}^+)$ *versus* $\epsilon^+$ (cm.$^{-1}$) for $CH_3NC^+$ for 300 and 600 models.

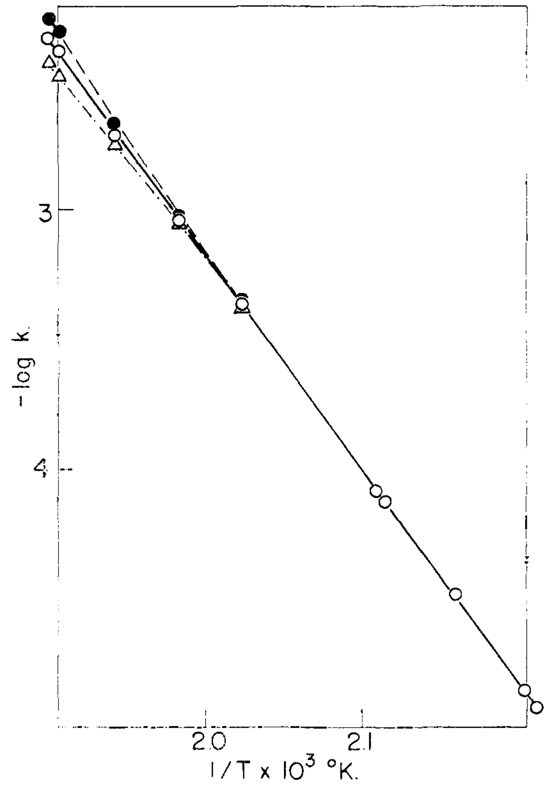

Fig. 6.—Log $k$ *versus* $1/T$ at 8 atm.; ●, uncorrected; △, corrected by eq. 10; ○, corrected by one-half of eq. 10.

An empirical correction factor $a$[20] to the semiclassical approximation[12] for vibrational levels summation is shown in Table VII. In practice such (or similar) corrections can with good accuracy obviate the need for machine calculations in many

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(40) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(41) S. Chapman and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge University Press, 1952.

cases. The $a$-values fall on a band with the earlier values of Rabinovitch and Current for other molecules.

**Calculation and Behavior of $k_{\mathrm{uni}}$.**—The principal summation of eq. 2 was carried out with a computer. The program obtained the summand at intervals starting at $E_0$ = 37.85 kcal./mole (300 model), or $E_0$ = 38.11 kcal./mole (600 model), and up to 54 kcal./mole where further contribution becomes negligible; at 44 kcal./mole the contribution is already ~95%.

**The Pressure Fall-off Region.**—The experimental fall-off curves are fairly well fitted by the 300 model (Fig. 1). No corrections or alternate definitions to the value of $\sigma$ = 4.5 Å. from viscosity measurements[11] were made. The calculated and observed curves overlap, and the agreement of the calculated and experimental pressure values is quite striking. The modest pressure correction factors which are used in the figure to bring the calculated curve into agreement with the experimental curve, at $k/k_\infty$ = 0.1, are listed in Table VIII. Marcus and Wieder[19] found for a number of reactions, including cyclopropane, that the computed rate constants were somewhat too high in the fall-off region. In a calculation of cyclopropane,[18] we have fitted the fall-off shape and have not found as large a pressure discrepancy as they reported; in addition, our discrepancy would be essentially wiped out[18b] by adoption of their value of the collision cross-section (3.9 Å. instead of 4.9 Å.). The calculational procedures used by us are somewhat more accurate and may account for the difference. However, within the somewhat uncertain limits of the inelastic collision cross-sections, such agreement can be fortuitous.

It is evident from eq. 2 that a change of $I_{\mathrm{r}}$ does not directly affect the *shape* of the fall-off curve but merely shifts it along the pressure axis.

The 600 model of the activated complex produces a small increase in curvature over the 300 model (Fig. 1). The degree of subjective control of the fit of calculated and experimental fall-off by manipulation of the sole significantly arbitrary parameter, the twist frequency, is in fact not large. Calculated values are compared in Table IX in terms of $s$, the classical fit parameter.

More generally, it is obvious that *gross* errors or distortions in several, or many, frequency assignments would be very serious for calculations of fall-off behavior and of $k_0$. Depending of course on the number and spread of the lower vibration frequencies of the molecule and of the complex, we estimate that three or probably four degenerate frequency groupings for each species is a minimum for accurate representation of the various aspects of unimolecular behavior of complex molecules.

**Effect of Temperature on Fall-off Behavior.**—In Slater theory,[14] the fall-off and shape parameter $n$ is independent of temperature. the fall-off curve merely being shifted along the pressure axis by change of temperature. In classical RRK theory, the fall-off parameter $s$ is fixed empirically, and for a fixed $s$ the theory then predicts *increased* fall-off curvature with temperature rise.[10] In the RRKM quantum statistical transition state formulation, the calculated behavior, which accords with the experimental observations here, gives a *decreased* curvature with rise of temperature at the conventional temperatures employed in such studies, corresponding to an increase in the empirical fit parameter $s$ (Table IX). Due to the modest temperature spread employed here, the experimental changes in the shape of the fall-off are very slight but are large enough to be detected relative to each other. The curvature decrease with temperature rise, due to relatively more classical behavior and reduction of quantum restrictions,[18a] is limited—since rise of temperature toward classical limiting behavior gives rise eventually, at the very high energies that then prevail, to a fall-off of increased curvature. With use of Slater's $n$-parameter[14] simply as a unique definition of fall-off *shape*, the calculated variation of fall-off curvature for methyl isocyanide as a double valued function of $T$ is illustrated in Table IX.

The experimental pressure shift for a temperature increase of 60° is $\Delta \log p$ = 0.12 at $k/k_\infty$ = 0.1. This is in good agreement with the calculated shift for the 300 model of 0.11.

**The $p_\infty$ Region; the Frequency Factor $A_\infty$.**—At infinite pressure the RRKM expression reduces to

$$k_\infty = \kappa \frac{kT}{h} \times \frac{I_{\mathrm{r}} Q_{\mathrm{v}}{}^{+} e^{-E_0/RT}}{Q_{\mathrm{v}}} \tag{5}$$

which is identical with the conventional formulation of Eyring theory; $\kappa$ was simply set at unity. Good agreement between experimental and calculated values of $A_\infty$ is particularly obtained for the 300 model (Table X). This further suggests that the frequency assignment in the 300 model (or, for that matter, the 600 model) is a reasonable one; particularly, since a small change within experimental error in $E_{\mathrm{a}}$ produces a relatively big change in the observed frequency factor, $A_\infty$, and makes such comparison somewhat inaccurate.

**The $p_0$ Region.**—The low pressure rate constant is

$$k_0 = \omega \int_{E_0}^{\infty} N(\epsilon)\, e^{-\epsilon/RT}\, \mathrm{d}\epsilon / Q_{\mathrm{v}} \tag{6}$$

The conventional activated complex does not enter, although the computed $E_0$ value depends upon it a little. The agreement between experimental and calculated values of $k_{\mathrm{bi}} = k_0/M$ (obtained by extrapolations to low pressure) is good for the 300 model (Table XI), the latter being a little low. At this point, the strong collision assumption appears justified. The average discrepancy (−40%) of the 300 model, relative to experiment, must be considered in the light of the uncertainty in $\sigma$; it will be subject to further reduction upon inclusion of anharmonicity.

The 600 model gives a low pressure rate constant which is too low by a factor of less than $^1/_2$; this is not as good.

**Activation Energies, $E_{\mathrm{a}}$.**—The dependence of activation energy on pressure has been determined continuously from the three calculated fall-off curves on the 300 model (Fig. 3). The resulting curve must, of course, coincide exactly with the experimental curve at $p_\infty$. At lower pressures, the calculation agrees well with the experimental curve; the theoretical spread of $E_{a\infty} - E_{a0}$ (1.8 kcal./mole) is slightly smaller than the experimental spread (2.1 kcal./mole), but is within experimental error (Fig. 3). The 600 model calculated activation energy spread is somewhat smaller (1.6 kcal./mole).

On all counts the harmonic 300 model is superior to the 600 model, although the over-all account provided by the latter may be considered not bad, and is improved significantly by considerations that follow.

**Anharmonicity Effects. General.**—The importance of anharmonicity has been noted above and leads to rapid intramolecular redistribution of vibrational energy.[13] Anharmonicity also enters in a second way, insofar as it may significantly alter the harmonic estimate of the internal energy level densities of the species. This section is concerned *only* with this second aspect. In general, it is most important for very small molecules having very large critical energies. Rice[42] estimated that anharmonicity causes an increase in rate at low pressures by a factor of 3–4 for $F_2O$. The critical energy for $F_2O$ is ~40 kcal./mole. For the larger $CH_3NC$ molecule at virtually the same critical energy, the effect tends to be greatly reduced since the average level populated by each mode is lower, while anharmonicity is enhanced only at the upper levels. Even more so for the decomposition of the large butyl radical, excited to these same energies, no need was found to take account of anharmonicity in order to obtain concordance of the theory with experiment.[22]

**Anharmonicity Calculations for $CH_3NC$ Molecule.**[7]—Due both to ignorance of the potential energy surfaces of polyatomic molecules and to earlier difficulties mentioned above in making accurate vibrational energy sums at the high energy level densities involved, the problem of anharmonicity in unimolecular rate calculations has scarcely received quantitative statistical treatment. A complete potential energy function for $CH_3NC$ includes all of the twelve vibrational modes, *i.e.*, stretching and bending vibrations as well as their interactions. Thus far workable and complete potential functions have been found only for some small triatomic molecules,[43] for which experimental values of anharmonic constants are accessible. For $CH_3NC$ the spectroscopic data available are insufficient for the construction of a complete potential energy function. Therefore the molecule was treated as consisting of a collection of anharmonic oscillators and cross terms in the potential energy were neglected. Fortunately for our purposes in chemical kinetics, this gross simplification should not prevent quantitative insights from being obtained here for methyl isocyanide, or for large molecules at low total energies in general, since the contribution of higher energy states is less important. For small molecules at high energies, good kinetic data could, optimistically, be used as a calibration of anharmonic and interaction effects.

Consider first the stretching motions. The energy levels for the stretching vibrations in $CH_3NC$ associated with the C—H, C—N and N≡C bonds were calculated by using the solution given by Morse[44] for his function

$$W(v) = \omega(v + {}^1/_2) - \frac{h\omega^2 c}{4D}(v + {}^1/_2)^2$$

where $D$ is the dissociation energy. $D$ was calculated from the quadratic and cubic force constants compiled by Herschbach and Laurie,[39a] $D = k_2^3/2k_3^2$. The range of validity of $v$ is $0 < v < (k\text{-}1)/2$, where

$$k = \frac{8\pi D}{h}\left(\frac{\mu}{k_2}\right)^{1/2}$$

where $\mu$ is the reduced mass. For example, the upper limit of $v$ used for the C–H stretching vibration is here $v = 20$. The Morse energy levels are most accurate for the lower quantum numbers, which are the more important ones here.

A general potential function describing an angle deformation vibration has the shape of a multiple minimum function.[43] The required information including higher order force constants for the angle deformation vibrations in $CH_3NC$ is not available. Known anharmonic constants for bending vibrations in some triatomic[43] and some polyatomic molecules[45–47] are usually negative in sign; *i.e.*, the energy level spacing decreases with increasing energy. Therefore, for lack of any procedure for evaluating the bending contribution, we have simply adopted a potential function for an angle deformation vibration of the Morse type, whose dissociation limit should exceed that of a pure stretching vibration by a considerable amount.

The splitting of the degeneracy of higher levels of degenerate vibrations due to anharmonicity was handled by taking the geometric mean of the corresponding group of levels as the representative group energy level, and assigning the appropriate degeneracy to the representative level; this reduces the anharmonicity correction relative to the result if such splitting were ignored and the degenerate group level were placed simply at the corresponding non-degenerate value.

Two anharmonic models were considered. Model 1 employs anharmonicity corrections which can be classified as possibly minimal. The corrections for the three stretching vibrations were calculated from the known quadratic and cubic force constants, whereas the bending corrections were assigned so as to result in "dissociation limits" (convergence of levels) at energies much larger than the limit characterizing stretching of the bond (App. III). Model 2 uses identical corrections for the stretching vibrations but increased anharmonicity corrections for the bending term values, whose dissociation limits are now comparable with the ones of the associated stretching vibrations. Model 2 is believed to be a maximum estimate. The resulting models are described as Anharm (300)1, Anharm (300)2, etc., where model 1 or 2 have been combined with the 300 or 600 model for the complex, which have been similarly corrected. The

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[42] O. K. Rice, *J. Phys. Chem.*, **65**, 1588 (1961); *Monatsh.*, **90**, 330 (1959).

[43] J. Pliva, *Coll. Czech. Chem. Commun.*, **23**, 777 (1958).

[44] P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

[45] S. J. Cyvin, *Spectrochim. Acta*, **16**, 1022 (1960).

[46] D. M. Dennison, *J. Chem. Phys.*, **20**, 313 (1952).

[47] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 207

latter correction is in fact negligible and thereby could be omitted with scarcely any effect.

The anharmonic energy level sum was calculated as previously[20] by exact count on a computer (IBM 709), using 5 groups of fundamental frequencies. The results are now described.

**Low Pressure Limit.**—Anharmonicity increases $N(\epsilon)$ markedly at the higher energy range above $E_0$. This results in enhanced rate of activation and of reaction in the low pressure region, since the normalizing partition function $Q_v$ (eq. 6) is tied in magnitude to the lower level spacing by the operation of the exponential factor in each term of its summation. In fact, $Q_v$(or $Q_v{}^+$) is increased in magnitude by only a few per cent. due to anharmonicity, at the temperatures of the present experiments (App. III). Tables XI and XII show that $k_{bi}$, and thus the energy level density at energies just above $E_0$, *i.e.*, 40 kcal. mole$^{-1}$, is increased by ~25–40% for these models. A plausible mean may be 30%. The agreement of all calculated values with experiment is enhanced as a result of the anharmonicity correction, and no indication contrary to the strong collision model is seen.

**Fall-off Region.**—In the fall-off region, the relative effect of anharmonicity on *both* the molecule and the activated complex enters. Since an anharmonic molecule behaves somewhat as if it consisted of oscillators of lower average frequency than the harmonic model, its behavior *tends* to be more classical at a given temperature. Thus anharmonicity might intuitively be thought to cause decreased curvature of the fall-off plot relative to the harmonic case. The calculations show that, in fact, use of either models 1 or 2 changes the fall-off shape as predicted by the RRKM theory very slightly, and mainly causes a shift of the curve to lower pressure (Tables VIII and IX). This may be seen by inspection of eq. 1: $N(\epsilon)$ (anharmonic) is appreciably increased, but $\Sigma P(\epsilon_v{}^+)$ is scarcely affected in magnitude at the low energies of the complex, $\epsilon^+$. The range of effective energies of $\epsilon$ is small enough, also, so as to cause little *differential* anharmonic increase in $N(\epsilon)$ over the range, even for model 2; so that $N(\epsilon)$ is increased virtually by a constant.

**High Pressure Limit.**—At the $p = \infty$ limit, since only the less-affected lower levels for *both* species are important and these also tend to be mutually compensating, as expressed by the partition function *ratio* $Q_v{}^+/Q_v$ in eq. 5, the net effect on the rate constant is only a few per cent. This is illustrated for the most extreme case in Table X. The calculation of $E_0$ is similarly only slightly affected, and amounts to a decrease of ~25 cal.

Evidently, since $N(\epsilon)$ does not appear explicitly in eq. 5, unlike eq. 6, the anharmonicity-enhanced rise in $N(\epsilon)$ at the high reaction energies is self-cancelling—physically this is so because the resulting effect of higher population of molecules above $E_0$ is opposed by their exactly compensating enhanced stability and reduced reaction probability. This may be made more evident by writing $k_\infty$ as

$$k_\infty = \int_0^\infty k_\epsilon \cdot K(\epsilon)\,\mathrm{d}\epsilon = \frac{P_1{}^+}{P_1h}\int \Sigma\,\frac{P(\epsilon_v{}^+)}{N(\epsilon)}\cdot\frac{N(\epsilon)e^{-\epsilon/kT}\mathrm{d}\epsilon}{Q_v}$$

$$= \frac{P_1{}^+}{P_1h}\int \Sigma\,\frac{P(\epsilon_v{}^+)}{Q_v}\,e^{-\epsilon/kT}\,\mathrm{d}\epsilon \qquad (7)$$

which reduces further to eq. 5. Thus there is a close correspondence between the reduction of the importance of the *rate* effects due to anharmonicity with pressure rise, and the occurrence of large *inverse isotope* effects at low pressures which disappear at high pressures.[18,48]

The effect of anharmonicity being strongest at low pressure, studies of the lower end of the fall-off curve, and especially of the limiting region, afford the best test both of anharmonicity effects and of the strong collision assumption.

**Conclusions.**—Despite the incompleteness of range and depth of the present results, they constitute one of the more thorough tests of unimolecular reaction theory presently available from thermal studies. The data bear out the general usefulness of the RRKM theory as a means of prediction and description. Absolute pressure fit of the fall-off is provided within a factor of less than two for a range of possible assumptions; the significance of closer fit is tempered by uncertainties in appropriate collision cross-sections. The variation of the fall-off pressure with temperature is given by the theory, as is also the activation energy decline. The low pressure rate constants in the non-equilibrium region are also reproduced in magnitude within the uncertainty of the collision cross-sections, particularly when vibrational anharmonicity is included in the calculations. Support for the substantial validity of the strong collision assumption is also provided by the low pressure fit.

The principal discrepancy of the theory concerns the fall-off shape. This discrepancy is actually rather modest when one considers that scarcely any gross adjustment factors have entered in a significant way. Furthermore, the total number of vibration modes were explicitly included in the calculations, *ab initio;* we do not believe that, for the present type of phenomenon, the evidence cited earlier permits the number of active vibration modes to be used as a variable parameter. The shape of the calculated fall-off is virtually independent of conventional anharmonicity assumptions which only affect the absolute pressure fit. The systematic experimental error mentioned in Tables X and particularly XI is part of the problem of the discrepancy between observed and calculated fall-off; the fall-off shape may thus have been fitted as closely as is reasonable at this time. However, some alterations of the calculational model can be considered.

First, one could invoke *special anharmonicity* of the activated complex, as might be appropriate for a shallow col. Insertion of gross anharmonicity into certain modes of the activated complex, corresponding, for example, to convergence of the spacings of the twist mode and of the C–N ring mode at very low levels of energy (15–25 kcal.), gives an improvement in the fit. As was found by us in trial calculations, the calculated equivalent Kassel *s* parameter is indeed raised toward the observed value. However, heavy appeal to such a model in our present state of knowledge of potential energy surfaces, while possibly justifiable in

(48) B. S. Rabinovitch and J. H. Current, *Can. J. Chem.*, **40**, 557 (1962).

principle to some degree, would reduce this part of the calculation to an entirely empirical procedure.

A related shortcoming of the model which may be mentioned here is the neglect of slightly better known effects associated with rotational–vibrational coupling in the molecule; and the use of vibrational level spacings corresponding to the ground states of the over-all rotations. The appropriate corrections would be at best very difficult to make from both the theoretical and the rate computational viewpoints, and are best frankly ignored at this stage.

Finally, a simple plausible deficiency of the calculations of our assumption[49a] regarding conservation of angular momentum,[49b] as was implicit in the assertion that all rotational degrees of freedom would be taken as adiabatic. Since the $C_{3V}$ symmetry of the methyl isocyanide molecule is lost in the activated complex, and due to the large Coriolis coupling[40] of the degenerate deformation modes (having net angular momentum) of the symmetric top group, the assumption of adiabaticity of the figure axis rotation is highly suspect. Employment of this degree of freedom as active in the present type of calculations will not ensure conservation of angular momentum in microscopic detail, but is a gross correction (overestimate) in the right direction.[49c] Its effect is to raise both the calculated equivalent $s$ parameter and $k_{bi}$, and to improve the fit to the fall-off shape and the account provided by the 600 model (Tables IX and XI). $k_\infty$ is not affected.

Other aspects of the experimental investigation of this reaction type are being pursued, and will be reported at a later time.

**Acknowledgment.**—B. S. R. thanks Dr. I. E. Puddington, Director, Applied Chemistry Division, National Research Council, Ottawa, Canada, for the hospitality enjoyed by him as a Visiting Scientist during which time part of this manuscript was written.

## Appendix I

**Self-heating.**—At high reaction rates, temperature gradients can be established in a reacting system due to self-heating. This effect is diminished by convection or turbulence. Self-heating occurred in the present work only in runs above 1000 mm. pressure at 230.4°, and in some determinations of activation energy at 8 atm. which extended to higher temperatures.

An expression for the relative average temperature rise over a vessel is[50]

$$\left(\frac{T - T_0}{T_0}\right) = \frac{R\Delta H r^2}{15\,\kappa\,T_0} \qquad (10)$$

where $r$ is the vessel radius; $\Delta H^0$, the heat of isomerization of methyl isocyanide, is $-15.0$ kcal./mole[51]; $\kappa$, the thermal conductivity (as calculated below), is $6.0 \times 10^{-5}$ cal./cm. °C. sec.; and $R$ is the reaction rate in moles/cc. sec.

The maximum correction made to the rate at 230° was 6%. Determination of corrected rate constants in vessels of different size provided some criterion of the validity of eq. 10. In addition, a further test was found by pushing the activation energy data at 8 atm. to higher temperatures. It is seen from Fig. 10 that at higher temperatures, where self-heating became important, the experimental points show upward curvature from the straight line obtained by extrapolation from runs at lower temperatures. The necessary correction (used henceforth) to restore straight line behavior was only one-half of that calculated by eq. 10. Apparently ideal conditions reflected in the equation were not fulfilled in the very small vessels used.

**Thermal Conductivity of $CH_3NC$.**—The thermal conductivity[52] $\kappa$ and viscosity[11] $\eta$ of acetonitrile have been reported at temperatures up to 140°. It is assumed that the transport properties of methyl isocyanide are similar to those of acetonitrile. The experimental values of $\eta$ were extrapolated to 230.4° where $\eta = 1.3 \times 10^{-4}$ g./cm. sec. With values[3] for $f_{\text{trans}} = 1.19$ and $f_{\text{int}} = 1.27$, $M = 41$, $C_{\text{v trans}} = 2.98$, and $(C_{\text{v rot}} + C_{\text{v vib}}) = 11.52$, then

$$\begin{aligned}\kappa &= \eta\,[f_{\text{trans}}\,C_{\text{v trans}} + f_{\text{int}}\,(C_{\text{v rot}} + C_{\text{v vib}})]/M \\ &= 6.0 \times 10^{-5}\ \text{cal./cm. °C. sec.}\end{aligned}$$

The variation of $\kappa$ with pressure was given up to one atmosphere by Vines and Bennett[52]

$$\kappa = \kappa^\circ\,(1 + \beta p/100)$$

An extrapolated value, $\beta = 0.34\%$ per atm., was obtained for acetonitrile at 230.4° and corresponds to a 5% increase in the thermal conductivity at 12 atmospheres, the highest pressure used in the present study, and is unimportant even if inaccurate.

**Association of Methyl Isocyanide.**—The association of acetonitrile at low temperatures and higher pressures has been reported in the literature. A similar association is expected for methyl isocyanide since it is isomeric with acetonitrile, and has similar symmetry and dipole moment. Because of a lack of data, the equilibrium constant for association of acetonitrile is employed for methyl isocyanide.

The variation of the equilibrium constant for acetonitrile with temperature is[53]

$$\log K_p = 4.505 - 1147/T$$

from which $K_p$ at 199.4° and 230.4° is 123 and 161 (atm.), respectively. Some error in the association correction is not serious in view of the fact that the fall-off curves $k/k_\infty$ approach unity asymptotically at the pressures involved. Apart from obtaining a corrected "pressure of isocyanide" as in Table II no further correction was made; change in the collision number due to changed identity, in part, of the inert gas tends to be self-compensating, since

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[49] (a) For the calculation of ethyl radical decomposition, J. H. Current and B. S. Rabinovitch (*J. Chem. Phys.*, submitted; J. H. Current, Ph.D. Thesis, University of Washington, 1961) have taken an over-all rotation as active, since figure axis and internal rotations interact strongly in this case. (b) S. Golden, private communication.

(49c) Reference 49a discusses this aspect and the summation of rotational levels in more detail.

(50) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960; valid for small rise.

(51) F. D. Rossini, "Selected Values of Thermodynamic Properties," N.B.S. Circular No. 500, 1952.

(52) R. G. Vines and L. A. Bennett, *J. Chem. Phys.*, **22**, 360 (1954); L. A. Bennett and R. G. Vines, *Austral. J. Chem.*, **8**, 451 (1955).

(53) J. S. Rowlinson, *Trans. Faraday Soc.*, **45**, 974 (1949).

collision cross-section rises concomitantly with doubling of weight on dimerization—which in the worst case caused only ~7% decrease in total pressure.

At 75 mm. pressure and 25°, association was calculated to be ~2.5%. Samples for runs were therefore measured out at lower pressure not exceeding 45 mm. where association is less than 1%.

## Appendix II

TABLE I

SAMPLE RUNS $CH_3NC \rightarrow CH_3CN$

| P, mm. | T, °C. | Conversion, % | $k \times 10^5$, sec.$^{-1}$ | P, mm. | T, °C. | Conversion, % | $k \times 10^5$, sec.$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1.05 | 230.8 | 9.8 | 3.81 | 7.46 | 230.2 | 13.5 | 15.1 |
| | | 13.2 | 3.84 | | | 21.6 | 14.6 |
| | | 18.8 | 3.98 | | | 30.0 | 14.8 |
| | | 22.2 | 3.84 | | | 37.8 | 14.9 |
| 2.11 | 229.6 | 11.4 | 6.30 | 17.6 | 230.7 | 10.4 | 25.9 |
| | | 16.6 | 6.29 | | | 23.4 | 25.9 |
| | | 21.0 | 6.16 | | | 33.6 | 25.9 |
| | | 25.9 | 6.29 | | | | |

TABLE II

PRESSURE DEPENDENCE OF ISOMERIZATION RATE CONSTANTS

| p, mm.[a] | k, sec.$^{-1}$ | $k/k_\infty$ | p, mm. | k, sec.$^{-1}$ | $k/k_\infty$ |
|---|---|---|---|---|---|
| $T = 199.4°$, $k \times 10^6$ | | | | | |
| 0.161 | 1.01 | 0.0134 | 5.21 | 13.2 | 0.176 |
| .172 | 0.89 | .0118 | 7.25 | 14.2 | .189 |
| P .190 | 1.03 | .0137 | Q 9.07 | 16.6 | .221 |
| .243 | 1.06 | .0141 | 10.0 | 18.0 | .240 |
| Q .297 | 1.36 | .0181 | 12.7 | 19.8 | .264 |
| .317 | 1.48 | .0197 | 15.7 | 21.6 | .288 |
| .323 | 1.45 | .0193 | 24.8 | 30.0 | .400 |
| .357 | 1.67 | .0222 | 35.7 | 34.0 | .453 |
| .448 | 2.09 | .0278 | 72.3 | 45.0 | .600 |
| P .496 | 2.06 | .0275 | 101.5 | 52.0 | .693 |
| Q .523 | 2.04 | .0272 | 120.1 | 55.8 | .744 |
| .538 | 2.35 | .0313 | 155.2 | 55.6 | .741 |
| .585 | 2.31 | .0308 | 208 | 60.2 | .803 |
| Q .648 | 2.83 | .0377 | 337 | 66.2 | .883 |
| .700 | 3.00 | .0400 | 570(575)[b] | 69.8 | .931 |
| .805 | 3.10 | .0413 | 948(962) | 67.9 | .905 |
| .93 | 3.43 | .0457 | 1143(1168) | 73.0 | .973 |
| 1.03 | 4.08 | .0544 | 1500(1530) | 72.5 | .967 |
| 1.14 | 3.70 | .0493 | 1780(1825) | 73.5 | .980 |
| 1.24 | 4.20 | .0560 | 2248(2322) | 73.7 | .983 |
| 1.41 | 4.55 | .0606 | P 2888(3075) | 74.5 | .993 |
| 2.03 | 5.91 | .0788 | 5010(5330) | 74.1 | .988 |
| 2.64 | 7.38 | .0984 | P 5980(6393) | 75.0 | 1.000 |
| 4.14 | 10.5 | .140 | 7106(7610) | 74.9 | 0.999 |
| 5.00 | 11.7 | .156 | 8800(9515) | 78.6 | 1.047 |
| | | | ∞ | 75.0 | 1.000 |
| $T = 230.4°$, $k \times 10^5$ | | | | | |
| 0.0255 | 0.145 | 0.00157 | 0.101 | 0.540 | 0.00584 |
| P .0266 | .166 | .00179 | .109 | .540 | .00584 |
| .0293 | .165 | .00178 | .124 | .628 | .00679 |
| .0348 | .205 | .00221 | .130 | .704 | .00761 |
| .0390 | .228 | .00246 | .130 | .653 | .00706 |
| P .0454 | .260 | .00281 | .131 | .721 | .00779 |
| .0470 | .256 | .00276 | .145 | .680 | .00735 |
| .0533 | .326 | .00352 | .224 | 1.10 | .0119 |
| .0632 | .323 | .00349 | .272 | 1.30 | .0140 |
| P .0654 | .339 | .00366 | .286 | 1.25 | .0135 |
| .0725 | .404 | .00436 | .410 | 1.79 | .0193 |
| P .0739 | .390 | .00421 | .560 | 2.20 | .0238 |
| P .0745 | .419 | .00453 | .581 | 2.32 | .0251 |
| .0876 | .453 | .00490 | .590 | 2.40 | .0259 |
| .0933 | .530 | .00573 | .950 | 3.80 | .0411 |

TABLE II (*continued*)

| $p$, mm.[a] | $k$, sec.$^{-1}$ | $k/k_\infty$ | $p$, mm. | $k$, sec.$^{-1}$ | $k/k_\infty$ |
|---|---|---|---|---|---|
| 1.05 | 3.76 | .0406 | 63.0 | 46.7 | .505 |
| 1.10 | 4.17 | .0451 | 79.5 | 48.4 | .523 |
| 1.11 | 4.20 | .0454 | 80.6 | 52.5 | .567 |
| 1.20 | 4.35 | .0470 | 82.0 | 50.3 | .544 |
| 1.39 | 4.84 | .0523 | 100 | 53.7 | .580 |
| 2.11 | 6.54 | .0707 | 103 | 57.0 | .616 |
| 2.20 | 6.54 | .0707 | 130 | 61.4 | .664 |
| 3.01 | 8.45 | .0913 | 157 | 68.4 | .740 |
| 3.02 | 8.24 | .0891 | 177 | 68.8 | .743 |
| 3.03 | 8.57 | .0926 | 191 | 69.8 | .754 |
| 5.08 | 12.0 | .130 | 222 | 68.5 | .740 |
| 5.10 | 12.2 | .132 | 240 | 68.2 | .737 |
| 5.20 | 12.4 | .134 | 265 | 72.5 | .784 |
| 5.23 | 12.0 | .130 | 309 | 73.5 | .794 |
| 5.04 | 11.6 | .126 | 323 | 71.6 | .774 |
| 7.14 | 14.0 | .151 | 337 | 74.0 | .800 |
| 7.25 | 15.0 | .162 | 372 | 73.0 | .789 |
| 7.37 | 14.5 | .157 | 479 | 76.8 | .830 |
| 7.46 | 15.0 | .162 | 486 | 80.0 | .865 |
| 7.48 | 14.9 | .161 | 607 | 79.7 | .861 |
| 8.00 | 15.6 | .169 | 635 | 82.0 | .886 |
| 8.04 | 15.7 | .170 | 659 | 77.4 | .830 |
| 8.76 | 15.8 | .171 | 775 | 86.0 | .930 |
| 10.1 | 18.8 | .203 | 1050 | 81.6(82.8)[c] | .882 |
| 17.6 | 25.3 | .273 | 1349(1355) | 87.1(88.4) | .941 |
| 18.0 | 27.4 | .296 | 1757(1795) | 86.6(88.0) | .936 |
| 18.1 | 25.8 | .279 | 3580(3679) | 89.5(91.5) | .967 |
| 23.3 | 27.2 | .294 | P 3610(3712) | 90.6(91.3) | .979 |
| 29.8 | 34.5 | .373 | 3850(3940) | 90.5(92.9) | .978 |
| 30.1 | 32.0 | .346 | 4020(4121) | 87.3(89.4) | .944 |
| 31.1 | 34.2 | .370 | 5880(6136) | 90.8(93.5) | .982 |
| 35.2 | 35.7 | .386 | 9880(10540) | 92.0(97.2) | .994 |
| 40.8 | 37.9 | .410 | 10250(10950) | 91.7(96.3) | .991 |
| 53.6 | 41.4 | .447 | P 10520(11290) | 93.0(94.7) | 1.005 |
| 59.6 | 45.4 | .491 | ∞ | 92.5 | 1.000 |
| $T$ = 259.8°, $k \times 10^5$ | | | | | |
| 0.0308 | 1.34 | 0.00175 | 0.938 | 24.7 | 0.0322 |
| P .0352 | 1.49 | .00194 | 1.07 | 30.8 | .0401 |
| .0432 | 1.82 | .00237 | 1.12 | 28.5 | .0371 |
| P .0463 | 2.06 | .00268 | 1.32 | 37.7 | .0491 |
| .0581 | 2.30 | .00300 | 1.36 | 33.0 | .0430 |
| .0745 | 2.88 | .00375 | 1.67 | 41.2 | .0537 |
| .0977 | 3.83 | .00499 | 1.98 | 46.6 | .0607 |
| P .105 | 3.90 | .00508 | 2 10 | 46.2 | .0602 |
| .116 | 4.43 | .00577 | 2.23 | 49.0 | .0639 |
| .146 | 5.07 | .00661 | 2.59 | 56.6 | .0738 |
| .182 | 6.12 | .00798 | 3.14 | 62.8 | .0819 |
| .212 | 7.58 | .00988 | 3.34 | 65.3 | .0851 |
| .220 | 7.50 | .00978 | 3.91 | 83.4 | .109 |
| .223 | 7.47 | .00974 | 4.63 | 88.0 | .115 |
| .231 | 8.05 | .0105 | 5.00 | 86.0 | .112 |
| .255 | 8.27 | .0108 | 5.49 | 96.1 | .125 |
| .278 | 10.2 | .0133 | 6.49 | 109 | .142 |
| .330 | 10.6 | .0138 | 7.21 | 127 | .165 |
| .396 | 12.7 | .0166 | 8.43 | 129 | .168 |
| .397 | 13.2 | .0172 | 9.71 | 150 | .195 |
| .508 | 15.0 | .0195 | 10.0 | 142 | .185 |
| .555 | 16.9 | .0220 | 10.9 | 138 | .180 |
| .675 | 19.2 | .0250 | 12.7 | 174 | .227 |
| .790 | 19.2 | .0250 | 15.3 | 206 | .268 |
| P .830 | 21.5 | .0280 | ∞ (calcd.) | (767) | (1.000) |

[a] P = packed vessel run, 10:1 surface/volume ratio; Q = quartz vessel. [b] Pressures in parentheses are uncorrected for association. [c] Rate constants in parentheses are uncorrected for self heating.

## Appendix III

**Anharmonicity Correction.**[7]—The anharmonicity correction constants and the dissociation constants $D$ for the isocyanide molecule, in a Morse-type equation for the energy levels measured from the zero level

$$W(n) = \omega n - \frac{hc\omega^2}{4D} \times n^2$$

are listed for two models in Table XII. Groups a and d represent geometric mean frequencies (with consequent "accidental" degeneracy) of close-lying vibration frequencies listed in Table IV. Splitting of accidental degeneracy was, of course, not introduced. The anharmonicity constants for vibration groups a, b and c were directly calculated with the use of the compilation of quadratic and cubic force constants of Herschbach and Laurie. The corresponding $D$ values are reasonably near to the correct values. For the estimation of the anharmonicity bending corrections, the deductions of Dennison[46] (ethane) concerning the lowering of the first excited levels and of Cyvin[45] (cyclopropane), for C–H motions, and of Pliva,[43] for skeletal bends in HCN and $H_2O$, are available. It was decided to make a frankly arbitrary empirical correction as the optimum procedure, rather than entertain tenuous correlations for such little known phenomena. "Dissociation" limits were assigned for the motions corresponding to frequency groups d, e and f, and the corresponding anharmonicity corrections determined. In the energy level density calculation by a multiple summation program on the IBM 709, groups c and e were further consolidated into a single group with composite correction coefficient of −4.0 for model 1, and − 7.8 for model 2. This is to be justified only as a mathematical simplification which does not alter the calculated values appreciably.

TABLE III

ARRHENIUS PARAMETERS FOR THE ISOMERIZATION OF $CH_3NC$

| $P$, mm. | log $A \pm \sigma$ | $E_a \pm \sigma$, kcal./mole |
|---|---|---|
| 6075 | 13.61 ± 0.09[a] | 38.35 ± 0.21[a] |
| 1500 | 13.49 ± .10 | 38.11 ± .21 |
| 150 | 13.17 ± .14 | 37.69 ± .31 |
| 10 | 12.17 ± .08 | 36.58 ± .18 |
| 5 | 11.82 ± .08 | 36.26 ± .18 |
| 0.1 | 10.46 ± .11 | 36.27 ± .27 |

[a] Standard deviation of the slope and intercept.

TABLE IV

VIBRATION FREQUENCIES FOR $CH_3NC$ MOLECULE AND ACTIVATED COMPLEX, CM.$^{-1}$

| Molecule[6] | | | Activated complex models[a] | | | |
|---|---|---|---|---|---|---|
| | | Grouping | | 300 | 600 | |
| C—H str. | 2966<br>3014(2) | 2998(3) | | 2998(3) | 2998(3) | |
| N≡C str. | 2161 | | Ring def. | 1990 | 1990 | |
| $CH_3$ def. | 1410<br>1459(2) | 1443(3) | | 1443(3) | 1443(3) | |
| $CH_3$ rock. | 1041(2) | | | 1041(2) | 1041(2) | |
| C—N str. | 945 | | Ring def. | 600 | 600 | |
| | | | Ring def. | Translation | | 580(2) |
| CNC bend. | 270(2) | | Twist | 270 | 560 | |

[a] $r_{cc}$ set at 1.46 Å., as in $CH_3CN$,[35] for the standard bond distance (Table V) for the calculation of activated complex force constants by Badger's rule.[39a] "Standard" frequencies for the C—N stretch, C≡N stretch and twisting mode, to which the reduced force constants were applied, were 945, 2160 and 880 cm.$^{-1}$, respectively.

TABLE V

STRUCTURE PARAMETERS FOR $CH_3NC$ MOLECULE AND ACTIVATED COMPLEX

| Bond | C—H | C—C | C—N | N≡C | HCH |
|---|---|---|---|---|---|
| Molecule[35] $r$, Å. | 1.094 | | 1.427 | 1.167 | 109° 46′ |
| Complex[a,c] $r$, Å. | 1.094[b] | 1.94(0.16)<br>1.64(0.5) | 1.61(0.5) | 1.20(2.5) | 109° 46′[b] |

[a] From Pauling's rule (L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947)), with the constant 0.6. [b] Molecule parameters have simply been transferred, although arguments can be made regarding small changes from the molecule. [c] Corresponding bond order given in parentheses.

The anharmonicity coefficients for the degenerate CNC bends, particularly, are somewhat too large ($D$ is too small) for model 1 to represent an extreme minimum anharmonicity model. Model 2 is an overestimate, or maximum model. Table XIII illustrates the energy level density increase for these two models, relative to the harmonic case, at various energies. It is evident by comparisons within the table that a decrease in the anharmonicity correction for the (f) frequency group would probably lower the relative correction to ~ 15% at 13,000 - 14,000 cm.$^{-1}$.

TABLE VI

MOMENTS OF INERTIA (A.M.U., Å.$^2$) FOR $CH_3NC$ MOLECULE AND ACTIVATED COMPLEX

| | $I_A$ | $I_B$ | $I_C$ | $I_r$ |
|---|---|---|---|---|
| 600 model | 12.53 | 25.77 | 35.08 | 3.532 |
| 300 model | 11.59 | 31.65 | 40.01 | 4.021 |
| Molecule | 3.23 | 50.29 | 50.29 | |

For consistency, and not from any feeling of conviction, similar anharmonicity correction models were also entered for the activated complex. Most of these corrections are unchanged from the models for the molecule; although, for example, the correction used for the C–N half-bond corresponded instead to $D = 56$ kcal. The details are scarcely worthwhile, since the contribution of conventional anharmonicity corrections in the activated complex to the calculated results is negligible in any case. This is discussed and illustrated in the text. In fact, for several of the calculations, *e.g.*, fall-off, only the anharmonicity correction to the molecule was included as significant; although evident, nonetheless this was verified directly in several instances. In the same vein, anharmonic partition functions are only slightly increased over harmonic quantities. The following illustration is for $CH_3NC$ at 230.4°.

| | Harmonic | Model 1 | Model 2 |
|---|---|---|---|
| $Q_v$ | 4.336 | 4.394 | 4.417 |
| Increase rel. to harmon. % | . . . | 1.34 | 1.87 |

The $Q_v{}^+$ values increase a little more strongly as

### TABLE VII

### HARMONIC OSCILLATOR ENERGY LEVEL SUMS ($LOG_{10}$)

$CH_3NC$, $\epsilon_z$ = 27.23 kcal. mole$^{-1}$, 270(2), 1008(3), 1443(3), 2161(1), 2998(3)

| $E$ (units $\epsilon_z$) | 0.3 | 0.5 | 1.0 | 1.5 | 2.0 | 3.0 | 5.0 |
|---|---|---|---|---|---|---|---|
| Class. | −4.28420 | −1.62236 | 1.99000 | 4.10308 | 5.60236 | 7.71544 | 10.37764 |
| Semiclass. | 3.35740 | 4.10308 | 5.60236 | 6.76528 | 7.71544 | 9.21472 | 11.32780 |
| Exact | 2.48572 | 3.48344 | 5.26724 | 6.54188 | 7.55056 | 9.10578 | 11.25870 |
| $a$[a] | 0.808 | 0.842 | 0.889 | 0.913 | 0.928 | 0.947 | 0.965 |

$CD_3NC$, $\epsilon_z$ = 21.23 kcal. mole$^{-1}$, 260(2), 823(3), 1033(3), 2192(4)

| $E$ (units $\epsilon_z$) | 0.3 | 0.5 | 1.0 | 1.5 | 2.0 | 3.0 | 5.0 |
|---|---|---|---|---|---|---|---|
| Class. | −4.48710 | −1.82406 | 1.78830 | 3.90150 | 5.40066 | 7.51386 | 10.17594 |
| Semiclass. | 3.15546 | 3.90150 | 5.40066 | 6.56358 | 7.51386 | 9.01302 | 11.12610 |
| Exact. | 2.35411 | 3.32899 | 5.10874 | 6.38364 | 7.39099 | 8.94505 | 11.09631 |
| $a$[a] | 0.815 | 0.844 | 0.891 | 0.915 | 0.930 | 0.948 | 0.966 |

[a] Defined in ref. 20 as the value which makes $(E + a\epsilon_z)^s/\Gamma(s + 1)\pi^i h\nu_i$ equal to the exact sum of all possible vibrational states up to the energy $E$, where $s$ is the number of vibration modes and $\nu_i$ is their frequency. The present values are virtually identical with those given earlier for cyclopropane and cyclopropane-$d_6$ at the same energy (in units of $\epsilon_z$).

### TABLE VIII

### PRESSURE CORRECTION FACTORS FOR CALCULATED FALL-OFF[a]

| $T$, °C. | Harmonic 300 | Harmonic 600 | Anharm. (300) Model 1 | Anharm. (300) Model 2 | Anharm. (600) Model 2 |
|---|---|---|---|---|---|
| 199.4 | 0.91 | 1.68 | 1.17 | 1.41 | 2.57 |
| 230.4 | 1.11 | 1.99 | | 1.58 | |
| 259.8 | 0.95 | 1.78 | | | |

[a] Since calculated and experimental curves do not have precisely the same shape, it is necessary to specify some reference point. The listed pressure correction factors give coincidence of the two curves at $k/k_\infty = 0.1$.

### TABLE IX

### EQUIVALENT CLASSICAL SHAPE PARAMETERS[a]

| $T$, °C. | 199.4 | 230.4 | 259.8 | 500 | 600 | 2400 | 3600 | 6000 |
|---|---|---|---|---|---|---|---|---|
| Kassel $s$-values | | | | | | | | |
| Exp. | 3.0 | 3.1 | | | | | | |
| 300 Model | 2.1 | 2.2 | 2.3 | | | | | |
| 300 Model + fig. rot. | 2.5 | 2.6 | 2.7 | | | | | |
| 600 Model | 2.0 | 2.1 | 2.2 | | | | | |
| 600 Model + fig. rot. | 2.2 | 2.3 | 2.4 | | | | | |
| Anharm (300)1 | 2.1 | 2.2 | 2.3 | | | | | |
| Anharm (300)1 + fig. rot. | 2.5 | 2.6 | 2.6 | | | | | |
| Anharm (300)2 | 2.1 | 2.2 | 2.3 | | | | | |
| Anharm (600)1 + fig. rot. | 2.2 | 2.3 | 2.4 | | | | | |
| Slater $n$-values | | | | | | | | |
| 300 Model | 3.2 | 3.4 | 3.6 | 4.6 | 5.0 | 3.6 | 3.2 | 2.8 |

[a] Decimals bear qualitative significance only.

### TABLE X

### COMPARISON OF EXPERIMENTAL AND CALCULATED HIGH PRESSURE FREQUENCY FACTORS,[a] SEC.$^{-1}$

| | 199.4° | 230.4° | 259.8° |
|---|---|---|---|
| Exp.[e] | 2.42 × $10^{13}$ | 2.50 × $10^{13}$ | (2.57 × $10^{13}$)[c] |
| 300 model[b] | 2.47 | 2.55 | 2.62 |
| 600 model | 1.47 | 1.49 | 1.51 |
| Anharm. (300) 2[d] | 2.39 | 2.47 | 2.54 |
| | 2.53 | 2.62 | 2.69 |

[a] Calculated from the equation, $k = Ae^{-E_0/RT}$, in which $E_0$ is the critical energy and not the observed activation energy. [b] This model may easily be perturbed just a little so as to yield almost exact coincidence with the experimental values. [c] Calculated value obtained by allowance for the discrepancy noted in footnote $b$. [d] The first value refers to inclusion of anharmonicity only in the molecule, while the second value includes comparable anharmonicity in the activated complex. [e] The consistency tests (Table XI, footnote $a$) indicate that the experimental values are systematically low by 0.5–1.5%.

### TABLE XI

### COMPARISON OF LOW PRESSURE EXPERIMENTAL (EXTRAPOLATED) AND CALCULATED RATES

$k_{\text{bi}}$, cc. mole$^{-1}$ sec.$^{-1}$

| | 199.4° | 230.4° | 259.8° |
|---|---|---|---|
| Exp. extrap.[a] | (180) | (2.0) × $10^3$ | (10) × $10^3$ |
| 300 model | 101 | 1.18 | 9.20 |
| 300 model + fig. rot. | 225 | 2.58 | 19.6 |
| Anharm (300)1 | 128 | 1.49 | 11.7 |
| Anharm (300)1 + fig. rot. | 269 | 3.09 | 23.5 |
| Anharm (300)2 | 147 | 1.73 | 13.5 |
| 600 model | 71.5 | 0.856 | 6.85 |
| 600 model + fig. rot. | 179 | 2.09 | 16.1 |
| Anharm (600)2 | 105 | 1.26 | 10.1 |
| Anharm (600)1 + fig. rot. | 215 | 2.51 | 19.4 |

[a] Obtained by extrapolation of an arbitrary calculated curve which gave best fit over the experimental pressure range, and which corresponds to s ≃ 3.0. The values were examined with the aid of the Johnston consistency tests (H. S. Johnston and J. R. White, *J. Chem. Phys.*, **22**, 1969 (1954)). The required inequalities are well obeyed, but $J$ values pass through a minimum with decrease of pressure from ∞ to 0. These tests are very sensitive at the extremes, and show some incompatibility of the high and low pressure regions of the fall-off (see Conclusions).

### TABLE XII

### ANHARMONICITY CONSTANTS FOR $CH_3NC$ MOLECULE

| | Vibration type | Frequency, cm.$^{-1}$ | Model 1 Constant, cm.$^{-1}$ | Model 1 $D$, kcal. mole$^{-1}$ | Model 2 Constant, cm.$^{-1}$ | Model 2 $D$, kcal. mole$^{-1}$ |
|---|---|---|---|---|---|---|
| (a) | C—H str. | 2998(3) | −72 | 90 | −72 | 90 |
| (b) | N≡C str. | 2161 | −17 | 195 | −17 | 195 |
| (c) | C—N str. | 945 | − 6.7 | 95 | − 6.7 | 95 |
| (d) | $CH_3$ def. | 1443(3) | − 3 | 500 | −16 | 93 |
| (e) | $CH_3$ rock. | 1041(2) | − 3 | 260 | − 9 | 86 |
| (f) | C—N≡C bend. | 270(2) | − 0.5 | 105 | − 0.6 | 87 |

### TABLE XIII

### PERCENTAGE INCREASE OF ANHARMONIC ENERGY LEVEL DENSITY RELATIVE TO HARMONIC VALUE

| Total energy, cm.$^{-1}$ | Increase, % Model 1 | Increase, % Model 2 |
|---|---|---|
| 6000 | 10 | 18 |
| 13000 | 20 | 36 |
| 14000 | 21 | 39 |
| 15000 | 23 | 43 |
| 16500 | 26 | 50 |
| 18000 | | 55 |

may be seen from the anharmonic $k_\infty$ values (Table X).

Consideration of cross-terms in the potential energy function, and of rotational interactions, would increase the anharmonicity correction relative to the above considerations. Despite this fact, however, and the complementary one that much of the assumptions entering bending mode calculations merely represents crystallized ignorance, we believe that the estimates provided by Table XIII must fall in the region of physical significance.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

# Electron Attachment and Solvation in Gamma Irradiated Organic Glasses at −196°[1]

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Gamma irradiation at −196° of organic glasses containing small amounts of solutes whose anion absorption spectra are known results in the formation of optically identifiable anions by electron attachment. Using a tetrahydro-2-methylfuran glass the limiting value for $G$(anions) was 2.6 for naphthalene and 3.2 for biphenyl. With a hydrocarbon glass, the limiting yields were 1.1 and 1.7, respectively. For biphenyl in ethanol, $G$(anion) = 2.94. In all media, $G$(anion) = 1 for about 0.05 mole % additive. Anions of nitrobenzene, benzophenone and tetracyanoethylene have also been prepared by both methods and identified while spectra of styrene and carbon tetrachloride molecular anions, which cannot be prepared chemically, appear to form in gamma irradiated glasses. Irradiation of glassed tetrahydro-2-methylfuran alone produces a structureless absorption band in the visible and near infrared. With less than 0.5 mole % of naphthalene, the solute anion and solvent spectra both appear. The solvent spectrum can be selectively bleached, with a concomitant increase in the solute anion absorption bands. These facts indicate that the solvent absorption is due to solvated electrons. Similarly one observes solvated electrons in gamma irradiated ethanol but not in glassed alkanes or alkenes.

## Introduction

The technique of isolating and stabilizing free radicals or other reactive entities for observation in rigid matrices at low temperature, although very useful in photochemistry, has received limited use in radiation chemistry.[2-4] The method has not been successful hitherto for the identification of ionic species produced by high energy radiation, to our knowledge. It occurred to us that electron attachment by solutes in gamma irradiated organic glasses at −196° offered attractive possibilities since many organic compounds are readily reduced by alkali metals to produce anions of intense and distinctive optical absorption in convenient spectral regions, examples being naphthalene,[5] benzophenone,[6] etc. Comparison of the optical absorption spectra of chemically prepared and gamma-irradiated samples provides a basis for identification and, within limits, of quantitative measurement.[7] Extensive measurements of e.s.r. spectra of such anions have been reported, although we are not now directly concerned with this technique.[8] Other solutes, for which anionic spectra are unknown, can also be tested for electron attachment in turn by employing them competitively with naphthalene or biphenyl as a reference reagent.

Such methods have proven feasible and have considerable interest in their own right. We plan to extend them further to investigate the role of ionic processes in radiation chemistry. For example, there is no *direct* evidence that electrons in gamma irradiated condensed phase chemical systems are involved in chemical changes, although such effects have been postulated on the basis of indirect evidence.[9] It has been assumed by most investigators, at least implicitly, that charge recombination occurs so quickly that other ionic processes can be ignored. We find the argument from chronology misleading and hope to demonstrate that other processes can intervene and that the chemistry of ions is relevant to radiation chemistry. Aqueous systems provide a notable exception since there is now good evidence for a relatively long-lived negative entity.[10] We also except from these generalizations the work on "ionic" polymerization, although the whereabouts of the electron or gegenion is altogether hypothetical, particularly in hydrocarbons,[11] and neither anion nor cation can be identified by e.s.r. spectra.[12]

## Experimental

**Solvents.**—In general, solvents were chosen for their ability to form clear glasses, transparent from the near ultraviolet to the near infrared regions. Tetrahydro-2-methylfuran was chosen both for its ability to glass and also because chemical reductions of aromatic compounds could also be carried out in this solvent at room temperature. The drying and purification of tetrahydro-2-methylfuran was carried out by several vacuum distillations from clean sodium mirrors and finally the solvent was distilled into a storage bulb containing sodium-potassium alloy. This procedure removed water and prevented formation of peroxides. Phillips pure grade 3-methylpentane, methylcyclohexane and isopentane were stored in air over sodium. Phillips pure grade 2-methylpentene-1 was treated in the same way as tetrahydro-2-methylfuran to prevent peroxida-

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