

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE 5, WASH.]

The Unimolecular Isomerization of Methyl- d_3 Isocyanide. Statistical-Weight Inverse Secondary Intermolecular Kinetic Isotope Effects in Nonequilibrium Thermal Systems¹

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

RECEIVED MARCH 27, 1963

The thermal isomerization of CD_3NC has been studied at 230.4° over a range of pressures from 10^{-2} to 10^4 mm. The fall-off corresponds to an enhanced value of the effective number of oscillators relative to CH_3NC . The difference in observed activation energy for the two species is very small (~ 0). The data were treated on an RRKM quantum statistical model. Calculations were made for various combinations of detailed assumptions in which vibrations were treated both on a harmonic basis and also with varying assumed degrees of anharmonicity and in which a figure axis rotation was treated both as active and as adiabatic. Various aspects of the calculations are in satisfactory agreement with experiment. The inverse intermolecular secondary isotope effect predicted earlier³ has now been found for the first time; k_H/k_D declines from 1.07 at $p = \infty$ to 0.28 at 10^{-2} mm.

Introduction

In a previous paper (herein called part I) a study of the isomerization of methyl isocyanide was described.² That work established the isocyanide-nitrile isomerization system as an important type of thermal unimolecular reaction. The desirability of attempting a thorough documentation of this thermal system was pointed out. One aspect of such a comprehensive program is the study of deuteriomethyl isocyanides. A number of interesting consequences follow from the change in frequency pattern of the molecule on substitution of H by D. Rabinovitch, Setser, and Schneider³ (RSS) described some effects of frequency lowerings and of differential quantal effects on nonequilibrium fall-off behavior and on other characteristics of thermal systems. These matters were amplified further in part I and elsewhere.⁴

A specific aspect of interest, which it was desired to investigate by deuterium substitution in methyl isocyanide, was a very large *inverse* intermolecular secondary kinetic isotope effect, of statistical nature, which RSS predicted is to be found for many thermal unimolecular reactions in the nonequilibrium region. This effect should be maximal in the limiting low pressure region. Its description as *statistical* is due to the fact that, unlike conventional secondary isotope effects in equilibrium systems whose origin is primarily mechanistic,⁵ the magnitude of the present effect should increase with increasing degree of isotopic substitution at positions remote from the reaction site.

Experimental data for test of such an effect were not available at the time. Blades⁶ had reported a decrease with pressure of the isotopic rate ratio for light cyclopropane, relative to cyclopropane- d_6 , from 1.96 at 10^2 cm. to 1.30 at 10^{-2} cm. (482°). However, at the lower pressure, the ratio of k/k_∞ for cyclopropane had only declined to ~ 0.2 , and for inversion to take place in the cyclopropane system, where an opposing primary isotope effect occurs, still lower pressures would be required,³ aided preferably by T substitution instead of D. Some earlier fall-off data by Weston⁷ for cyclopropane- t_1 , apart from intrinsically involving only a small effect because of monosubstitution, was not considered of usable accuracy for test of theory. More accurate data from this Laboratory⁸ for light cyclopropane and cyclo-

propane- d_2 in the fall-off region, down to $k/k_\infty = 0.08$, reveal only a very small possible effect; however, these data, as was pointed out at the time, are also inadequate for very accurate isotopic rate comparisons, and this isotopic pair suffers from the further disadvantage of displaying only a disubstitution effect. A study of the cyclobutane-cyclobutane- d_8 system⁹ revealed a decrease of k_H/k_D from 1.37 to 1.19 as pressure dropped from 50 mm. ($\approx p_\infty$) to 1.2 mm., but k/k_∞ for the light compound is still quite high, ~ 0.7 , even at the lowest pressure.

By contrast, the isomerization of methyl isocyanide had been extended down to $k/k_\infty = 0.0016$. Study of deuteriomethyl isocyanides offered availability of both the high pressure equilibrium region, where the isotopic rate ratio should be close to unity, and a lower pressure portion well into the nonequilibrium region. Although trisubstitution is the maximum that can be attained in methyl isocyanide, and use of longer chain isocyanides is being pursued, there should be no opposing primary effect to be overcome here, and inversion of rates was calculated to be readily attainable.

The present paper reports the temperature and pressure dependence of the CH_3NC - CD_3NC kinetic isotope effect and verifies the existence of the predicted inverse effect.

Experimental

Materials.—Methyl- d_3 isocyanide was prepared in the manner described in I, by use of CD_3I and $AgCN$. Its chemical purity was $> 99.9\%$; its isotopic purity was 97% and it contained 3% of CD_2HNC and CDH_2NC . The CD_3I was obtained from Merck Sharp and Dohme of Canada.

Apparatus and Procedure.—The apparatus used and the experimental procedure were in part similar to the earlier work. Different reactors were used in various overlapping pressure regions, with no evident systematic disparity in the overlap. In the first experiments (group 1) separate CD_3NC runs were made over a pressure range. This *external* comparison method was later complemented by *internal* comparison studies for greater accuracy. In the earlier internal comparison runs (group 2), approximately 50–50 reactant isotopic mixtures were used. The products were separated from the reactant by g.l.p.c. on a tetraglyme column. The amounts of CH_3CN and CD_3CN were determined with a Consolidated 21–103 mass spectrometer, by use of the parent ion peaks (masses 41 and 44, respectively) at low electron energies (10 e.v.). Calibrations were made with standard CH_3CN - CD_3CN mixtures. In later work (group 3), the mixture proportions of isotopic reactants were varied to give maximum analytical accuracy. The reaction mixture was passed through a short column of $AgCN$ which quantitatively removed unreacted isocyanide and the residual nitrile products were analyzed on the mass spectrometer with use of parent peak intensity at 70-e.v. electron energies. Analysis of nitrile mixtures of known composition, before and after passage through the $AgCN$ column, indicated no change in composition. They showed a 1:1 sensitivity of parent peaks which obviated the need of a calibration curve at the high electron energies.

Another method of isotopic analysis was developed also, analogous to the method of Falconer and Cvetanović for alkanes.¹⁰ The products CH_3CN and CD_3CN were very adequately resolved

(1) Presented at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962. This work was supported by the National Science Foundation.

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

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

(4) (a) B. S. Rabinovitch and J. H. Current, *ibid.*, **40**, 557 (1962); (b) J. H. Current and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 1967 (1963).

(5) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961).

(6) A. T. Blades, *Can. J. Chem.*, **39**, 1401 (1961).

(7) R. E. Weston, *J. Chem. Phys.*, **26**, 975 (1957).

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

(9) J. Langrish and H. O. Pritchard, *J. Phys. Chem.*, **62**, 761 (1958).

(10) W. E. Falconer and R. J. Cvetanović, *Anal. Chem.*, **34**, 1064 (1962).

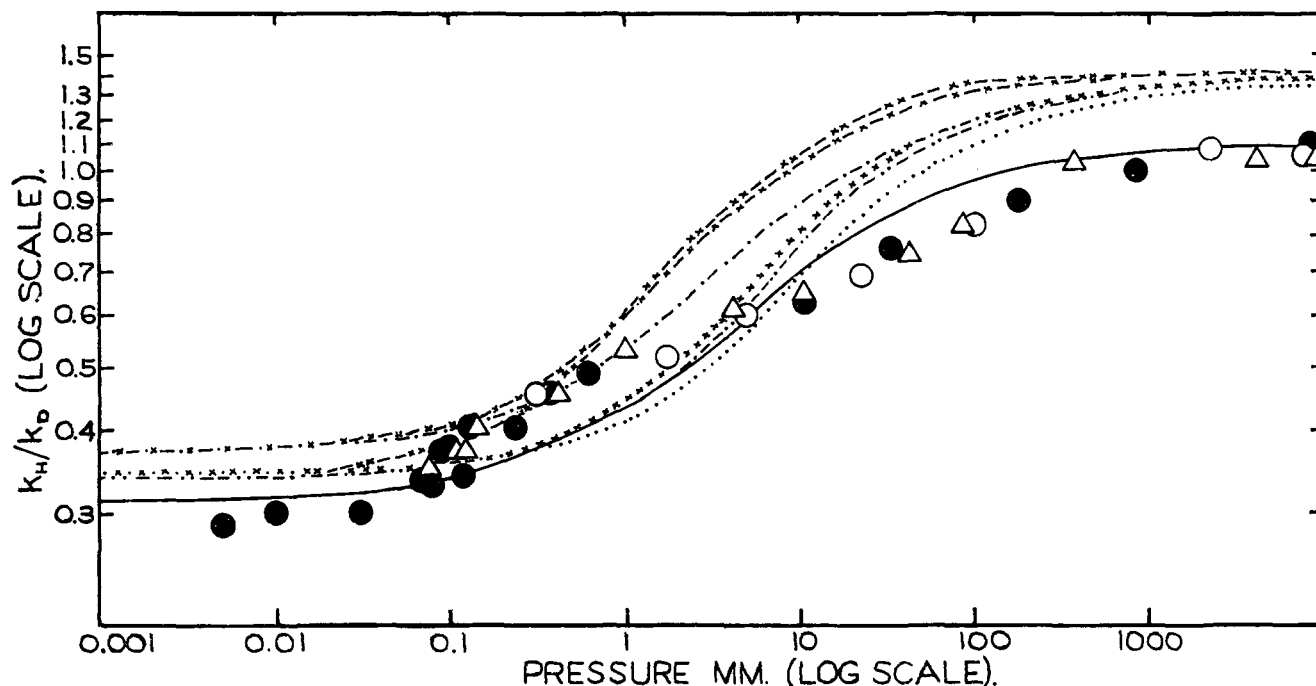


Fig. 1.—Plot of k_H/k_D vs. pressure. Experimental: group 1, Δ ; group 2, \circ ; group 3, \bullet . Calculated: 300,; 300 + fig. rot., - - - -; 300 + fig. rot. ($\Delta E_a = -0.1$ kcal.), ———; Anharm (300)2, - · - · -; 600, $\times \times \times \times$; 600 + fig. rot., $\times \cdot \times \cdot$; Anharm (600)1, $\times \times \cdot \cdot$.

on a 150-ft. unpacked copper tube column (i.d. 0.065 in.) coated with tetraglyme. The reproducibility of analysis, however, was not considered adequate for the desired purposes and the method was eventually discarded.

Results

Corrections to the Data.—The same experimental corrections as were listed in part I were applied to the present data. Allowance was made in the analytical calculations for the presence of the small percentage of d_2 -isomer, the principal impurity in the sample.

Isotopic Rate Ratio.—The relative rates of isomerization of CH_3NC and CD_3NC at 230.4° are summarized in Fig. 1. The group 1 data are the ostensibly less accurate external comparison, by independent measurements, of the light and heavy species. They are in

good agreement with the results of groups 2 and 3, which are the separate sets of data determined by internal comparison. The third group is believed to be the most accurate, but the harmony of all the determinations have led us to give them equal weight. The rate data are given in Table I. The group 1 CD_3NC data were compared with the smoothed values for CH_3NC of paper I; since the latter are quite numerous, the smoothing is reasonably unequivocal and is not a significant variable.

The limiting extrapolated high pressure ratio (k_H/k_D) $_{\infty}$ is 1.07. The corresponding limiting low pressure ratio (k_H/k_D) $_0$ is taken as 0.28. The data extend over a range in excess of ten decades of pressure, from 5×10^{-3} mm. to 9550 (8900 when corrected for association) mm. The values at the two lowest pressures were determined at 246.6° and 260.1° , respectively, because of the onerously slow rates of reaction at these pressures at lower temperatures. This procedure appeared acceptable in the present system because the temperature coefficient of the rate ratio, described in the next section, is very small. Correction of the ratio to the standard temperature engenders only small probable error: A 100% error in ΔE_a would cause an error of 0.6% at the lowest pressure and 0.3% at the next higher pressure; even a 500% error in ΔE_a would occasion errors of only 3% and 1.5% in the temperature-corrected ratios.

Temperature Dependence of Rate Ratio.—Measurements of the ratio (k_H/k_D) were made over a range of temperatures from 180° to 250° at 10 atm. pressure. This is virtually the high pressure limit and will be considered as such. Several groups of measurements were made at different times during the course of the work. The observed ΔE_a values fluctuated somewhat, both as between and within the group 2 and 3 runs (Fig. 2). The latter are more consistent. The value of $\Delta E_{a\infty}$ from group 3 is 147 ± 36 cal. mole $^{-1}$, where the uncertainty is the formal standard deviation of the slope; the rate ratio from this group is $k_H/k_D = (0.91 e^{(147 \pm 36)/RT})$. The ratio from the group 2 set is $k_H/k_D = 1.01 e^{(48 \pm 190)/RT}$. A set of six group 3 runs over the range 180 – 250° , which were also analyzed in the group 2 manner, gave $k_H/k_D = 0.92 e^{(97 \pm 40)/RT}$. A value of

TABLE I
PRESSURE DEPENDENCE AND RELATIVE ISOTOPIC MAGNITUDES OF EXPERIMENTAL ISOMERIZATION RATE CONSTANTS FOR CD_3NC (230.4°)

p , mm.	$k_D \times 10^5$, sec. $^{-1}$	$k_D/k_{D\infty}$	k_H/k_D	p , mm.	$k_D/k_{D\infty}$	k_H/k_D
Group 1				Group 3		
0.074	1.12	0.0129	0.348	0.0050	0.286 ^c	
.089 ^e	1.26	.0146	.371	.0100	0.00220	0.300 ^d
.103	1.43	.0165	.374	.0305	.00659	.300
.122 ^e	1.68	.0194	.372	.070	.0126	.339
.138	1.73	.0200	.402	.077	.0142	.330
.411	3.97	.0459	.456	.085	.0138	.372
.996	7.02	.0812	.531	.117	.0203	.342
4.18	17.6	.204	.614	.124	.0182	.404
10.3	29.7	.343	.646	.225	.0307	.407
41.1	52.2	.604	.747	.360	.0350	.454
86.7	65.0	.752	.831	.600	.0501	.493
372	75.0	.867	1.027	10.5	.354	.637
4154(4280) ^a	88.0(92.9) ^b	1.018	1.034	32.5	.535	.757
8900(9550) ^a	87.7(93.7) ^b	1.015	1.049	173	.867	.90
Group 2				834	.983	1.00
0.30		0.0413	0.451	8000(8500) ^a	.998	1.06
1.73		.127	.517			
5.0		.233	.60			
22.4		.491	.69			
96.5		.784	.828			
2200		.964	1.08			
7100(7600) ^a		1.00	1.051			

^a Pressures in parentheses are uncorrected for association (see part I). ^b Rate constants in parentheses are uncorrected for self-heating (see part I). ^c Corrected from 260.1° to 230.4° . ^d Corrected from 246.6° to 230.4° . ^e Packed vessel run, 10:1 surface/volume ratio.

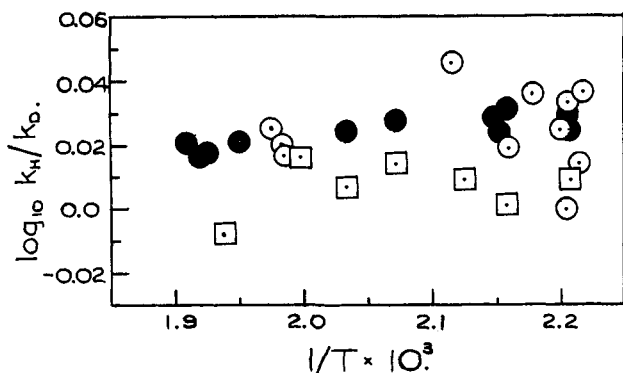


Fig. 2.—Arrhenius plots for CD_3NC : group 2, \circ ; group 3, \bullet ; combined technique, \square .

$\Delta E_{a\infty} = 0.1$ kcal. has been taken as the experimental value. Somewhat better agreement of observed and theoretical models described in the Discussion (*cf.* Fig. 1) would be found for a value of ΔE of opposite sign, *i.e.*, $\Delta E_{a\infty} = -0.1$ or -0.2 . We do not rule out these values. The results exhibit such large relative fluctuations because the total variation of the rate ratio over the whole temperature range is only a few per cent, while the standard deviation of an individual measurement is much larger than this magnitude.

A few measurements of the temperature dependence were made in the low pressure region around 0.01–0.03 mm. These measurements were not pursued because the rates were very slow, which made practicable only a limited range of temperatures from 230–260° with existing technique, and because of larger cumulative experimental errors at the lower pressures. Four measurements at 0.03 mm. over this temperature range gave a maximum fluctuation in k_H/k_D of 1.5%. This means that ΔE_{a0} is some small quantity, ~ 0 , whose precise magnitude is not given by our data.

CD_3NC Fall-off Behavior.—Of the three groups of runs, only group 1 gave independent values of $k_D/k_{D\infty}$ as a function of pressure. The CD_3NC fall-off was calculated for groups 2 and 3 with use of the smoothed CH_3NC curve as the standard. A value of k_D cannot be found at $p = 0.005$ mm. (group 3) because a very long extrapolation of the CH_3NC fall-off curve would be required.

From part I the value of $k_{H\infty} = 92.5 \times 10^{-5}$ sec. $^{-1}$. The value of $k_{D\infty}$ from the data of groups 2 and 3 is 86.5×10^{-5} sec. $^{-1}$. The corresponding group 1 value is 88.0×10^{-5} sec. $^{-1}$. By reason of some systematic error in the fall-off for CH_3NC , which we noted on the basis of consistency tests (see part I, footnotes to Tables X and XI), $k_{H\infty}$ is probably higher by $\sim 1\%$ than the value given. This largely reconciles the difference between $k_{D\infty}$ obtained from group 1 and $k_{D\infty}$ obtained from groups 2 and 3, if we were naively to regard the data literally. The relative values from the latter two groups are more reliable, and therefore the value $k_{D\infty} = 86.5 \times 10^{-5}$ sec. $^{-1}$ has been used here, since it would be premature to attempt formal correction of the CH_3NC values at the present stage of experimental progress.

The experimental fall-off curve (Fig. 3) corresponds formally to a curvature and shape characterized by a Slater¹¹ n -value of 6.1, and a classical Kassel¹² s -parameter of 3.9. Footnote 13 should be consulted for an *erratum* relating to s -values described in part I and for comment on the precision of the values of s and n .

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

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

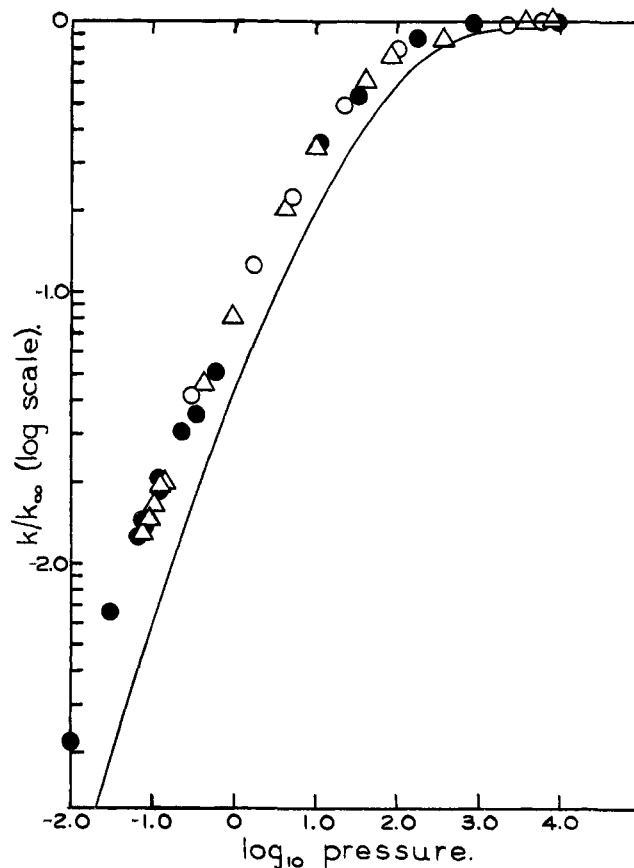


Fig. 3.—Experimental fall-off for CD_3NC : group 1, Δ ; group 2, \circ ; group 3, \bullet . The solid curve summarizes the earlier CH_3NC experimental data.

Discussion

Quantum Statistical Effects. Low and High Pressure Limits.—As was noted by Waldmann¹⁴ and quantitatively discussed by Bigeleisen and Goepfert-Mayer,¹⁵ classical statistics cannot describe important aspects of kinetic isotope effects. Some interesting behavior of unimolecular reactions is also overlooked by discussions in terms of classical formulations; even in the correct quantum statistical treatment, the most interesting features are only fully developed in the limiting nonequilibrium low pressure region.^{1,2}

Low Pressures.—The prediction by RSS that relatively large low-pressure intermolecular secondary isotope effects should occur in hydrogen-deuterium or

(13) It was called to our attention by Dr. D. F. Swinehart, whom we thank, that the s -values given in part I, Table 9, are somewhat in error. As may be seen from that table, the s -values were obtained from n -values by simply applying the "ideal" relation¹¹ $s = (n + 1)/2$, stated to be valid below $s \sim 4$ by E. W. Schlag, B. S. Rabinovitch, and F. W. Schneider, ref. 10, part I. This statement now appears not quite correct; moreover, the comparison of ref. 10 was restricted to a range of fall-off above that being considered in this paper, so that the ideal relation proves valid only below $s \sim 2$ here, instead. The resulting changes may be exemplified in a few cases:

Expt: For $s = 3.1$ read $s = 3.6$ as a more correct estimate

300 model: for $s = 2.2$ read $s = 2.4$ as the new estimate

Other values change correspondingly.

We emphasize that comparison of the shapes of s and n fall-off curves between themselves is imprecise because of the different curvatures of such plots in different pressure regions. A similar remark applies to comparison of the RRKM fall-off plots with $I_n(\theta)$ plots, so that the n -values given are possibly accurate only to ± 1 , although the error may well be less. In this connection, for example, the value of n in Table 9 is implicitly given as $n = 5.2$ for the experimental results at 230°; our present re-estimate is closer to $n = 5.5$.

The present calculations have, of course, been done on a quantum statistical basis. The citation of "equivalent" classical s fall-off shape values is given to make a connection with this familiar parameter. The citation of n -values is given for the same reason, and because n provides a useful unique definition of fall-off curvature.

(14) L. Waldmann, *Naturwiss.*, **31**, 205 (1943).

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

other isotopic unimolecular systems was based on the form of quantum statistical rate ratio

$$\left(\frac{k_H}{k_D}\right)_0 = \frac{\frac{(M_D)^{1/2}}{Q_H} \int_{E_0}^{\infty} K(E)_H dE}{\frac{(M_H)^{1/2}}{Q_D} \int_{E_0}^{\infty} K(E)_D dE} = \frac{(M_D)^{1/2} \cdot Q_D \cdot \int_{E_{0H}}^{\infty} N(E)_H e^{-E/RT} dE}{(M_H)^{1/2} \cdot Q_H \cdot \int_{E_{0D}}^{\infty} N(E)_D e^{-E/RT} dE} \quad (1)$$

Here the M terms are a residue from a ratio of collision numbers and represent the total mass of the molecules; any collisional inefficiency factor ratio must be very close to unity; the $K(E)$ are Boltzmann-type distribution functions for active degrees of freedom, explicitly normalized by the partition function quantities Q . For a "pure" secondary isotope effect, $E_{0H} = E_{0D} = E_0$. The enhancement of the rate constant k_D relative to k_H is based on the large difference in the quantum statistical densities of active energy states, $N(E)$, for the two molecules at energy levels $E \geq E_0$, as contrasted with the lesser opposing ratio of the normalizing partition function quantities Q . The latter ratio, which is vibrational in nature, apart possibly from a few internal and over-all rotational degrees of freedom, is frequently not much larger than unity: the magnitude of each quantity of the ratio is dependent on the contributions from the energy levels near zero because of the operation of the exponential factor in every term of the sum of states; for vibrational degrees of freedom under conditions where only the ground state level makes a significant contribution to each partition function, *i.e.*, for all $h\nu_i \gg kT$, this ratio is unity. By contrast, the limit of $N(E)_H/N(E)_D$ for vibrational degrees of free-

dom, as $E \rightarrow \infty$, is the large ratio $\prod_i (\nu_{iH}/\nu_{iD})$. Complication of these expressions due to active rotational degrees of freedom has been described elsewhere.^{4b} Thus for the limiting case of E_0 very large, but T (the reaction temperature) very small, one has

$$(k_H/k_D)_0 \rightarrow \left(\frac{M_D}{M_H}\right)^{1/2} \prod_i (\nu_{iH}/\nu_{iD}) \quad (2)$$

This limit would involve considerable patience on the part of the experimentalist for its realization, but large statistical-weight inverse effects may still be observed in practical systems.

By contrast, classical statistics¹² give a ratio which is very close to unity

$$\left(\frac{k_H}{k_D}\right)_0 = \frac{(M_D)^{1/2} \int_{E_0}^{\infty} (E)^{s-1} e^{-E/RT} dE}{(M_H)^{1/2} \int_{E_0}^{\infty} (E)^{s-1} e^{-E/RT} dE} = \left(\frac{M_D}{M_H}\right)^{1/2} \approx 1 \quad (3)$$

where E is the total energy and s is the number of vibrational modes.

High Pressures.—At the low pressure limit the effective reaction coordinate is collisional activation. At the high pressure limit, the rearrangement of an activated complex is the reaction coordinate and the customary Eyring equilibrium expression applies. So for the secondary isotope ratio

$$(k_H/k_D)_\infty = I_{rH} Q_H^+ Q_D / I_{rD} Q_H Q_D^+ \quad (4)$$

where each I_r is itself the ratio of rotational partition functions (moments of inertia) of the activated complex and the molecule, and the Q^+ terms represent the partition functions for the active degrees of freedom of activated complexes. Since I_r and the (Q^+/Q) ratio of ratios are both close to unity in this case, only small isotope effects occur for this equilibrium situation even in the quantum statistical formulation.

The quantum statistical partition functions in eq. 4 are readily evaluated in analytical form, as opposed to the difficult problem of evaluation of the incomplete integrals of the type in eq. 1. Hence classical statistics have not had as wide use for the $p = \infty$ limit as they have had for the low pressure limit and fall-off region, for which accurate quantum statistical evaluations have only been described comparatively recently.^{16, 17}

Whether the isotope effect at high pressures is normal or inverted will depend principally on whether there is bond tightening or bond loosening in the activated complex relative to the molecule.

Fall-off Region.—In the intermediate fall-off region the quantum statistical formulation of Marcus and Rice¹⁵ (RRKM theory) is used

$$\frac{k_H}{k_D} = \frac{I_{rH} Q_D}{I_{rD} Q_H} \cdot \frac{\int_{E^+}^{\infty} \frac{\Sigma P(E_v^-)_H e^{-E^-/kt} dE^+}{1 + \frac{I_{rH}}{\omega h} \cdot \frac{\Sigma P(E_v^+)_H}{N(E_0 + E^+)_H}}}{\text{Den}}$$

where the summations Σ are over the range $E_v^+ \leq E^+$, and where the denominator term, Den, is another integral identical with that in the numerator but with subscript D replacing H. $\Sigma P(E_v^+)$ is the sum over the degeneracy of active energy levels of the activated complex at all internal energies up to E^+ . ω is the collision frequency. When all 3 over-all rotations are taken as *adiabatic*, the inertial ratio is

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

the σ being symmetry numbers. For an *active* figure axis rotation, I_r is a product of only two ratio terms.

The effect of free or hindered internal rotation (which we rule out for methyl isocyanide) would not alter the I_r expression. In the case of an active figure axis rotation in the activated complex this sum includes the contribution from the rotational energy levels E_J where the degeneracy is $d = 1$ for $J = 0$ and $d = 2$ for all other J . Finally $N(E_0 + E^+)$ is the energy level density at energy $(E_0 + E^+)$ of the molecule, which for an active over-all rotation also includes the contribution of a one-dimensional quantized rotor.

Calculated Fall-off Behavior for CD₃NC.—The fall-off for CD₃NC was calculated for various models, characterized and described in detail in part I. Various combinations of the activated complex twist frequency together with anharmonicity and active rotation assumptions have been used—sufficient to illustrate the effects involved and to permit deduction of others, whose explicit calculation seemed not worthwhile. The molecular constants, frequencies, and anharmonicity constants used, are given in App. I. Equivalent classical shape parameters are presented in Table II. The experimental shape is best approximated by the "300 + fig. rot." and "Anharm (300) + fig. rot." models (Table II). Agreement between experimental and theoretical shape factors is better in general for CD₃NC than it was for CH₃NC; it would overestimate the accuracy of the data considerably to regard this as due to anything other than experimental error (quite possibly in the light species).

In the same way as was done earlier for CH₃NC, the theoretical and experimental curves were superimposed at the arbitrarily chosen value of $k/k_\infty = 0.1$. The pressure correction factors which must be applied to calculated curves to bring about coincidence with experi-

(16) B. S. Rabinovitch and J. H. Current, *J. Chem. Phys.*, **35**, 2256 (1961).

(17) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962);

R. E. Harrington, B. S. Rabinovitch, and R. W. Diesen, *J. Chem. Phys.*, **32**, 1245 (1960).

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

TABLE II
EQUIVALENT CLASSICAL FALL-OFF SHAPE PARAMETERS *s* AND *n*
FOR CD₃NC (230.4°)

	<i>s</i>	<i>n</i>
Expt.	3.9	6.1
300	2.9	4.2
300 + fig. rot.	3.5	5.7
Anharm (300)2	2.8	4.1
600	2.7	3.9
600 + fig. rot.	3.5	5.6
Anharm (600)1 + fig. rot.	3.4	5.3

TABLE III
PRESSURE CORRECTION FACTORS FOR CALCULATED
CD₃NC FALL-OFF (230.4°)

Model	300 +		600 +		Anharm (600)1 + fig. rot.
	300	fig. rot. (300)2	600	fig. rot.	
Factor(0.1)	1.52	3.03	2.23	5.64	7.70
Factor(0.01)	0.80	1.75	1.19	3.29	4.31

ments at $k/k_{\infty} = 0.1$ are given in Table III. These factors are reduced to almost half their value, if the comparison point is taken at $k/k_{\infty} = 0.01$, instead. This variation occurs because experimental and theoretical shapes are not identical. For the value of 4.5 Å. for the molecular diameter,² the "300 harmonic" and "300 anharmonic" models give the best absolute pressure fits. The agreement is satisfactory.

The study of isotopically substituted methyl isocyanides is related to an aspect of the Slater theory.¹¹ This theory is usually identified with the postulate of effective orthogonality of the normal mode motions of molecules. The fall-off parameter *n* describes the number of vibration modes which interact effectively with the molecular reaction coordinate. Without performing a Slater-type analysis in this connection, it follows, since perdeuteration maintains the C_{3v} molecular symmetry, that the CD₃NC molecule should be characterized by the same value of *n* as the light molecule. However, consideration of the differential quantal effects leads to the prediction of an increase in *n* for CD₃NC. A related prediction of the Slater theory in the case of dideuteration of cyclopropane has previously been shown not to be supported by experiment.⁸ The present work provides a specific test of these matters, although not a strong one. The experimental value of *n* does increase from 5.5 for CH₃NC (old estimate, 5.2 in I) to 6.1 for CD₃NC. However, neither the experimental nor theoretical increase for this system is large enough to provide a good test, in view of the experimental error.

Isotopic Rate Ratio.—In Fig. 1, various theoretical evaluations of k_H/k_D are compared with the observed behavior. The broad agreement is good; the detailed agreement seems not as good. In general, $(k_H/k_D)_{\infty}$ and $(k_H/k_D)_0$ are too high for all models. However, recalculation of the 300 model with the slightly altered value of $\Delta E = -0.1$ kcal. mole, instead of the nominal value of 0.1 kcal., reduces these ratios in this model from 1.35 and 0.35 to 1.08 and 0.29, respectively, in excellent agreement with the observations. The active figure rotation models also give fairly satisfactory over-all fit, as well as concordance for the high and low pressure limiting ratios, if ΔE is taken as -0.1 kcal. (the effect of this change is to lower all calculated curves by an almost constant factor of 1.22 and improve all fits). Close inspection of the shape of the experimental fall of k_H/k_D with pressure almost reveals an apparent double inflection that we believe is nothing more than experimental error and which belies reliance upon details of the exact experimental shape. In the preceding sections, evidence for existence of some systematic error has been noted. Clearly, the general agreement with the theoretical cal-

culations is as good as the data warrant. Some defects of the theoretical calculations, themselves, have been noted previously in I.

The research thus bears out the occurrence of a large statistical inverse isotope effect which is in accord with theory in regard to both magnitude and pressure dependence. The study of higher deuterated isocyanides now being undertaken may lead to improvements in relative experimental accuracy.

Acknowledgment.—The authors thank Mr. Peter Gilderson for his helpful assistance with the experimental work.

Appendix I

The mechanism of the isomerization and the structure parameters of the molecule and activated complex were presented in part I. The relevant moments of inertia are given in Table IV.

TABLE IV
MOMENTS OF INERTIA (A.M.U. Å.²) FOR THE CD₃NC AND
ACTIVATED COMPLEX

	<i>I</i> _A	<i>I</i> _B	<i>I</i> _C
600 model	15.76	32.07	41.38
300 model	14.86	38.65	47.06
Molecule	6.45	58.91	58.91

TABLE V
VIBRATION FREQUENCIES FOR THE CD₃NC MOLECULE AND
ACTIVATED COMPLEX

	Molecule		Activated complex	
			"300"	"600"
C—D str	2251	2235(4)	2259(3)	2259(3)
	2263(2)			
N=C str	2165		ring def 1990	1990
CD ₃ def	1117	1077(3)	1077(3)	1077(3)
	1058(2)			
CD ₃ rock	900(2)	892(3)	900(2)	900(2)
	900(2)			
C—N str	877		ring def 562	562
CNC bend	249(2)	249(2)	twist 249	540
				550(2)

TABLE VI
ANHARMONICITY CONSTANTS^a FOR THE CD₃NC MOLECULE

Frequency, cm. ⁻¹	Model 1		Model 2	
2259(3)	2235(4)	-45	-35.3	-35.3
2165		-17		
1077(3)		-1.7		-9.0
900(2)	892(3)	-2.2	-3.0	-6.7
877		-5.8	-5.8	-6.4
249(2)		-0.43		-0.51

^a Found for grouped frequencies as geometric mean of individual constants. As in paper I, the grouping of anharmonicity constants for different types of modes having coincidentally close-lying frequencies is to be understood as a mathematical simplification, and not a physical assumption.

The fundamental frequencies for CD₃NC were obtained by a combination of values, obtained by an FG matrix calculation of the values of Pillai and Cleveland for CH₃NC,¹⁹ with values given by Mottern and Fletcher²⁰ published later.

This assignment and that for the activated complexes are given in Table V. Various frequency lowerings in the activated complex, relative to the molecule, correspond mainly to the C=N stretch and the C-N stretch which become ring deformation frequencies in the activated complex. The only significantly variable vibrational parameter of the calculation here is the perpendicular twist vibration in the complex (the out-of-plane

(19) M. E. K. Pillai and F. F. Cleveland, *J. Mol. Spectry.*, **5**, 212 (1960). We thank Dr. B. Kirtman for the use of his 709 program and for his advice.

(20) J. G. Mottern and W. H. Fletcher, *Spectrochim. Acta*, **18**, 995 (1962).

CNC bending mode in the molecule) set at 249 and 540 cm.^{-1} in the so-called "300" and "600" models, comparable to CH_3NC .

For the calculation of the anharmonic sum of energy states, in analogy to part I, we have used again two anharmonic models characterized by anharmonicity con-

stants according to a "minimum" model 1 and a "maximum" model 2. The constants for a Morse-type expression for the energy and dissociation limits of the various bonds in CD_3NC are given in Table VI.

Other parts of the rate calculations were made as before.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILL.]

Pulse Radiolysis Studies. III. Elementary Reactions in Aqueous Ethanol Solution^{1,2}

BY LEON M. DORFMAN AND I. A. TAUB

RECEIVED MARCH 27, 1963

The kinetics of the elementary reactions of two transient species, the hydrated electron and the α -ethanol radical, have been observed in irradiated deaerated aqueous ethanol solution using the pulse radiolysis technique. Absolute rate constants at 23° have been determined for the reaction of the hydrated electron with a hydrogen ion and for the first-order decay of the electron: $e_{\text{aq}}^- + \text{H}_{\text{aq}}^+ = \text{H}$, $k_{e_{\text{aq}}^- + \text{H}_{\text{aq}}^+} = (2.26 \pm 0.21) \times 10^{10} M^{-1} \text{sec.}^{-1}$; $e_{\text{aq}}^- + \text{H}_2\text{O} = \text{H} + \text{OH}^-$, $k_{e_{\text{aq}}^- + \text{H}_2\text{O}} \leq 4.4 \times 10^4 \text{sec.}^{-1}$. The molar extinction coefficient at 577–579 $m\mu$ of the hydrated electron in water, based on $G_{e_{\text{aq}}^-} = 2.7$ molecules/100 e.v., was determined as: $\epsilon_{577} = (9.7 \pm 1.5) \times 10^3 M^{-1} \text{cm.}^{-1}$. Experiments with $\text{C}_2\text{H}_5\text{OD}$ in strongly basic D_2O establish that the product of the bimolecular reaction of two hydrated electrons is a molecule of hydrogen: $e_{\text{aq}}^- + e_{\text{aq}}^- = \text{H}_2 + 2\text{OH}^-$. The isotopic data also give $G_{e_{\text{aq}}^-} = (2.9 \pm 0.3)$ molecules/100 e.v. in D_2O . The molar extinction coefficient of the α -ethanol radical at 2967 Å. was determined as: $\epsilon_{2967} = 240 \pm 45 M^{-1} \text{cm.}^{-1}$. The absolute rate constant for the bimolecular reaction of two α -ethanol radicals at 23° was determined as: $2k_b = (1.4 \pm 0.4) \times 10^9 M^{-1} \text{sec.}^{-1}$.

Introduction

This report in the series^{3,4} of pulse radiolysis studies of organic and aquo-organic systems is concerned with the elementary reactions in deaerated aqueous ethanol solution. Two aspects, in particular, of the radiation chemistry of this system are dealt with. The reaction kinetics of the hydrated electron, of which the absorption spectrum in irradiated water has recently been observed,^{5,6} have been studied. These reactions are of general importance in the radiation chemistry of aqueous systems. The kinetics of the disappearance of the α -ethanol radical, the absorption spectrum of which has already been reported,⁴ have now been studied in acid solution.

A number of isotopic experiments, involving $\text{C}_2\text{H}_5\text{OD}$ in D_2O over a pH range of 0.4 to 13, have been carried out. The results provide the basis for the determination of the molar extinction coefficients of both the hydrated electron and the α -ethanol radical. In the latter case, the molar extinction coefficient, which has been estimated in neutral solution,⁴ may be determined to a higher degree of certainty in acid solution. The isotopic data, furthermore, furnish definitive information concerning the nature of one of the reactions of the hydrated electron.

Experimental

The technical details of the pulse radiolysis method used in these fast reaction studies have been described in the first paper³ of this series. Only the particular conditions pertaining to the present investigation will be outlined.

Pulse Irradiation.—A 15-Mev. electron pulse from the linear accelerator was used throughout. The work on the α -ethanol radical was done with a 5- $\mu\text{sec.}$ pulse, with the exception of a few runs where a 3- $\mu\text{sec.}$ pulse was used. The kinetics of the hydrated electron were observed after a 0.4- $\mu\text{sec.}$ pulse. The time-profile of the pulse, which is very nearly rectangular, has been shown elsewhere.³

The electron beam used in this work was more nearly collimated than in the previous work, having an incident diameter of 16 mm. and an emergent diameter of about 18 mm. in a 4-cm. long cell.

Cylindrical quartz cells of various sizes were used in the irradiations. In those runs where it was desirable to define the irradiated

volume precisely, cells of 4 cm. length and inside diameter 15 mm., thus smaller than the actual beam diameter, were used. Cells of 4 cm. diameter were also used. In the determination of bimolecular rate constants, where a uniform concentration of transient species along the axis of the beam was highly desirable, a number of runs were carried out in cells of 2 cm. length to ensure that this condition would be satisfied. In the observations of the kinetics of the hydrated electron at high pulse intensity, a cell of only 1 cm. length was used because of the very high extinction coefficient of this species.

Dosimetry.—The pulse was monitored on a relative basis by integrating the current in the beam sensor⁷ which has been mentioned previously.⁴ The absolute dose was determined in two ways. The usual bulk dosimetry with the Fricke dosimeter containing $10^{-2} M$ ferrous ion and 0.8 N sulfuric acid was used. This solution was saturated with oxygen and contained no chloride ion. The yield of ferric ion in this solution at the high dose rates^{8,9} is 15.6 molecules/100 e.v. The ferric ion concentration was measured on a Beckman DU spectrophotometer. In addition a type of *in situ* dosimetry was used involving the optical detection system itself in a fast spectrophotometric measurement of the total ferric ion formation in the above dosimeter solution. This method was considered worthwhile in the determination of the molar extinction coefficients, where the actual concentration (or energy deposition) in the path of the analyzing light beam was the particular information required. This information was obtained by calculating the ferric ion concentration from the optical density corresponding to the plateau in the formation rate curve. This optical density represents the concentration of ferric ion formed from all reactions in the dosimeter, which in these experiments are completed within about 2 sec. after the pulse. The rate curve for ferric ion formation was determined at either 302 or 366 $m\mu$ depending upon the length of the irradiation cell. The ferric ion concentrations were calculated using $\epsilon_{302} = 2200 M^{-1}$ and $\epsilon_{302}/\epsilon_{366} = 8.57$. This ratio of the molar extinction coefficients was determined with a Cary spectrophotometer, type 14R, using a solution approximately $2 \times 10^{-4} M$ in ferric sulfate and 0.8 N in sulfuric acid.

Optical Detection.—The fourfold reflection system was used in most of the experiments. In a number of observations of the hydrated electron a twofold reflection was used for optical detection. The 2.25-m. spectrograph was used with two separate gratings. For detection in the ultraviolet region a grating blazed at 370 $m\mu$ with a dispersion of 15 Å./mm. was used. For the kinetic studies of the hydrated electron at 577–579 $m\mu$ a grating blazed at 600 $m\mu$ with a similar dispersion was used.

The steady light source in the fast spectrophotometric measurements was an Osram mercury lamp, type HBO 107/1, monitored with a 1 P28 photomultiplier tube. At 2967 Å., where the α -ethanol kinetics were observed, a 1-mm. slit was placed in front of the photomultiplier, giving a band width of 15 Å. For the hydrated electron, which exhibits a very broad absorption

(1) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963; see Abstracts of Papers, p. 11P.

(2) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(3) L. M. Dorfman, I. A. Taub, and R. E. Bühler, *J. Chem. Phys.*, **36**, 3051 (1962).

(4) I. A. Taub and L. M. Dorfman, *J. Am. Chem. Soc.*, **84**, 4053 (1962).

(5) J. W. Boag and E. J. Hart, *Nature*, **197**, 45 (1963).

(6) E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.*, **84**, 4090 (1962).

(7) K. Johnson, T. Klippert, and W. J. Ramler, *Nuclear Instr. Methods*, **14**, 125 (1962).

(8) J. Rotblat and H. C. Sutton, *Proc. Roy. Soc. (London)*, **A255**, 49 (1960).

(9) J. K. Thomas and E. J. Hart, *Radiation Res.*, **17**, 408 (1962).