

Table IV. Values for Slopes and Intercepts Derived from Figure 6^a

Temp., °K.	Slope × 10 ² , sec.	Intercept × 10 ⁶ , mole l. ⁻¹ sec.	α × 10 ⁻³ mole ⁻¹ l.
1350	1.62	0.42	3.09
1415	0.618	0.12	5.73
1612	0.197	0.047 ₅	2.98

^a Emission data at 3195 cm.⁻¹; ⟨α⟩ = 3.93 × 10³ mole⁻¹ l.

sets of shock tube data taken over a long period of time, wherein two distinct calibrations for emission intensi-

ties are involved. We must conclude that θ is essentially unity within our absolute error. Equation 12 leads to

$$\frac{k_1 k_3}{k_2} = 2.8 \times 10^7 \exp(-32,500/RT) \text{ (mole}^{-1} \text{ l. sec.}^{-1}\text{)}$$

One may argue that the association rate (1) probably has a collision efficiency of 10⁻¹ to 10⁻², while the quenching step (2) has unit collision efficiency. This leads to an internal conversion efficiency (step 3) of 10⁻³ to 10⁻², which is inherently reasonable.

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The Thermal Unimolecular Isomerization of Methyl-*d*₁ Isocyanide. Fall-Off and Inverse Isotope Effect¹

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Earlier work (parts I and II) on the study of methyl and methyl-*d*₃ isocyanides has been extended to the methyl-*d*₁ compound. A brief study has been made of the fall-off at 245° at pressures from 9.3 atm. down to 0.05 mm., and values of k/k_∞ from ~1 down to 0.0042. No significant effect on the fall-off behavior due to the splitting of the four doubly degenerate modes of methyl isocyanide by the deuterium substituent is observed; the variation of fall-off behavior for the three compounds, methyl, methyl-*d*₁, and methyl-*d*₃ isocyanides, are as expected from differential quantum statistical factors. With decrease of pressure an inverse statistical-weight isotope effect is found which is in good agreement with the theoretical formulation in II; $k_{\text{CH}_3}/k_{\text{CH}_2\text{D}}$ is measured as 0.75 at the lowest pressure studied and is extrapolated down to ~0.70; the limiting low pressure value is calculated to be $(k_{\text{CH}_3}/k_{\text{CH}_2\text{D}})_0 = 0.67$, on a quantum statistical basis. At the high pressure limit, $k_{\text{CH}_3}/k_{\text{CH}_2\text{D}} \simeq 1$, as expected.

Introduction

The thermal unimolecular isomerization of methyl^{2a} and methyl-*d*₃^{2b} isocyanide has been reported earlier. In continuation of the study of the isocyanide reaction system, the methyl-*d*₁ isocyanide system has now been examined. Unlike the methyl-*d*₃ molecule which has C_{3v} symmetry similar to the light methyl compound, monodeuteration introduces a new structural feature by splitting the degeneracy of the four doubly degenerate modes, a C-H stretch, a methyl rock and methyl deformation, and the skeletal bend.

This molecule also provides another potential example of the inverse intermolecular secondary isotope

effects described earlier for nonequilibrium (*i.e.*, low pressure conditions) thermal systems.³ The present study is brief, but adequate for illustrating the differential quantum effects in this series of isotopically substituted molecules.

Experimental

Materials. CDH₂NC was prepared by allowing CDH₂I (from Merck Sharp and Dohme, Ltd., Montreal) to react with silver cyanide in the molar ratio 1:2 by the modified Gautier method.^{2a} It was purified by gas chromatography on a tetraglyme-Fluoropak column. The isotopic purity of the material was determined by parent peak analysis with a Consolidated 21-103 mass spectrometer and was found to contain 3.4% CH₃NC. Acetonitrile was also purified on the gas chromatographic column.

Procedure. An internal comparison method similar to that described in II was employed. A reactant mixture of CH₃NC and CH₂DNC of composition 3:1 was prepared under mercury-free conditions, by using a glass diaphragm click gauge. Runs were carried out in a conventional high vacuum apparatus at an average temperature of 245°. Reaction vessels of different sizes varying from 0.8 ml. at the highest pressure up to 12 l. at the lower pressures were used. No corrections were necessary for small deviation from the average temperature because of the negligible temperature coefficient found in II for this isotope effect. Temperature over the reactors was usually constant to ±0.5° in the worst case. The vessels were seasoned and "exchanged" before use, as in II. The conversion of reactants was kept as low (average 20%) as was convenient for analysis.

In the run at highest pressure, 1.14 × 10⁴ mm., in order to conserve reactant the vessel was pressurized

(1) This work was supported by the National Science Foundation.
(2) (a) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **84**, 4215 (1962), called I; (b) *ibid.*, **85**, 2365 (1963), called II. In II, on p. 2366, right column, second paragraph, line 4, *ten* decades should be replaced by *six* decades.

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

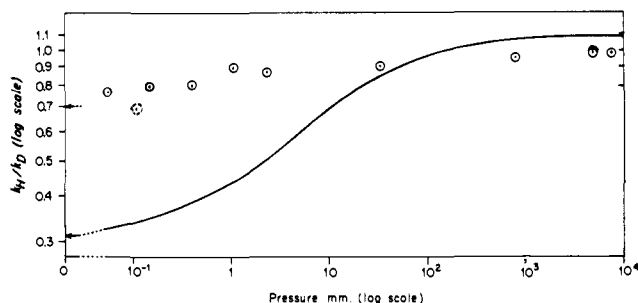


Figure 1. Plot of k_H/k_D for $\text{CH}_3\text{NC}-\text{CH}_2\text{DNC}$ (circles) at 245° , together with a solid curve summary of the system $\text{CH}_3\text{NC}-\text{CD}_3\text{NC}$ at 230° : the latter is part of the solid curve of Figure 1, part II, which actually goes to lower pressure than was attained in the present work; the dashed circle is a doubtful experimental point.

with ethane in a 18:1 ratio. From the relative efficiency of ethane = 0.62 determined in I, this corresponds to an effective pressure of 7100 mm. The lowest pressure was 0.053 mm.

Analysis. After reaction, the products were separated from isocyanides on a 2-ft. silver cyanide column which complexed the remaining reactants but allowed the nitriles to pass unchanged. The nitriles were analyzed mass spectrometrically. The relative sensitivities of the parent peaks in the mass spectrometer were determined at 70 v. by calibration with standard mixtures prepared after completely converting samples of the reactant mixture to nitriles. The parent peaks were corrected for C^{13} and N^{15} contributions.

Results

The data were treated in the manner described in I.

Isotopic Rate Ratio. The experimental values of $k_{\text{CH}_3}/k_{\text{CH}_2\text{D}}$ (i.e., k_H/k_D) are summarized in Figure 1. In II, the experimental high pressure limiting value of $(k_{\text{CH}_3}/k_{\text{CD}_3})_\infty$ was found to be 1.07, and the expected⁴ limiting ratio for the present comparison would be slightly greater than unity, ~ 1.02 . The observed average value for the runs at the three highest pressures was approximately unity. In view of the great difficulty of measuring the rate ratio with an accuracy better than a few per cent, a high pressure limiting ratio of 1.02 has been assumed; this enters into the limiting value of $k_{\text{D}\infty}$ described for CH_2DNC in the following section, although this scarcely affects any other quantities or considerations.

Fall-Off Ratio. Since only relative rate measurements, k_H/k_D , were accurately made, the fall-off behavior for CH_2DNC is found by relating the isotopic rate ratio to the fall-off data determined in I for CH_3NC at 230° . Figure 2 gives the data and also compares the fall-off for CH_3NC and CD_3NC .

Discussion

Nonequilibrium Inverse Isotope Effect. Inverse intermolecular secondary isotope effects in nonequilibrium (i.e., low pressure) thermal activation systems have previously been verified experimentally for the methyl-methyl- d_3 isocyanide system^{2b} and for the cyclopropane-

(4) A little uncertainty derives from the fact that ΔE_a , i.e., $(E_{a\text{CH}_3} - E_{a\text{CD}_3})$, the observed activation energy difference, was measured in II as 0.1 kcal. mole⁻¹ but is uncertain to at least a few tenths of a kilocalorie; the corresponding zero point or critical energy difference, ΔE_0 , is similarly affected.

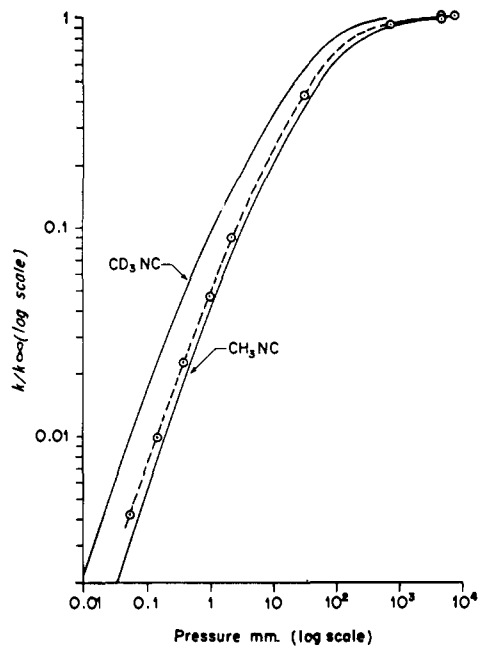


Figure 2. Experimental values of k/k_∞ (log scale) vs. pressure in mm. (log scale) for CH_3NC , CH_2DNC , and CD_3NC at 230° : the continuous lines represent smooth curves through the experimental points for CH_3NC and CD_3NC since use of the numerous data points would clutter the graph; the circles are actual data points for CH_2DNC brought to 230° from 245° .

cyclopropane- d_6 pair.⁵ A detailed formulation and extensive discussion of the nature of the effect in terms of the RRKM theory was given in II.⁶ Parts I and II also gave, for the first time, a quantitative treatment and application of both harmonic and anharmonic oscillator models to the accurate calculation of rates and nonequilibrium isotope effects in thermal systems, including the over-all rotational contributions to the rate. We need not recapitulate the treatment here. It is sufficient to recall eq. 1 of II

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

where the M terms are the molecular weights, the Q terms are the molecular partition functions for active degrees of freedom, and the $N(E)$ quantities are densities of active energy levels at the energy E . For the present case, $E_{0H} \approx E_{0D}$, so that mechanistic differences in the decomposition of this isotopic methyl series are virtually absent; this is a favorable feature not originally emphasized when the advantages of these systems were being enumerated.^{2a}

It is seen from eq. II-1 that one deals with a quantum statistical-weight effect which increases with increasing degree of isotopic substitution, i.e., $N(E)_D$ thereby increases relative to $N(E)_H$. Hence the magnitude of the

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

(6) For some further considerations on low pressure inter- and intramolecular primary and secondary isotope effects in unimolecular systems see ref. 5, and also B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

inversion is expected to be less for CH₂DNC than for CD₃NC. Figure 1 bears this out.

The low pressure limiting value $(k_H/k_D)_0$ was calculated with the following frequency models for CH₂DNC (cm.⁻¹): 3016, 2972, 2260, 2150, 1443, 1305, 1205, 1040, 970, 910, 257 (2). The value of E_{cH} is equal to E_{0D} . The frequencies for CH₃NC were given in I. It was demonstrated previously^{2a} that anharmonicity effects are as large as 30% at the energies of interest just above E_0 (38 kcal.). However, the harmonic oscillator calculation can be used since the anharmonicity corrections have been shown^{2b} to virtually cancel for the ratio of rates in eq. II-1; the uncertainty in bending anharmonicity constants makes the simpler procedure even more desirable. Inclusion of over-all figure-axis rotation as active in the theoretical calculations similarly largely cancels in the rate ratio.^{2b}

The agreement between the calculated limit, 0.67, and the extrapolation of experimental values given in Figure 1 is evidently quite good; the earlier experimental comparison of CH₃NC and CD₃NC was carried a decade lower in pressure and, by comparison, the present results (0.75 at 0.053 mm.) extrapolate to ~0.70. It is very gratifying that an observed inversion of correct magnitude has been observed in this system with a single D substituent. However, since the total effect is quite small, and the accuracy of the details of the experimental decline of k_H/k_D with pressure is not great, there is no point in making the detailed comparisons with theory that were warranted in II for CD₃NC. An interesting fact is that the experimental limiting low pressure value was a little lower than theoretical for CD₃NC, and is a little higher than theoretical here; since the rather small discrepancies are not even consistent, we may ascribe them simply to errors in experiment or to trifling error (<0.1 kcal.) in the assumed identity here of the ΔE_0 values.

Fall-Off of k_D/k_{D_∞} with Pressure. The values of the familiar fall-off parameters—Kassel's s or Slater's⁷ n —were reported at 230° as 3.6 and 5.5, respectively, for CH₃NC, and 3.9 and 6.1 for CD₃NC. The variation between the two compounds is due to the lower average vibration frequencies of the deuterio compound and represents a differential quantum statistical effect^{2,3} in reasonable agreement with RRKM theory.

Although we believe that the question of the validity of the Slater⁷ postulate of normal coordinate orthogonality in reacting molecules has already been essentially resolved,^{2,8} nevertheless it is of interest to

(7) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Reinhold Publishing Corp., New York, N. Y., 1932; N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

(8) B. S. Rabinovitch, R. F. Kubin, and R. E. Harrington, *J. Chem. Phys.*, **38**, 405 (1963).

examine the relation of the present study to this matter. The Slater theory predicts that no change in n will occur on perdeuteration of methyl isocyanide, since the original C_{3v} symmetry is retained.⁹ The observed change is small in magnitude, from 5.5 to 6.1, and this isotopic pair thus provided only an inadequate test.

The situation for the monodeuterio compound, CH₂DNC, provides a little stronger criterion. Degenerate modes which interact with the reaction coordinate are to be counted⁷ only once in n ; thus, the maximum value of n for CH₃NC and CD₃NC is predicted as 8; the observed values around 6 imply that on a Slater basis the reaction coordinate has a significant contribution from two of the degenerate modes. (Actually, by contrast, although three of the four degenerate modes involve H motions the comparative invariance of E_0 suggests that C-H participation is not great.) The splitting of these on monosubstitution should enhance the effective value of n since splitting could double each contribution. From the nature of the transition state proposed previously for this reaction² (or any reasonable variant thereof) it seems clear, even without a detailed analysis, that n includes at least the degenerate skeletal bending mode. The value of $n = 5.5$ for CH₃NC would then be expected to increase to ≥ 6.5 on monosubstitution; alternatively, the value of $n = 6.1$ for CD₃NC might be expected to increase to ≥ 7.1 for monosubstitution. Although the determination of the absolute values of n from the shape of fall-off is probably accurate only to ± 1 , the relative values in this series are more precisely determined. It is evident that n for CH₂DNC does not exceed n for CD₃NC; in fact it is actually measured as 5.5 or 5.6 by superposition on the CH₃NC curve.

Because of the inaccuracy of fall-off shape comparison, the pressure shift of the fall-off is a clearer experimental measure of the decrease in molecular frequencies accompanying deuteration. Figure 2 illustrates quite nicely the increased "effective number of oscillators" (in the sense of the s parameter) with increasing degree of deuteration for these three members: the fall-off curves appropriately shift to progressively lower pressure as expected on the RRKM basis. Thus the curve for the dideuterio compound, CHD₂NC, is predicted to fall between those for CH₂DNC and CD₃NC.

We expect that our studies of longer chain isocyanides will provide still better examples of these effects for test of theory.

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(9) This assumes that none of the normal mode contributions is marginal in effective magnitude.