($\sim$0.9 p.p.m.) of methyl isocyanide,[24] yet the dipole moments of these two compounds are almost indistinguishable.[25] If the dipole moments of the two compounds can be located anywhere near the same position, this must mean that the anisotropy effect for methyl isocyanide is less than that for acetonitrile. If this is so, then the hydrogen bond length must be greater for the isocyanide, since the Δ_{AD} values are essentially the same, and ζ for the carbon is less than that for nitrogen. This is not surprising in light of the lower boiling points of isocyanides, though infrared

(24) I. D. Kuntz, P. von R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, **35**, 1533 (1961).

(25) C. P. Smith, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

spectral shifts upon hydrogen bond formations are smaller for the cyanide.[26]

In conclusion, we feel that the electric field effect and the neighbor-anisotropy effect are sufficient to explain the n.m.r. shift upon complex formation for weak hydrogen bonds. Thus, where anisotropy is constant, this shift could be used to compare hydrogen bond lengths and, as far as the two are proportional, strengths. Furthermore, a fair estimate of the actual length can be obtained. The connection between the weaker basicity of nitriles compared with amines and the prediction of longer hydrogen bond lengths is being investigated.

(26) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 866 (1963).

Inverse Secondary Intermolecular Isotope Effects in the Low Pressure Thermal Isomerization of Cyclopropane[1a]

BY B. S. RABINOVITCH,[1b] P. W. GILDERSON,[1b] AND A. T. BLADES[1c]

The experimental study of quantum statistical intermolecular secondary isotope effects in the rate of thermal decomposition of cyclopropane and of cyclopropane-d_6 has been extended down to pressures of 10^{-4} mm. at 510° by an internal comparison method. The expected inversion of the ratio $k(h_6)/k(d_6)$ occurs at $\sim 10^{-2}$ mm. Below this pressure complications attributed to wall effects obscure the behavior, and a limiting value of $k(h_6)/k(d_6) \simeq 0.8$ was obtained. The results are discussed briefly, along with mixed isotope effects, and are compared with theoretical computations.

Kinetic isotope effects for the thermal unimolecular isomerization of cyclo-C_3H_6 and cyclo-C_3D_6 were first measured by Blades.[2] His experiments at 482°, made at pressures down to 0.18 mm., gave ratios which declined with pressure from the limiting high pressure value $[k(h_6)/k(d_6)]_\infty = 1.96$ to $[k(h_6)/k(d_6)]_{c \cdot 18} = 1.35$. Rabinovitch, Setser, and Schneider[3] (RSS) pointed out that this inequality, which at high pressures reflects a primary isotope effect mainly, should invert at sufficiently low pressures, where opposing secondary quantum statistical isotope effects would eventually overtake the primary effect. They calculated a low pressure limiting value on a harmonic oscillator model of $[k(h_6)/k(d_6)]_0 = 0.25$. This inverse isotope effect is a quite general phenomenon, and explicit confirmation of its existence has since been given for the isomerization of the pair CH_3NC and CD_3NC.[4]

The present paper describes the extension of the cyclopropane system to lower pressures. Although the expected inversion has been realized, wall effects at still lower pressures[5] obscure the quantitative aspects.

(1) (a) This work was supported by the National Science Foundation; (b) University of Washington; (c) Research Council of Alberta, Contribution No. 253.

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

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

(4) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963); this effect has now also been demonstrated for CH_2DNC, unpublished results of P. W. Gilderson.

(5) A. D. Kennedy and H. O. Pritchard, *J. Phys. Chem.*, **67**, 161 (1963); B. S. R. thanks Dr. Pritchard for a private communication which clarified the fact that a k_∞ value derived from data of W. E. Falconer, T. E. Hunter, and A. F. Trotman-Dickenson [*J. Chem. Soc.*, 609 (1961)] has been used in the log k/k_∞ plot of this reference.

Experimental

Materials.—The mixture of cyclo-C_3H_6 and -C_3D_6, in the proportions of 4.00:1, was the same as that used previously.[2] The C_3D_6 component was of 93% isotopic purity, with the remainder chiefly C_3HD_5.

Apparatus and Procedure.—The reactor was a 12-l. spherical Pyrex flask, fitted with a thermometer well, and heated in a stirred air furnace to an average temperature of 510.7°. The maximum temperature variation from the mean over the vessel was ±2°. A conventional vacuum system was employed.

After production of a sticking vacuum, the reactor was seasoned as follows: Following a flush with 1 mm. of C_3H_6, the reactor was allowed to stand at 510° and 1 mm. pressure for 2 hr. The procedure was repeated. After evacuation of the reactor, any exchange of a surface film was allowed to occur by flushing for 10 min. with the isotopic mixture. After the first exchange treatment, no isotopic alteration of the mixture or products could be detected.

Measured samples were expanded into the reactor from a trap at Dry Ice temperature in order to prevent transport of mercury vapor. At the end of the run, the contents of the reactor were analyzed.

Analytical.—Analysis of products was made by g.l.p.c. on an 80-ft. silver nitrate-glycol column.[6] Standard mixtures of propene-h_6 and -d_6 were prepared for the calibration of peak heights and their ratios. Three mixtures, of h_6/d_6 composition 0.971:1, 2.305:1, and 4.96:1, were used. The calibration factor (actual ratio/measured ratio) was found to be the same for each mixture. There was no recognizable trend of the factor with sample size. A calibration run was performed with each set of analyses. Variations were within ±2%.

Parent peak analysis with a Consolidated 21–103 mass spectrograph of the propene-d_6 used in the calibrations showed that there was 6% propene-d_5 present; this did not introduce appreciable inaccuracy because its retention time is virtually identical with that of propene-d_6.

(6) R. J. Cvetanovic, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963).

Results

Side Reaction.—The products of the runs down to 4×10^{-2} mm. contained a small side product with the same retention time on the silver nitrate column as *trans*-butene-2. It occurred in amounts varying from trace quantities to about 4.5% of the total propene peaks. There was also a small quantity of propane, usually in trace amounts, and less than 0.5% of total product.

Another trace of lower side product was found at pressures below 3×10^{-3} mm. It was not CO_2, ethylene, or ethane and was not identified.

Treatment of the Data.—Where possible, the percentage reaction was kept below 10%. However, in many cases this value was greatly exceeded and calculation was made with the relation[2]

$$\frac{k(h_6)}{k(d_6)} = \frac{f_h}{f_d} \frac{\left(1 + \dfrac{f_h}{2} + \dfrac{f_h^2}{3} + \dfrac{f_h^3}{4} + \ldots \right)}{\left(1 + \dfrac{f_d}{2} + \dfrac{f_d^2}{3} + \dfrac{f_d^3}{4} + \ldots \right)}$$

where f_h and f_d are the fractional conversions of light and heavy cyclopropane. Since all the values of $k(h_6)/k(d_6)$ were relatively close to unity, the correction terms were only a few per cent.

The measured k_H/k_D values were converted from $510.7°$ to the temperature of Blades' experiments $(482°)$. His temperature coefficient of the isotope effect (fortunately small—$\Delta E_a = 1.3$ kcal. mole^{-1} from which $\Delta E_0 = 1.4$ kcal. mole^{-1}) was employed, amounting to a correction of $\sim 4.3\%$.

The isotope effect is shown as a function of pressure in Fig. 1. The higher pressure values overlap satisfactorily with the solid curve which summarizes the results of Blades.

Discussion

Variation of k_H/k_D with Pressure.—The theoretical fall with pressure of the isotopic ratio $k(h_6)/k(d_6)$ was recalculated on the Rice–Ramsperger–Kassel–Marcus theoretical basis used by RSS. The same molecular and activated complex vibration frequency and structural models as used previously[3,7] were employed, but more accurate evaluation of sums and densities of active rotation–vibrational (harmonic) eigenstates was made with an improved 709 program. The numerical values are altered a little, but not significantly, from those of RSS and the limiting low and high pressure values are essentially unchanged; the high pressure ratio is 2.12.

The low pressure (harmonic) limit is 0.25; it may be worthwhile to examine the composition of this value: The rate ratio expression is[3]

$$[k(h_6)/k(d_6)]_0 = \frac{\omega_h}{\omega_d} \frac{Q_{vd}}{Q_{vh}} \frac{\displaystyle\int_{E_{0h}}^{\infty} N(E_v)_h e^{-E/RT} dE}{\displaystyle\int_{E_{0d}}^{\infty} N(E_v)_d e^{-E/RT} dE}$$

The first ratio, in the collisional rates, is close to unity. The second ratio, in the respective molecular vibrational partition functions, is $\sim 4:1$. The third ratio involves the vibrational energy level densities, $N(E_v)$, which at 65 kcal. is $\sim 1:40$; it also involves the difference in zero point energies, $\Delta E_0 = E_{0d} - E_{0h}$, which

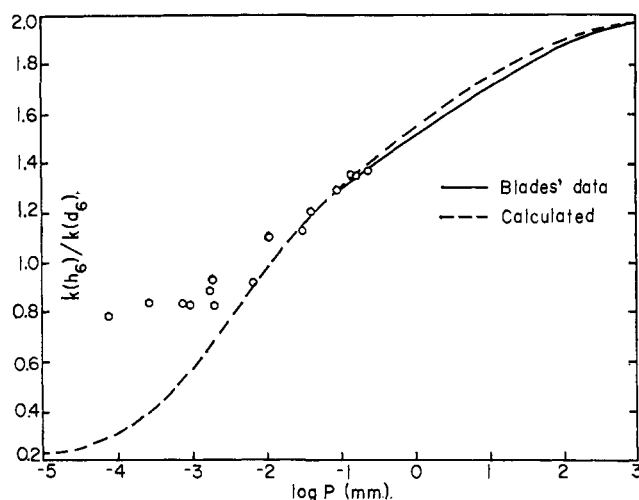(7) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

Fig. 1 —Plot of $[k(h_6)/k(d_6)]$ *vs.* pressure (mm.) on a log scale; O, present data.

provides the opposing ratio, $e^{\Delta E_0/RT}$ which is $\sim 2.5:1$. The product of all these values is 0.25, as given.

The calculated pressure dependence curve is compared to experiment in Fig. 1 by arbitrarily scaling from 2.12 to Blades' value of 1.96 at $p = \infty$, in order to make clearer the correspondence between the two sets of values as a function of pressure.[8] Excellent agreement with the experimental results exists down to a pressure below 10^{-2} mm.; the disagreement is marked for the measurements below 7×10^{-3} mm. The experimental values of Fig. 1 show a premature leveling off in the lowest pressure region.

A plausible explanation of this behavior is that it is due to the wall-activated reaction (which has the same energy parameter as the gas reaction), as observed by Kennedy and Pritchard[5] for cyclopropane at pressures below 3×10^{-2} mm. in a 1-l. vessel. For the present 12-l. reactor, the mean-square diffusion path length in the gas phase between wall collisions would be increased by a factor of $(12)^{1/3} = 5$; from the Einstein diffusion equation, this factor corresponds to a similar decrease in the wall–gas collision ratio. The onset of the experimental inflection at low pressures in the present work cannot be specified precisely, but the differential behavior between our system and that of Kennedy and Pritchard[5] is in the correct direction for this explanation.

Mixed Isotope Effects.—The structural isomerization of deuterated cyclopropanes offers interesting cases of mixed primary and secondary isotope effects[9]; such effects are discussed more generally elsewhere.[10] Figure 2 shows the quantum statistical effect on calculated low pressure *total* rate ratios $[k(h_6)/k(d_x)]_0$ as a function of x, where the individual rate constants refer to the *total* structural isomerization rate. Since no cognizance was taken of possible very small variations in the critical energy E_0 for the cases $x \leq 5$ (it should be noted that for $x \leq 5$, the critical threshold corresponds

(8) The value of $[k(h_6)/k(d_6)]\infty = 1.96$ at $482°$ was directly measured by Blades. By contrast, the value calculated here depends on his measured activation energy difference, ΔE_a; the absolute agreement of the experimental and calculated values in Fig. 1 is considered to be good; a change in ΔE_a of only 0.1 kcal. encompasses the difference.

(9) D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 564 (1964); the additional simultaneous existence of inter- and intramolecular isotope effects for the partially deuterated species complicates these systems.

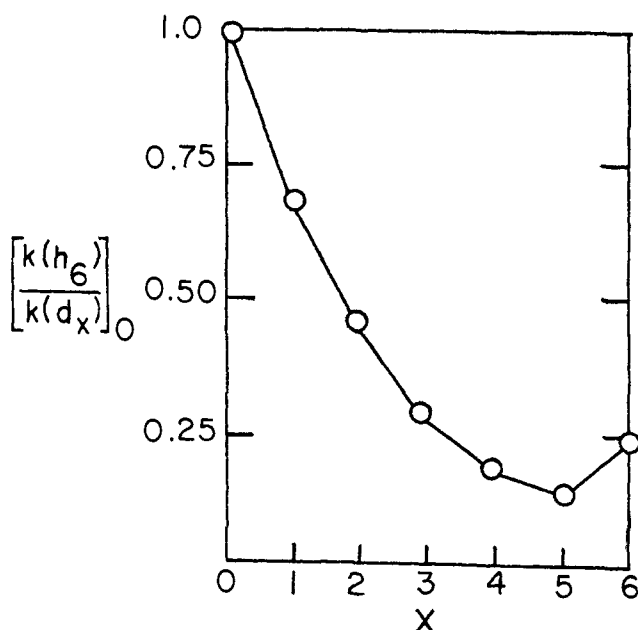(10) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, to be published.

Fig. 2.—Representation of the variation of the ratio $[k(h_6)/k(d_x)]_0$ as a function of x (after Rabinovitch and Setser, ref. 10).

to H migration in all cases), the computational results cannot be exact, but undoubtedly give the correct magnitudes. The rise shown in Fig. 2 between $x = 5$ and $x = 6$ corresponds to a primary effect due to the gross alteration in the collisional activation reaction coordinate attendant upon the *complete* replacement of H atoms by D atoms. Although information on primary intermolecular isotope effects can be obtained[11,12] at the higher pressures from the measurements of the

(11) (a) R. E. Weston, J. Chem. Phys., **23**, 988 (1955); **26**, 975 (1957); (b) R. H. Lindquist and G. K. Rollefson, ibid., **24**, 725 (1956).

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

total rates of isomerization for the cases, $1 \leq x \leq 5$, the change in the nature of the reaction coordinate precludes the possibility of finding similar information from such measurements at the low pressure limit; detailed knowledge of the proportions of the various possible isotopic products would be necessary, in addition, in order to decipher the intramolecular rate ratios.

Weston[11a] has studied the variation with pressure of the isotope effect for cyclopropane–cyclopropane-t_1 at 775°K. He found that the primary isotopic rate ratio per bond, k_H/k_T, had a high pressure value of 3.7, under the approximation of no secondary isotope effects; the *total* observed isotopic ratio was reported as declining to the limiting classical statistical low pressure value, unity, at 0.4 mm.

This observed unity ratio also appears to have been identified[13] as the limiting primary isotope value corresponding to $p = 0$. However, it should be noted that the limiting low pressure regime actually lies well below 0.4 mm. (cf. Fig. 1 and ref. 14). Also the experimental method of Weston did not isolate primary and secondary intermolecular kinetic isotope effects from each other, and, if it were carried to the true low pressure region, the technique could provide a measure of intermolecular secondary effects only.

A curve similar to Fig. 2 but of more exaggerated shape applies to tritiated compounds, and the ratio $[k(h_6)/k(t_1)]_0$ should be even more substantially less than one (and order of magnitude 0.55); also, $E_0(h_6) - E_0(t_1) = \Delta E_0$ probably is unmeasurably different from zero, when $p = 0$. The lowest pressure measurement of Weston at 0.4 mm. is substantially affected by the present quantum statistical secondary intermolecular effects.

(13) J. Bigeleisen and M. Wolfsberg, Advan. Chem. Phys., **1**, 15 (1958).

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

Catalysis over Supported Metals. I. Kinetics of Ethane Hydrogenolysis over Nickel Surfaces of Known Area

BY D. J. C. YATES, W. F. TAYLOR, AND J. H. SINFELT

A method of determining the specific catalytic activity of a supported metal, i.e., the activity per unit area of the metal, has been demonstrated for a Ni-on-SiO$_2$ catalyst used in the hydrogenolysis of ethane. The method involves hydrogen chemisorption measurements of the metal surface area, coupled with reaction rate determinations obtained at low conversions in a flow reactor. Samples of the catalyst were heated in air at various temperatures prior to reduction of the nickel. After reduction at a standard set of conditions, these samples had nickel surface areas which varied over a threefold range. It was observed that the rate of hydrogenolysis of ethane was proportional to the nickel surface area; i.e., the specific catalytic activity of the nickel was essentially unchanged by heating in air prior to reduction. Furthermore, the apparent activation energy and reaction orders were also unchanged.

I. Introduction

Supported metal catalysts are of great technical interest. However, as pointed out by Bond,[1] very little information has been reported on the specific catalytic activities of supported metals, i.e., the activity per unit surface area of the dispersed metal. A major part of the difficulty in determining the specific catalytic activity of supported metals, until

(1) G. C. Bond, "Catalysis by Metals," Academic Press, Inc., New York, N. Y., 1962, p. 239.

recent years, has been the unavailability of direct methods for determining the surface area of the metal itself, as distinguished from the total surface area which is readily determined by the B.E.T. method.[2]

Electron microscopy, for example, is rendered useless for this purpose because of the obscuring effect of the support. The only practical method appears to be to find a gas which will adsorb on the metal and not

(2) S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc., **60**, 309 (1938).