# Isotope Effects in the Reaction $C_2D_5 + D_2 = C_2D_6 + D$[1]

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**Abstract:** Complementing a recent study of the reaction of ethyl radicals with molecular hydrogen, a similar study has been made of the reaction of ethyl-$d_5$ radicals with molecular deuterium in the range 240–320°. The mercury $6(^3P_1)$ photosensitized decomposition of deuterium in the presence of ethylene-$d_4$ was used to generate ethyl-$d_5$ radicals. The rate constant ($cm^3$ mole$^{-1}$ sec$^{-1}$) is given by $\log k_D = 11.75 - (12.9/\theta)$. The ratio $k_H/k_D$ was treated by a transition state theory model using bond-energy–bond-order methods. Theory and experiment are in reasonably good agreement when allowance is made for quantum mechanical tunneling.

The interpretation of reaction rate constants in terms of transition state theory requires knowledge of the structure and mechanical properties of the activated complex as well as of the reagents. In many cases this is forbiddingly complicated, particularly for those parts of the potential energy surface which are directly related to the reaction coordinate. However, substitution of H atoms by D atoms in ordinary hydrocarbons will not change the structure or mechanical properties, except for those arising from the change in masses. Errors caused by using an approximate model will then cancel to some extent when the ratio of two isotopic reaction rate constants is treated.

In a recent paper from this laboratory, Reid and Le Roy[2] reported kinetic data on the reaction $C_2H_5 + H_2 = C_2H_6 + H$ in the form $\log k_H = 12.57 - (13.7/\theta)$. In the present paper we report on the evaluation of $k_D$ for the analogous reaction $C_2D_5 + D_2 = C_2D_6 + D$. In line with our current studies on the three-center reactions of atomic and molecular hydrogen and deuterium,[3] the present results are interpreted in terms of transition state theory and with the object of ascertaining the importance of quantum effects.

## Results and Discussion

The procedure used in the present work was closely analogous to that used previously,[2] in which experimental conditions were chosen to minimize extraneous reactions and to permit the results to be interpreted in terms of a basic mechanism which, for the present reaction, is as follows.

$$Hg(6^3P_1) + D_2 = Hg(6^1S_0) + 2D \tag{1}$$

$$D + C_2D_4 = C_2D_5 \tag{2}$$

$$2C_2D_5 = C_4D_{10} \tag{3}$$

$$2C_2D_5 = C_2D_4 + C_2D_6 \tag{4}$$

$$C_2D_5 + D_2 = C_2D_6 + D \tag{5}$$

Allowing for nonuniform absorption of light in the reaction cell, the observed rates of formation of ethane and butane are related by the expression

$$\frac{R_{C_2D_6}}{R_{C_4D_{10}}} = \frac{k_4}{k_3} + \frac{k_5(D_2)\delta}{k_3^{1/2}(R_{C_4D_{10}})^{1/2}} \tag{6}$$

in which

$$\delta = \frac{2[1 - \exp(-\epsilon(Hg)L)/2]}{\{\epsilon(Hg)L[1 - \exp(-\epsilon(Hg)L)]\}^{1/2}} \tag{7}$$

The absorption cross sections, $\epsilon$, varied from $9 \times 10^{-15}$ $cm^2$ atom$^{-1}$ at 240° to $11 \times 10^{-15}$ $cm^2$ atom$^{-1}$ at 320°, at the constant working pressure of 95 Torr of $D_2$, very similar to the data obtained for $H_2$.[2] The presence of $C_2D_4$ had no influence on $\epsilon$. The values of $\delta$ were very close to unity in all experiments.

Linear curves conforming to eq 6, obtained at 240, 260, 280, 300, and 320°, are shown in Figure 1. The slopes of these curves are listed in Table I and plotted in Arrhenius form in Figure 2. The derived parameters, together with their standard deviations, are given by

$$\log (k_5/k_3^{1/2}) = (5.09 \pm 0.07) - (12.9 \pm 0.4)/\theta$$

where $\theta = 2.303 \times 10^{-3}RT$, and $k$'s are in $cm^3$ mole$^{-1}$ sec$^{-1}$. By assuming $k_3$ to be equal to the value previously taken[2] for the corresponding reaction of $C_2H_5$ radicals divided by the square root of the ratio of the reduced masses

$$\log k_D \equiv \log k_{5(D)} = (11.75 \pm 0.07) - (12.9 \pm 0.4)/\theta \tag{8}$$

This is to be compared to

$$\log k_H \equiv \log k_{5(H)} = (12.57 \pm 0.13) - (13.7 \pm 0.3)/\theta \tag{9}$$

obtained for the protonated species.[2]

The experimental values of $k_H/k_D$ are plotted in Figure 4. Instead of using smoothed values derived from eq 8 and 9, we have used observed values for each of the five temperatures used in the present and previous[2] work. Allowance was made for the factor $(k_3^{1/2})_D/(k_3^{1/2})_H$.

The isotope effect can be treated in terms of transition state theory as follows.

$$\frac{k_H}{k_D} = \frac{\Gamma_H}{\Gamma_D}\frac{Q_{D_2}}{Q_{H_2}}\frac{Q^{\ddagger}{}_{C_2H_7}Q_{C_2D_5}}{Q_{C_2H_5}Q^{\ddagger}{}_{C_2D_7}} \times \exp\left[\frac{(\Delta E_0°)_D - (\Delta E_0°)_H}{RT}\right] \tag{10}$$

The quantities $\Gamma_H$ and $\Gamma_D$ are tunneling factors. The partition functions, $Q$, are assumed to be evaluated

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[1] (a) This research was supported by a grant from the National Research Council of Canada; (b) submitted in honor of Dr. W. D. Walters.

[2] L. E. Reid and D. J. Le Roy, *Can. J. Chem.*, **46**, 3275 (1968).

[3] D. J. Le Roy, B. A. Ridley, and K. A. Quickert, *Discussions Faraday Soc.*, **44**, 92 (1967).

**Table I.** Experimental Values of $(k_5/k_3^{1/2})_H$, $(k_5/k_3^{1/2})_D$, and the Ratio $k_H/k_D = (k_5)_H/(k_5)_D$

| Temp, °K | $(k_5/k_3^{1/2})_D$, cm³ mole⁻¹ sec⁻¹ | $(k_5/k_3^{1/2})_H$,[a] cm³ mole⁻¹ sec⁻¹ | $k_H/k_D$ |
|---|---|---|---|
| 513.2 ± 0.2 | 0.381 ± 0.015 | 1.284 ± 0.069 | 3.51 ± 0.22 |
| 533.2 ± 0.2 | 0.624 ± 0.022 | 2.170 ± 0.018 | 3.62 ± 0.15 |
| 553.2 ± 0.2 | 0.878 ± 0.024 | 3.459 ± 0.042 | 4.10 ± 0.15 |
| 573.2 ± 0.15 | 1.463 ± 0.067 | 5.271 ± 0.095 | 3.75 ± 0.22 |
| 593.2 ± 0.15 | 2.083 ± 0.073 | 7.946 ± 0.044 | 3.97 ± 0.14 |

[a] L. E. Reid, Ph.D. Thesis, University of Toronto, 1967, and ref 2.

using the zero-point energy levels as origins, and so the exponential term is comprised of the zero-point energy terms.

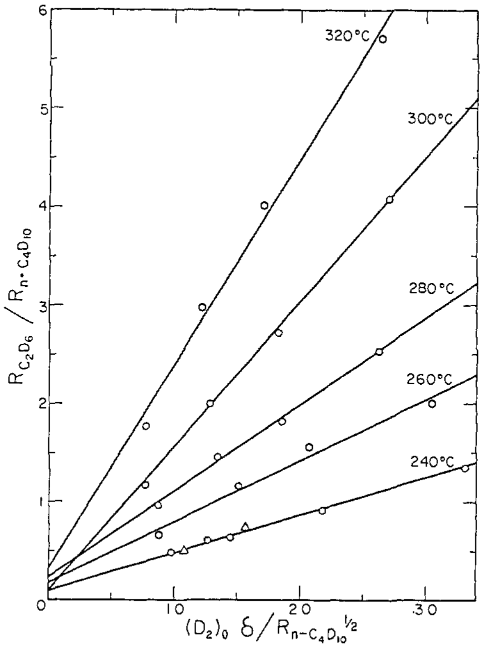

Figure 1. Ratio of the rates of formation of ethane to butane in terms of eq 6: ○, 95 Torr of $D_2$, 0.78 Torr of $C_2D_4$; Δ, 93 Torr of $D_2$, 2.3 Torr of $C_2D_4$.

Instead of using the rigid rotator–harmonic oscillator approximation to evaluate $Q_{H_2}$ and $Q_{D_2}$, we have adopted the more accurate approach of calculating the ratio from the thermodynamic data of Woodley, *et al.*[4] The free energy function $-(G° - E_0°)/T$ for $D_2$ and $H_2$ in the ideal state at 1 atm pressure for various temperatures, $T$, are related to the corresponding partition functions, $Q$, through the equation

$$-\frac{G° - E_0°}{T} = R[\ln Q - \ln A] \qquad (11)$$

where $A$ is Avogadro's number and $Q$ is calculated relative to the zero-point energy levels. In their calculations Woodley, *et al.*,[4] have included the contributions to the partition functions made by nuclear spin, $Q_{\text{nuc spin}} = \pi_i(2s_i + 1)$, for all nuclei. Since these must cancel out in the expression of both $k_H$ and $k_D$, and will not be taken into account in calculating $Q^{\ddagger}_{C_2H_7}/Q_{C_2H_5}$ or $Q^{\ddagger}_{C_2D_7}/Q_{C_2D_5}$, it was necessary to eliminate these from the data of Woodley, *et al.*,[4] in order to obtain the value of $Q_{D_2}/Q_{H_2}$ to be used here. In Table II are shown values of the free energy functions for various temperatures,[4] together with values of $Q_{D_2}/Q_{H_2}$, from which the $Q_{\text{nuc spin}}$ contributions have been removed.[5]

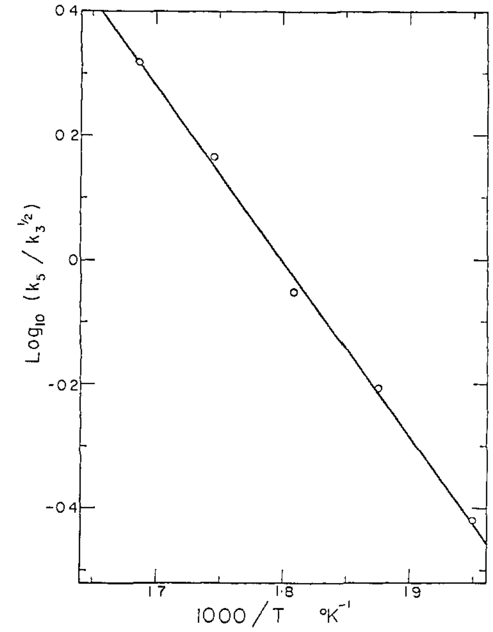

Figure 2. Arrhenius plot for $k_5/k_3^{1/2}$.

The translational components of the ratio lead to $(31/29)^{3/2}(38/34)^{-3/2}$, or a factor of 0.935 in the expression for $k_H/k_D$, independent of temperature. The rotational components will be assumed to cancel.

**Table II.** Free Energy Functions for $D_2$ and $H_2$ and Ratios of Their Partition Functions

| Temp, °K | $-[(G° - E_0°)/T]_{D_2}$,[a] cal mole⁻¹ deg⁻¹ | $-[(G° - E_0°)/T]_{H_2}$,[a] cal mole⁻¹ deg⁻¹ | $Q_{D_2}/Q_{H_2}$[b] |
|---|---|---|---|
| 300 | 32.161 | 27.217 | 5.35 |
| 400 | 34.142 | 29.175 | 5.41 |
| 500 | 35.683 | 30.702 | 5.45 |
| 600 | 36.946 | 31.955 | 5.48 |
| 700 | 38.018 | 33.018 | 5.50 |

[a] Reference 4. [b] Omitting zero-point energies and contributions from $Q_{\text{nuc spin}}$.

It is assumed that all the vibrational components of the partion functions for a complex will cancel those for the corresponding ethyl radical except for those re-

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(4) H. W. Woodley, R. B. Scott, and F. G. Brickweddle, *J. Res. Nat. Bur. Std.*, **41**, 387 (1948).

(5) The harmonic oscillator–rigid rotator approximation gives $Q_{D_2}/Q_{H_2} = 5.65$ without the nuclear spin contribution. Hence the error caused by this approximation is about 4% at 500°K.

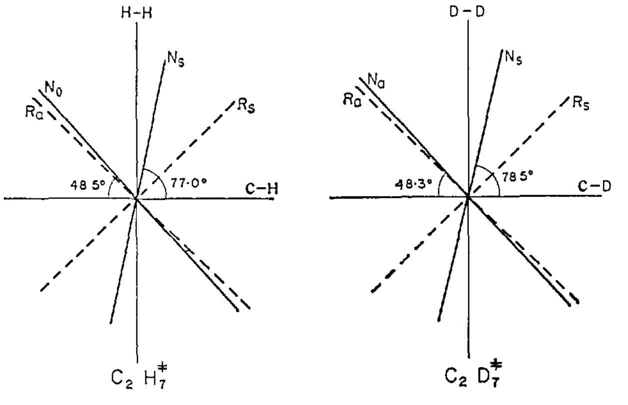

Figure 3. The normal coordinates $N_a$ and $N_s$ for $C_2H_7^{\ddagger}$ and $C_2D_7^{\ddagger}$, assuming $F_{11} = F_{22} = 2.68 \times 10^5$ dyn/cm and $F_{12} = 3.25 \times 10^5$ dyn/cm.

lated to the symmetric stretching, doubly degenerate bending and wagging vibrations associated with -C-H-H and -C-D-D; the asymmetric stretching vibrations are included in the Γ terms rather than $Q^{\ddagger}$, as these belong to the reaction coordinates. The complex will be treated as a linear three-atom system insofar as the stretching modes are concerned, and as a linear four-atom system in treating the bending and wagging motions, *viz.* $C_2H_5$-H-H and $CH_3$-$CH_2$-H-H, respectively. The wagging vibrations will be doubly degenerate. The Wilson *FG* matrix method[6] of vibrational analysis was made for this model.

The stretching force constant was estimated from Badger's rule,[7] $F = F_s n$, where $F_s$ is the force constant for the corresponding single bond and $n$ is the bond order. Using the values of $F_s$ given by Johnston[8] ($5.74 \times 10^5$ dyn cm$^{-1}$ for H-H; $5.00 \times 10^5$ dyn cm$^{-1}$ for C-H), and the bond orders estimated by the BEBO method[9] (0.43 for -H-H; 0.57 for -C-H-), the force constants $F_{11}$ and $F_{22}$ for the -H-H and -C-H- fractional bonds of the complex were found to be almost equal. To simplify the calculations we assumed they were equal and used the average value $F_{11} = F_{22} = 2.68 \times 10^5$ dyn cm$^{-1}$. The interaction force constant $F_{12} = 3.25 \times 10^5$ dyn cm$^{-1}$ was estimated from the potential energy function obtained by the BEBO method.[9]

Johnston's bending and wagging force constants[8] ($0.13 \times 10^{-11}$ and $0.26 \times 10^{-11}$ erg radian$^{-2}$, respectively) were used for the *F* matrix. The length of a bond of a given order (0.94 Å for -H-H; 1.28 Å for -C-H-) was calculated by Pauling's rule[10] for the *G* matrix. The calculated vibrational frequencies are shown in Table III.

In Figure 3 are shown the results of the normal mode analysis[3] using the force constants obtained above. At the saddle point, the normal coordinates $N_s$ and $N_a$ for symmetric and asymmetric stretching are expressed in terms of the bond distances. In spite of the very large asymmetry of the complexes with respect to the reaction center, the normal coordinates for asymmetric stretching of the complexes are found to be at an angle of about 48–49°, which is very close to the value obtained for D-H-H.[3] The angles for $N_s$ were found to be very large compared to 45°; however, this would not have any effect on $Q^{\ddagger}$.

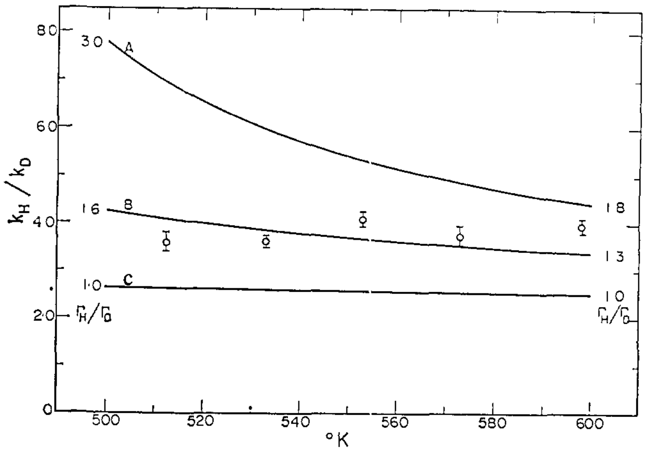

Figure 4. Calculated and observed rate constants ratio, $k_H/k_D$, with quantum correction, $\Gamma_H/\Gamma_D$. Theoretical values are obtained assuming $F_{11} = F_{22} = 2.68 \times 10^5$ dyn/cm and $F_{12} = 3.59$ (A), 3.25 (B), and $2.68 \times 10^5$ dyn/cm (C).

Table III. Calculated Frequencies for the Symmetric Stretching, Asymmetric Stretching, Bending and Wagging Vibrations of $C_2H_7^{\ddagger}$ and $C_2D_7^{\ddagger}$,[a] and Tunneling Factors at 550°K

| Complex | $\nu_s$, cm$^{-1}$ | $\nu_a$, cm$^{-1}$ | $\nu_b$, cm$^{-1}$ | $\nu_w$, cm$^{-1}$ | Γ at 550°K |
|---|---|---|---|---|---|
| $C_2H_7^{\ddagger}$ | 2252 | 1468i | 1001 | 586 | 1.99 |
| $C_2D_7^{\ddagger}$ | 1641 | 1054i | 710 | 447 | 1.39 |

[a] $F_{11} = F_{22} = 2.68 \times 10^5$ dyn cm$^{-1}$; $F_{12} = 3.25 \times 10^5$ dyn cm$^{-1}$; $F_b = 0.13 \times 10^{-11}$ erg radian$^{-2}$; $F_w = 0.26 \times 10^{-11}$ erg radian$^{-2}$.

The vibrational partition function component of the quantity $(Q^{\ddagger}_{C_2H_7}/Q_{C_2H_5})/(Q^{\ddagger}_{C_2D_7}/Q_{C_2D_5})$ in eq 10 was calculated using the harmonic oscillator approximation

$$\frac{\Omega_H}{\Omega_D} = \frac{(1 - e^{-\theta_s/T})_H^{-1}\,(1 - e^{-\theta_b/T})_H^{-2}\,(1 - e^{-\theta_w/T})_H^{-2}}{(1 - e^{-\theta_s/T})_D^{-1}\,(1 - e^{-\theta_b/T})_D^{-2}\,(1 - e^{-\theta_w/T})_D^{-2}} \qquad (12)$$

where $\theta = hc\nu/k$ and s, b, and w refer to the symmetric stretching, bending, and wagging vibrations.

The quantum corrections $\Gamma_H$ and $\Gamma_D$ were approximated by the relation

$$\Gamma = (|\theta_a|/2T)/\sin(|\theta_a|/2T) \qquad (13)$$

where a refers to the asymmetric vibration.[3,9,11]

Since most of the potentials and zero-point energies are assumed to be the same in a complex and in the corresponding ethyl radical, and since the potential energy along the reaction path will be the same for the two isotopic reactions, the numerator of the exponent in eq 10 will be given by

$$(\Delta E_0{}^{\circ})_D - (\Delta E_0{}^{\circ})_H = R[(\theta_s/2 + \theta_b + \theta_w)_D - (\theta_s/2 + \theta_b + \theta_w)_H] - [ZPE(D_2) - ZPE(H_2)] \qquad (14)$$

Using the data of Table III and exact spectroscopic values for $D_2$ and $H_2$, $(\Delta E_0{}^{\circ})_D - (\Delta E_0{}^{\circ})_H = -2.11 - (-1.79) = -0.32$ kcal mole$^{-1}$.

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(6) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(7) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1933); **3**, 710 (1934).

(8) H. S. Johnston, *Advan. Chem. Phys.*, **3**, 131 (1960).

(9) H. S. Johnston, "Gas Phase Reaction Rate Theory," The Ronald Press Co., New York, N. Y., 1966, p 339 ff.

(10) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(11) R. P. Bell, *Trans. Faraday Soc.*, **55**, 1 (1959).

The calculated values of $k_H/k_D$ are plotted in Figure 4. Curve B corresponds to the parameters found from the BEBO calculations described above. Variation of $F_{12}$ above and below the value $3.25 \times 10^5$ dyn cm$^{-1}$ (while keeping $F_{11} = F_{22}$ constant) had little effect on $\nu_s$, but a rather strong effect on $\nu_a$, and hence on $\Gamma$. For $F_{12} = 2.68 \times 10^5$ dyn cm$^{-1}$, very little tunneling is predicted for either reaction.

It does not seem possible, using a transition state theory model, to account for the apparent increase in $k_H/k_D$ with temperature found experimentally. The assumption of tunneling accentuates the apparent discrepancy in the slopes. However, the magnitude of $k_H/k_D$ found experimentally can best be explained, at least within the framework of transition state theory, if tunneling is assumed to occur.

The difference in the Arrhenius activation energies of the two reactions was calculated from the relation

$$(E_A)_H - (E_A)_D = -R\,\mathrm{d}\ln(k_H/k_D)/\mathrm{d}(1/T) \qquad (15)$$

The values were quite sensitive to the force constants assumed, and particularly to $F_{12}$, and hence the frequency of the asymmetric vibration. They varied from 0.3 kcal mole$^{-1}$ for $F_{12} = 2.68 \times 10^5$ dyn cm$^{-1}$ to $-0.9$ kcal mole$^{-1}$ for $F_{12} = 3.25 \times 10^5$ dyn cm$^{-1}$, which can be compared to the observed value of $0.8 \pm 0.7$.

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# Kinetics of the Thermal Decomposition of 1-Methylcyclopentene[1]

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**Abstract:** The thermal decomposition of 1-methylcyclopentene has been investigated over the temperature region 470–512° and a pressure range of 5–18 mm. The major products in the early stages of the pyrolysis were hydrogen and methylcyclopentadiene isomers. Other products found in small amounts were ethene, 2-methylpropene, methane, cyclopentene, cyclopentadiene, and 3-methylcyclopentene. The rate of pressure increase followed closely, but not exactly, the behavior of a first-order reaction. The reaction did not appear to be affected by the addition of propene or nitric oxide, or an increase in the surface to volume ratio by a factor of 7. The quantitative results indicated that in the initial portion of the pyrolysis the rate of disappearance of 1-methylcyclopentene was about equal to the rate of pressure increase. The first-order constant for the rate of pressure increase can be expressed as $k = (2.64 \pm 0.12) \times 10^{13} \exp(-60{,}000/RT)$ sec$^{-1}$. Approximately 90% of the pressure increase was due to hydrogen and methylcyclopentadiene, with a slightly greater amount of methylcyclopentadiene.

Thermal gas-phase reactions where a molecular detachment of hydrogen appears to be the predominant process have been receiving attention recently. Cyclopentene,[3] 2,5-dihydrofuran[4a] and its 2-methyl derivative,[4b] and 1,4-cyclohexadiene[5a–c] and its 1-methyl[5d] and 3-methyl[5e] derivatives undergo dehydrogenation as the major, if not sole, reaction. As a part of a continuing investigation in this laboratory of this type of reaction, a study of the kinetics of the thermal decomposition of 1-methylcyclopentene was undertaken.

## Experimental Section

**Materials.** 1-Methylcyclopentene was purchased from the Aldrich Chemical Co. and was purified further by gas chromatography. Subsequent analysis using a Perkin–Elmer 154D chromatograph with a Golay "R" column showed that the purified compound had a purity greater than 99.9%. The mass spectrum and gas-phase infrared spectrum of the purified sample were in good agreement with the corresponding spectra (liquid phase for the infrared spectra) previously reported.[6] A mixture of the methylcyclopentadiene isomers was prepared by cracking the dimer (Aldrich Chemical Co.) over glass helicies followed by redistillation with further purification by gas chromatography. The retention times of the 1- and 2-methylcyclopentadiene from the unpurified mixture (relative to cyclopentadiene) were in good agreement with previous reports with a dimethylsulfolane column.[7] Also the relative ratio of 1-methylcyclopentadiene to 2-methylcyclopentadiene for an unpurified mixture was 0.82, in satisfactory agreement with prior values. The ultraviolet spectrum (made with a Beckman DU spectrophotometer) in Mallinckrodt SpectrAR *n*-heptane of purified methylcyclopentadienes exhibited a maximum at 248 m$\mu$, which agrees with the results of Mironov and coworkers.[8]

Matheson Co. 2-methylpropene and K & K Laboratories 3-methylcyclopentene were purified by gas chromatography. Cyclopentene, purchased from the National Bureau of Standards with a stated purity of 99.97%, was used after outgassing. Cyclopentadiene, which had been prepared from Kodak technical grade dicyclopentadiene, was provided by D. Knecht of this laboratory. Deuterated cyclopentadiene supplied by Merck Sharp and Dohme of Canada was used without further purification. The amounts of the various deuterated isomers (analysis provided by the supplier) were: cyclopentene-$d_8$ 72.43%, cyclopentene-$d_7$ 23.32%,

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[1] This work was supported in part by a grant from the National Science Foundation.

[2] Abstracted in part from the Ph.D. Thesis of N. H. Turner, University of Rochester, 1968.

[3] (a) D. W. Vanas and W. D. Walters, *J. Am. Chem. Soc.*, **70**, 4035 (1948); (b) H. Tanji, M. Uchiyama, A. Amano, and H. Tokuhisa, *Kogyo Kagaku Zasshi*, **70**, 307 (1967); (c) D. A. Knecht, Ph.D. Thesis, University of Rochester, 1968.

[4] (a) C. A. Wellington and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 4888 (1961); (b) T. L. James and C. A. Wellington, *J. Chem. Soc.*, *A*, 2398 (1968).

[5] (a) R. J. Ellis and H. M. Frey, *ibid.*, 553 (1966); (b) M. S. Mutter and S. M. E. Kellner, Northern New England Academy of Science Bulletin, May 1966, p 3; (c) S. W. Benson and R. Shaw, *Trans. Faraday Soc.*, **63**, 985 (1967); (d) H. M. Frey and D. H. Lister, *J. Chem. Soc.*, *A*, 509 (1967); (e) *ibid.*, 1800 (1967).

[6] American Petroleum Institute Research Project 44: (a) Mass Spectrum Serial No. 1286; (b) Infrared Spectra Serial No. 1834 and 1835.

[7] (a) S. M. Csicsery, *J. Org. Chem.*, **25**, 518 (1960); (b) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2312, 2329 (1965).

[8] V. A. Mironov, E. V. Sobolov, and A. N. Elizarova, *ibid.*, **19**, 1939 (1963).