

# Kinetic Isotope Effects for Hydrogen Abstraction from a Series of Cycloalkanes and Branched Alkanes by Hydrogen Atoms in the Gaseous Phase

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**Abstract:** Hydrogen atoms produced in the radiolysis of water vapor were used to determine the kinetic isotope effects for the reactions  $H \cdot + RH(RD) \rightarrow H_2(HD) + R \cdot [k_H(k_D)]$ , where RH is a perprotiated alkane and RD is the corresponding perdeuterated alkane. The alkanes studied include a homologous series of cycloalkanes, cyclopentane through cyclododecane, and isobutane, 2,3-dimethylbutane, 2,3,4-trimethylpentane, and neopentane. The results were expressed in terms of the Arrhenius-type equation  $k_H/k_D = A_H/A_D \exp[(E_D - E_H)(\text{kJ mol}^{-1})/RT]$ , over the temperature range of 363–463 K. The values for the ratio  $A_H/A_D$  range from 0.32 to 0.75, and the activation energy differences  $E_D - E_H$  vary from 6.8 to 11.0 kJ/mol, depending on the molecular structures of the reactants. The variation in the values of  $E_D - E_H$  was correlated with the bond dissociation energies of the C–H bond being broken. Theoretical calculations based on transition-state theory combined with the London–Eyring–Polanyi–Sato potential energy surfaces could reproduce the major features of the experimental results when tunnel effects were taken into consideration.

The primary kinetic isotope effects (KIEs) have been studied both theoretically and experimentally by a number of investigators,<sup>1a–5</sup> since they provide considerable insights into reaction mechanisms. However, it is not easy to find a relationship between the magnitude of the KIE and some property of the reactants from existing data. Only a few research groups<sup>6–8</sup> have been able to relate the variation in the magnitude of the KIEs to that in the thermodynamic properties of reactions.

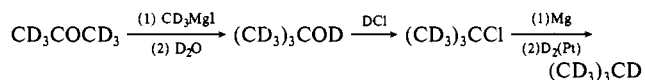
For some time we have been engaged in the studies of the KIE for hydrogen abstraction from saturated hydrocarbons by hydrogen atoms.<sup>9,10</sup> In the present work we have systematically determined the KIEs as a function of temperature for the reactions of hydrogen atoms with a series of cycloalkanes and some branched hydrocarbons. An attempt has been made to find a relationship between the variation in the magnitude of  $E_D - E_H$  values and the nature of structural changes in the organic reactants.

The study of the deuterium KIE also provides us with an opportunity of revealing the role played by the tunnel effect.<sup>1b,11</sup> We have tried a theoretical interpretation of our experimental results using transition-state theory<sup>12</sup> and found that tunnelling has to be included in order to interpret the transfer of light atoms such as hydrogen.

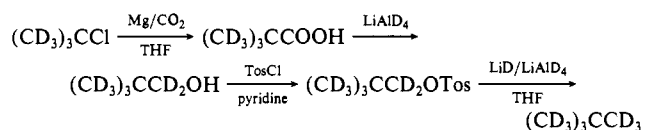
## Experimental Section

**A. Materials.** Triply distilled water was available from our previous works.<sup>9,10,13,14</sup> Most of the nondeuterated hydrocarbons were obtained

from commercial sources. The perdeuterated hydrocarbons, with the exception of isobutane-*d*<sub>10</sub> and neopentane-*d*<sub>12</sub>, were produced in a homemade exchange reactor.<sup>15,16</sup> The deuterated forms of isobutane and neopentane were prepared as follows. Isobutane-*d*<sub>10</sub>



Neopentane-*d*<sub>12</sub>



All of the deuterated and nondeuterated hydrocarbons were rigorously purified to >99.9% by preparative gas chromatography. The isotopic purities of the perdeuterated hydrocarbons were determined by mass spectrometry to be  $\geq 99\%$  D. The 100-MHz <sup>1</sup>H NMR spectrum of the deuterated isobutane was recorded to deduce the position of the H-atom impurity in this compound.<sup>17</sup> A comparison of the integrals of the NMR signals in the tertiary C–H region ( $\delta$  1.70) and primary C–H region ( $\delta$  0.90) indicated that the deuterium content of the tertiary group in the isobutane was greater than 98%. A similar NMR result was obtained for the deuterated 2,3-dimethylbutane. Corrections for the isotopic impurities were made in the kinetic treatment of experimental results.

**B. Irradiation and Product Analysis.** The value of the mole fraction of the deuterated compound in the hydrocarbon mixtures was usually 0.6, 0.7, 0.8, 0.9 and 1.0. In typical runs 0.50 g of water and a small amount of the hydrocarbon mixtures were admitted to a spherical Pyrex vessel of 0.5 L after degassing the samples. The samples were irradiated in a <sup>60</sup>Co  $\gamma$ -ray source at a dose rate of 0.5 Mrad/h to a total dose of 0.50 Mrad. The irradiation temperatures were 363, 393, 423, and 463 K unless otherwise specified. The isotopic hydrogen produced was collected by means of a Toepler pump and subsequently analyzed at 77 K by gas chromatography on a column packed with etched glass beads.<sup>18</sup>

## Results

**A. Reaction Mechanism.** The mechanisms for the  $\gamma$ -radiolysis of water vapor containing a small concentration of alkane have

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(17) We thank Dr. E. Gassmann for the measurements of NMR spectra.

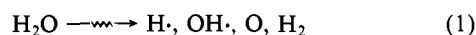
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**Table I.** Experimental Kinetic Isotope Effects for Abstraction of Hydrogen and Deuterium Atoms from Alkanes by Hydrogen Atoms

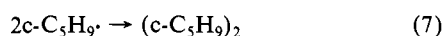
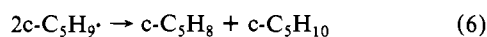
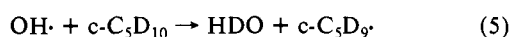
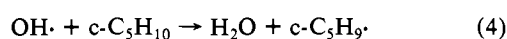
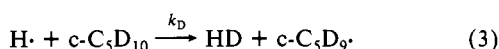
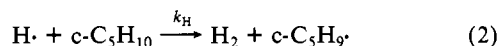
reaction	$k_H/k_D^d$		temp range, K	ref
	$A_H/A_D$	$(E_D - E_H), \text{kJ mol}^{-1}$		
H + neo-C <sub>5</sub> H <sub>12</sub> /neo-C <sub>5</sub> D <sub>12</sub> <sup>a</sup>	0.32 ± 0.04	11.00 ± 0.46	373–483	e
H + c-C <sub>5</sub> H <sub>10</sub> /c-C <sub>5</sub> D <sub>10</sub>	0.54 ± 0.04	9.00 ± 0.25	363–463	e
H + c-C <sub>6</sub> H <sub>12</sub> /c-C <sub>6</sub> D <sub>12</sub>	0.43 ± 0.03	9.67 ± 0.25	363–463	10
H + c-C <sub>7</sub> H <sub>14</sub> /c-C <sub>7</sub> D <sub>14</sub>	0.50 ± 0.04	9.00 ± 0.25	363–483	e
H + c-C <sub>8</sub> H <sub>16</sub> /c-C <sub>8</sub> D <sub>16</sub>	0.56 ± 0.03	8.45 ± 0.17	363–463	e
H + c-C <sub>10</sub> H <sub>20</sub> /c-C <sub>10</sub> D <sub>20</sub>	0.55 ± 0.05	8.41 ± 0.33	363–463	e
H + c-C <sub>12</sub> H <sub>24</sub> /c-C <sub>12</sub> D <sub>24</sub>	0.48 ± 0.05	9.29 ± 0.33	363–463	e
H + n-C <sub>6</sub> H <sub>14</sub> /n-C <sub>6</sub> D <sub>14</sub>	0.45 ± 0.04	9.46 ± 0.29	363–463	10
H + n-C <sub>7</sub> H <sub>16</sub> /n-C <sub>7</sub> D <sub>16</sub>	0.46 ± 0.05	9.37 ± 0.38	363–473	10
H + n-C <sub>8</sub> H <sub>18</sub> /n-C <sub>8</sub> D <sub>18</sub>	0.44 ± 0.06	9.58 ± 0.46	373–463	10
H + n-C <sub>9</sub> H <sub>20</sub> /n-C <sub>9</sub> D <sub>20</sub>	0.45 ± 0.03	9.54 ± 0.25	373–463	10
H + n-C <sub>10</sub> H <sub>22</sub> /n-C <sub>10</sub> D <sub>22</sub>	0.47 ± 0.03	9.41 ± 0.21	363–463	10
H + i-C <sub>4</sub> H <sub>10</sub> /i-C <sub>4</sub> D <sub>10</sub>	0.60 ± 0.11	7.78 ± 0.63	373–463	e
H + (CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> ) <sub>2</sub> / (CD <sub>3</sub> ) <sub>2</sub> CDCD(CD <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	0.70 ± 0.08	7.07 ± 0.38	363–463	e
H + (CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> )CH(CH <sub>3</sub> ) <sub>2</sub> / (CD <sub>3</sub> ) <sub>2</sub> CDCD(CD <sub>3</sub> )CD(CD <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	0.75 ± 0.05	6.82 ± 0.21	363–463	e

<sup>a</sup> Abbreviations of H + neo-C<sub>5</sub>H<sub>12</sub> → H<sub>2</sub> + C<sub>5</sub>H<sub>11</sub>· ( $k_H$ ) and H + neo-C<sub>5</sub>D<sub>12</sub> → HD + C<sub>5</sub>D<sub>11</sub>· ( $k_D$ ). <sup>b</sup> 2,3-Dimethylbutane. <sup>c</sup> 2,3,4-Trimethylpentane. <sup>d</sup>  $k_H/k_D = A_H/A_D \exp[(E_D - E_H)(\text{kJ mol}^{-1})/RT]$ . <sup>e</sup> This work.

been described at length in a previous publication.<sup>9</sup> In brief, H<sub>2</sub>O\*, H<sub>2</sub>O<sup>+</sup>, and e<sup>-</sup> are generated in the primary processes occurring during the radiolysis of water vapor, but subsequent unimolecular and bimolecular reactions of these species lead predominantly to H· and OH· radicals. Therefore, the radiolysis of water vapor may be depicted as follows



where H<sub>2</sub> refers to “unimolecular” hydrogen. The formation of both the oxygen atom and the unimolecular hydrogen are of minor importance here. In the presence of a small concentration of the protiated and deuterated hydrocarbon mixture, for instance, c-C<sub>5</sub>H<sub>10</sub> ~ c-C<sub>5</sub>D<sub>10</sub>, the H· and OH· radicals produced in reaction 1 efficiently undergo abstraction of H and D atoms from the additives at temperatures above ~360 K.



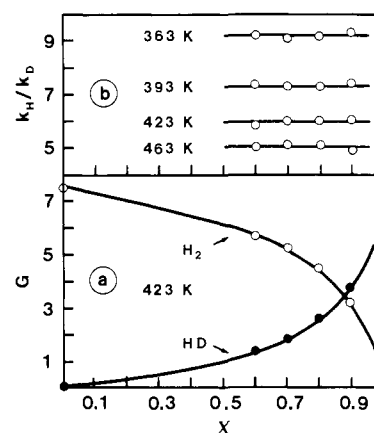
In the case where cyclopentane was taken as an additive, we have quantitatively measured not only hydrogen but also cyclopentene and bicyclopentyl yields,<sup>14</sup> and the material balance confirms the above scheme, i.e.,  $G(\text{hydrogen}) = G(\text{cyclopentene}) + G(\text{bicyclopentyl})$ .<sup>19</sup> Furthermore, we have shown that both the energy transfer from H<sub>2</sub>O\* to the hydrocarbon additive and the ion-molecule reaction between H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> and the additive can be excluded from the reaction scheme.<sup>9</sup>

**B. Kinetic Isotope Effects.** As typical results, the yields of H<sub>2</sub> and HD formed in the radiolysis of water vapor with 0.40 mol % c-C<sub>8</sub>H<sub>16</sub> ~ c-C<sub>8</sub>D<sub>16</sub> are shown in Figure 1a as a function of  $x$  where  $x = [\text{c-C}_8\text{D}_{16}]/([\text{c-C}_8\text{H}_{16}] + [\text{c-C}_8\text{D}_{16}])$ . It has been shown<sup>9</sup> that the H<sub>2</sub> and HD yields in Figure 1a can be presented by eq 8 and 9, respectively,

$$G(\text{H}_2) = g(\text{H}_2) + g(\text{H}) \frac{k_H[\text{c-C}_8\text{H}_{16}]}{k_H[\text{c-C}_8\text{H}_{16}] + k_D[\text{c-C}_8\text{D}_{16}] + k_Y[\text{Y}]} \quad (8)$$

$$G(\text{HD}) = g(\text{H}) \frac{k_D[\text{c-C}_8\text{D}_{16}]}{k_H[\text{c-C}_8\text{H}_{16}] + k_D[\text{c-C}_8\text{D}_{16}] + k_Y[\text{Y}]} \quad (9)$$

(19) The term  $G$  value stands for the number of molecules formed per 100 eV of energy absorbed by the system.



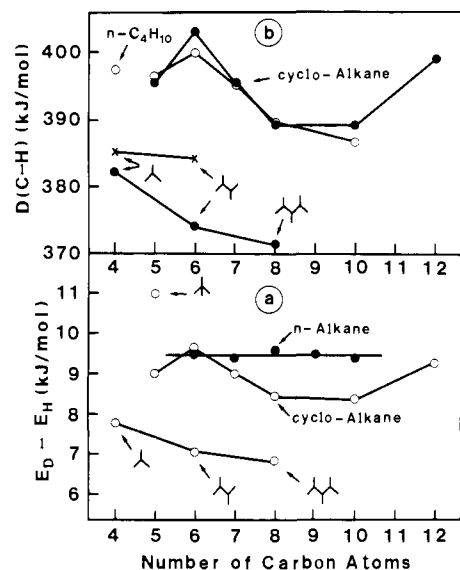
**Figure 1.** (a) The yields of H<sub>2</sub> and HD formed in the gas-phase radiolysis of H<sub>2</sub>O-(c-C<sub>8</sub>H<sub>16</sub>-c-C<sub>8</sub>D<sub>16</sub>) mixtures as a function of  $x$  where  $x = [\text{c-C}_8\text{D}_{16}]/([\text{c-C}_8\text{H}_{16}] + [\text{c-C}_8\text{D}_{16}])$ .  $G(\text{D}_2)$ , not shown, is less than 0.1 over the whole range of  $x$ . Dose = 0.50 Mrad,  $P = 1356$  torr,  $V = 0.54$  L, the total concentration of the added cyclooctane = 0.40 mol %. (b) The kinetic isotope effects at various temperatures calculated by eq 10.

where the measured yield is designated by  $G$  and the primary yield in water vapor by  $g$ . The  $g(\text{H}_2)$  is equal to the unimolecular hydrogen yield and amounts to 0.51.<sup>9,10</sup> The term  $k_Y[\text{Y}]$  means that some reaction intermediates such as OH· radicals compete with the added hydrocarbons for hydrogen atoms. Combination of eq 8 and 9 gives

$$\frac{k_H}{k_D} = \frac{G(\text{H}_2) - g(\text{H}_2)}{G(\text{HD})} \frac{[\text{c-C}_8\text{D}_{16}]}{[\text{c-C}_8\text{H}_{16}]} = \frac{G(\text{H}_2) - g(\text{H}_2)}{G(\text{HD})} \frac{x}{1-x} \quad (10)$$

Figure 1b illustrates the  $k_H/k_D$  values computed by applying eq 10 to the H<sub>2</sub> and HD yields obtained at different temperatures. The invariability of the  $k_H/k_D$  ratios over a large variation in  $x$  is indicative of the validity of eq 10. We have shown<sup>9</sup> that the  $k_H/k_D$  ratios calculated by eq 10 are influenced by both the concentration and percentage conversion of the added hydrocarbons. In order to obtain reliable  $k_H/k_D$  values the total doses must be small enough to make the change in the ratio  $[\text{c-C}_8\text{D}_{16}]/[\text{c-C}_8\text{H}_{16}]$  inappreciable. The additive concentration must also be small so that the effects of its direct radiolysis are negligible. Our experiments were performed under conditions which satisfied the above constraints.

Since the KIEs for various alkanes have been measured as a function of temperature as shown in Figure 1b, the ratios of  $A_H/A_D$  and the differences in activation energies  $E_D - E_H$  were deduced from the least-squares treatment of the experimental data. The



**Figure 2.** (a) The values of  $E_D - E_H$  vs. the number of carbon atoms in the saturated hydrocarbons. (b) The C-H bond dissociation energies vs. the number of carbon atoms.  $D(C-H)$  calculated by eq 11 (O), by eq 12 (X), and by eq 16 (●).

results are summarized in Table I along with the data previously determined for the reactions of hydrogen atoms with *n*-alkanes.<sup>10</sup>

## Discussion

**A. The Values of  $E_D - E_H$  and Molecular Structures.** To facilitate a comparison, the values of  $E_D - E_H$  listed in Table I are plotted in Figure 2a as a function of the number of carbon atoms present in the alkane. A rough classification of the  $E_D - E_H$  values into three groups seems to be possible (Figure 2a): the first group consists of only neopentane which exhibits a large  $E_D - E_H$  value for the abstraction of an H atom from a primary C-H bond. A homologous series of *n*-alkanes belongs to the second group which shows typical  $E_D - E_H$  values for abstraction from a secondary C-H bond. The third group includes branched alkanes; these are considered to yield representative  $E_D - E_H$  values for the tertiary C-H bond. This classification seems to suggest that the strength of C-H bonds being broken is a dominant factor in determining the magnitudes of  $E_D - E_H$  values, since the  $E_D - E_H$  values and the C-H bond strengths for the first, second, and third groups decrease congruently. We can assume a correlation between the strength of the C-H bond and the  $E_D - E_H$  value (see also under heading B). Thus, for example, the constant  $E_D - E_H$  value for various *n*-alkanes is interpreted to imply that abstraction of hydrogen takes place predominantly from the secondary hydrogens and that the average bond energies of the secondary hydrogen atoms scarcely depend on the chain lengths of the *n*-alkane studied.

**B. The Values for  $E_D - E_H$  for Cycloalkanes.** Figure 2a shows that an increase in the  $E_D - E_H$  value from cyclopentane to cyclohexane is followed by a decrease for cycloheptane and a further decrease for cyclooctane and then by an increase for cyclododecane. This variation in  $E_D - E_H$  is conjectured to be associated with the C-H bond strengths in the cycloalkanes. In fact, available bond energies<sup>20</sup> for cyclopentane, cyclohexane, and cycloheptane are respectively 394, 400, and 387 kJ/mol in line with the fact that within this group the largest  $E_D - E_H$  value is found for cyclohexane together with the strongest C-H bond.

For the medium ring compounds, reliable C-H bond energies are not available, but they can be inferred from the strain energies of the intermediates. It has been recognized by several investigators<sup>21,22</sup> that the ring strains have pronounced effects on the

**Table II.** C-H Bond Dissociation Energies

compound	strain energy, kJ mol <sup>-1</sup>		C-H bond energy, kJ mol <sup>-1</sup>		
	alkane	alkene <sup>c</sup>	exptl	eq 11	eq 16
c-C <sub>5</sub> H <sub>10</sub>	25.9 <sup>a</sup>	23.8 <sup>a</sup>	394.1 <sup>e</sup>	396.5	395.7
c-C <sub>6</sub> H <sub>12</sub>	0.0 <sup>a</sup>	5.4 <sup>a</sup>	399.6 <sup>e</sup>	400.2	403.2
c-C <sub>7</sub> H <sub>14</sub>	25.9 <sup>a</sup>	21.3 <sup>a</sup>	387.0 <sup>e</sup>	395.2	395.7
c-C <sub>8</sub> H <sub>16</sub>	40.2 <sup>a</sup>	24.3 <sup>a</sup>		389.6	389.6
c-C <sub>10</sub> H <sub>20</sub>	51.5 <sup>a</sup>	29.3 <sup>d</sup>		386.4	389.1
c-C <sub>12</sub> H <sub>24</sub>	16.7 <sup>a</sup>				399.0
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	0.0 <sup>a</sup>	0.0 <sup>a</sup>	397.5 <sup>e</sup>	397.5	
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	0.0 <sup>a</sup>	0.0 <sup>a</sup>	384.9 <sup>f</sup>	384.9 <sup>g</sup>	382.1 <sup>h</sup>
2,3-dimethylbutane	6.7 <sup>b</sup>	4.6 <sup>a</sup>		383.9 <sup>g</sup>	374.1 <sup>h</sup>
2,3,4-trimethylpentane	16.4 <sup>a</sup>				371.3 <sup>h</sup>

<sup>a</sup> Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970; pp 166, 571, 579, 580, 590. <sup>b</sup> Benson, S. W. "Thermochemical Kinetics"; John Wiley: New York, 1968; p 179. <sup>c</sup> The strain energy for the least strained alkene, if several isomeric alkenes are conceivable. <sup>d</sup> Hay, J. M. "Reactive Free Radicals"; Academic Press: London, 1974; p 83. <sup>e</sup> Reference 20. <sup>f</sup> Reference 25. <sup>g</sup> Equation 12. <sup>h</sup> Tertiary C-H bond.

reaction rates. Systematic studies of the effects of the strains on reaction rates led Brown to propose the I-strain (Internal strain) and the F-strain (Frontal strain) hypotheses,<sup>21,23</sup> for example. In the I-strain hypothesis the Arrhenius activation energy is considered to be largely influenced by the change in steric energy occurring during the course of the reaction. The differences in ring strains between the reactants and transition states are crucial factors which have considerable influence on the magnitude of the activation energies. Since we are unable to estimate the strain energies for activated complexes, it has become common practice to approximate them by means of the strain energy differences between the reactants and products. Thus, Stein and Rabinovitch<sup>24</sup> supposed that the C-H bond energies in cycloalkanes can be expressed in terms of the conventional strain energies (SE) in the reactant and product, viz,

$$D(\text{cycloalkane C-H}) = D(\text{standard secondary C-H}) + [\text{SE}(\text{cycloalkene}) - \text{SE}(\text{cycloalkane})]/2 \quad (11)$$

This equation includes the concept of the I-strain to a certain extent. In eq 11 the change in strain energy due to conversion from cycloalkane to cycloalkene carrying two sp<sup>2</sup> carbon atoms is assumed to be twice as large as that due to conversion from cycloalkane to the cycloalkyl radical with one sp<sup>2</sup> carbon atom. The C-H bond energies in the cycloalkanes are calculated with the aid of eq 11 and the use of a bond dissociation energy of 397.5 kJ/mol for a secondary hydrogen in *n*-butane<sup>20</sup> as  $D(\text{standard secondary C-H})$ . They are listed in Table II and plotted in Figure 2b. The correlation between the calculated C-H bond energies and  $E_D - E_H$  values is rather good from cyclopentane to cyclooctane, though it is less satisfactory for cyclodecane as can be seen in Figure 2b. This situation is presumably due to the lack of reliable strain energies needed for the calculation.

The magnitude of the  $E_D - E_H$  value is appreciably larger for isobutane than for congested molecules such as 2,3-dimethylbutane (2,3-DMB) and 2,3,4-trimethylpentane (2,3,4-TMP). This suggests that the tertiary C-H bond is stronger in isobutane than in 2,3-DMB and 2,3,4-TMP. We try to rationalize our findings by using an equation similar to eq 11. When applied to the tertiary C-H bond, eq 11 may be modified as follows

$$D(\text{tertiary C-H}) = D(\text{standard tertiary C-H}) + [\text{SE}(\text{alkene}) - \text{SE}(\text{alkane})]/2 \quad (12)$$

The bond strength of the *t*-C-H bonds in 2,3-DMB with double gauche interactions was estimated by taking the bond energy of 384.9 kJ/mol for the tertiary C-H bond in isobutane<sup>25</sup> as  $D$ -

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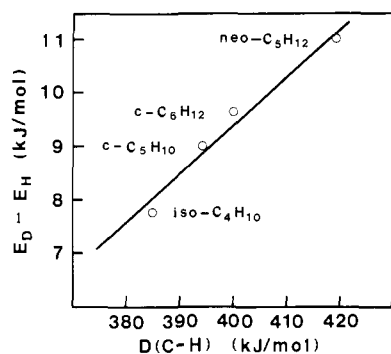


Figure 3. The linear relationship between  $E_D - E_H$  values and the C-H bond energies of the alkanes.

(standard tertiary C-H). The results are listed in Table II and shown in Figure 2b. Equation 12 indicates that the tertiary C-H bond is slightly weaker in 2,3-DMB than in isobutane in qualitative accord with the experimental findings.

**C. The Evans-Polanyi Relation.** For a series of related reactions, Evans and Polanyi derived an empirical linear relation between the activation energy  $E$  and the enthalpy change of reaction  $\Delta H_r$ . For the attack of hydrogen atoms on a C-H bond in the homologous series of the protiated alkanes, the change of enthalpy of reaction can be replaced by the bond dissociation energy  $D(\text{C-H})$  of the C-H bond involved

$$E_H = a_H[D(\text{C-H})] + b_H \quad (13)$$

where  $a_H$  and  $b_H$  are constants. Similarly, for the attack of H atoms on C-D bonds in the respective deuterated alkanes we have

$$E_D = a_D[D(\text{C-D})] + b_D \quad (14)$$

Subtraction of eq 13 from eq 14 leads to

$$E_D - E_H = a_D[D(\text{C-D})] - a_H[D(\text{C-H})] + b_D - b_H \quad (15)$$

$D(\text{C-D})$  should be larger than  $D(\text{C-H})$  by at least the amount corresponding to the difference in the zero-point energies between the C-D and C-H stretchings. Further details of the difference between  $D(\text{C-D})$  and  $D(\text{C-H})$  are not well-known. However, with the assumption that  $D(\text{C-D}) - D(\text{C-H}) = \text{constant}$  for a series of related alkanes, we arrive at a quasi-Evans-Polanyi type of equation

$$E_D - E_H = a[D(\text{C-H})] + b \quad (16)$$

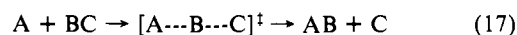
where  $a = (a_D - a_H)$  and  $b = (b_D - b_H) + (\text{constant}) a_D$ . Thus, we can expect a linear relation between  $D(\text{C-H})$  and  $E_D - E_H$  values unless  $a_D = a_H$ . In Figure 3 the experimental values of  $E_D - E_H$  are plotted vs. the known C-H bond energies for neo-C<sub>5</sub>H<sub>11</sub>-H,<sup>25</sup> c-C<sub>5</sub>H<sub>9</sub>-H,<sup>20</sup> c-C<sub>6</sub>H<sub>11</sub>-H,<sup>20</sup> and t-C<sub>4</sub>H<sub>9</sub>-H.<sup>25</sup> A good correlation is found. The values for  $a$  and  $b$  in eq 16 are determined to be  $0.089 \pm 0.013$  and  $-26.4 \pm 5.1$  kJ/mol from the least-squares analysis. It is worthwhile in this context to note that Johnston<sup>1a</sup> predicted theoretically the existence of a correlation between the magnitude of the  $k_H/k_D$  value and bond dissociation energy. Equation 16 can be of value in deducing unknown C-H bond energies of the alkanes from the experimental  $E_D - E_H$  values. Thus, estimation of the unknown secondary C-H bond energies for c-C<sub>7</sub>H<sub>14</sub> to c-C<sub>11</sub>H<sub>24</sub> as well as tertiary C-H bond energies for 2,3-DMB and 2,3,4-TMP are listed in the last column of Table II and plotted in Figure 2b by using eq 16. The C-H bond energies determined in this way for the cyclanes agree within  $\pm 3$  kJ/mol with those calculated from the consideration of strain energies, i.e., eq 11.

As seen in Figure 2b and Table II, the tertiary C-H bond energy calculated by the quasi-Evans-Polanyi relation, eq 16, is appreciably larger for isobutane than for 2,3-DMB and 2,3,4-TMP. If the tertiary C-H bond is stronger in isobutane than in

2,3-DMB and 2,3,4-TMP, it should be detectable, when one measures the Arrhenius activation energies for H abstraction by radical species other than hydrogen atoms. However, no conclusive results are known.<sup>26</sup>

Isobutane has nine primary hydrogen atoms and one tertiary hydrogen atom, and when adopting the recommended rate constants for H abstraction from the primary and tertiary C-H bonds in alkanes by hydrogen atoms,<sup>27</sup> one can estimate that at a temperature of 423 K the tertiary hydrogen atom in isobutane contributes about 93% to the reaction. Therefore, to a good approximation the experimental  $E_D - E_H$  value for isobutane is thought to represent the value for abstraction of a tertiary hydrogen atom from isobutane. Similar conclusions also apply to 2,3-DMB and 2,3,4-TMP.<sup>28</sup>

**D. Theoretical Calculation of the Kinetic Isotope Effects.** One of the strong points of the transition-state theory is its capability of allowing quantitative predictions of the kinetic isotope effect. We have recently carried out the theoretical estimation of the KIE for H abstraction from cyclohexane by hydrogen atoms within the framework of transition-state theory<sup>1a-3,12</sup> and found good agreement between experimental and calculated  $k_H/k_D$  values.<sup>10</sup> An attempt is made in the present work to calculate the KIE for H-abstraction reactions from primary hydrogen in neopentane and tertiary hydrogen in isobutane. To calculate the theoretical KIE based on transition-state theory we have to know all the vibrational frequencies for the reactant and the activated complex. However, in order to simplify the calculation, we use a simple collinear three-atom model<sup>10</sup> depicted by



where A stands for an attacking hydrogen atom, B is the atom undergoing the metathesis reaction, and C is considered to be a structureless alkyl group. The theoretical formula of the KIE for the aligned three-atom model takes the form<sup>1a-3</sup>,

$$\frac{k_H}{k_D} = \frac{\nu_{iH}}{\nu_{iD}} \left( \frac{\Gamma_H}{\Gamma_D} \right)^* \left( \frac{\Gamma_{sH}\Gamma_{bH}}{\Gamma_{sD}\Gamma_{bD}} \right)^\ddagger \left( \frac{\Gamma_{sD}}{\Gamma_{sH}} \right)^r \quad (18)$$

where  $\nu_i$  is the imaginary frequency corresponding to motion along the reaction coordinate,  $\Gamma^*$  represents the tunnel correction factor,  $\Gamma^\ddagger$  and  $\Gamma^r$  denote quantum correction factors for each of the real vibrations of the activated complex and reactant and are of the form  $\Gamma = (u/2)/\sinh(u/2)$  with  $u = h\nu/kT$ , and subscripts s and b refer to the stretching and bending vibrations. The first step in setting up the theoretical calculation is to construct the potential energy surface for the reaction. For this purpose, use is made of the semiempirical London-Eyring-Polanyi-Sato (LEPS) equation<sup>1c,10</sup> which is computationally convenient. The LEPS potential energy surface with a single adjustable parameter is given by

$$V = \frac{U_1 + U_2 + U_3 - (J_1^2 + J_2^2 + J_3^2 - J_1J_2 - J_2J_3 - J_3J_1)^{1/2}}{1 + \zeta} \quad (19)$$

where  $\zeta$  means formally the overlap integral (Sato parameter) and  $U$  and  $J$  are well defined elsewhere.<sup>1c,10</sup> One can calculate the LEPS potential with a few physicochemical constants of the reactant and product. Table III summarizes the molecular properties needed such as the bond dissociation energy  $D^\circ_{298}$ , the C-H stretching frequencies  $\nu_s$ , and the equilibrium internuclear

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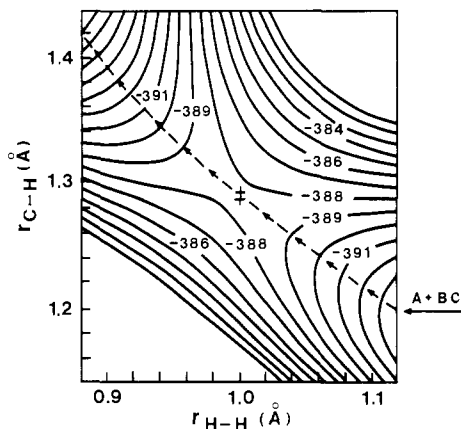
(28) Admitting the recommended rate constants for hydrogen abstraction from the primary and secondary C-H bonds in *n*-alkanes by hydrogen atoms,<sup>27</sup> it is estimated that only 6% of hydrogen abstraction from *n*-hexane takes place from the primary C-H bonds at 423 K. Consequently, the experimental value of  $E_D - E_H$  for *n*-hexane is considered to reflect the value for hydrogen abstraction from the secondary C-H bonds. Needless to say, H abstraction from the primary C-H bonds in *n*-alkanes becomes less important in going from *n*-hexane to *n*-decane.

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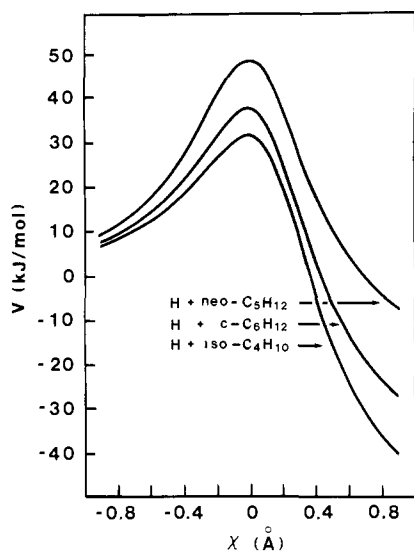
**Table III.** Molecular Properties of neo-C<sub>5</sub>H<sub>11</sub>-H, c-C<sub>6</sub>H<sub>11</sub>-H, t-C<sub>4</sub>H<sub>9</sub>-H, and H-H

property	neo-C <sub>5</sub> H <sub>11</sub> -H	c-C <sub>6</sub> H <sub>11</sub> -H <sup>a</sup>	t-C <sub>4</sub> H <sub>9</sub> -H	H-H <sup>a</sup>
$D_0^{298}$ , kJ mol <sup>-1</sup>	419.66 <sup>d</sup>	399.57	384.93 <sup>d</sup>	431.56
$\bar{\nu}_3$ , cm <sup>-1</sup>	2959 <sup>e</sup> (2218)	2933 (2206)	2880 <sup>e</sup> (2067)	4395.2
$D_e$ , kJ mol <sup>-1 a</sup>	437.36	417.1	402.17	457.86
$r_0$ , Å	1.114 <sup>f</sup>	1.119	1.122 <sup>h</sup>	0.7417
$\beta$ , Å <sup>-1</sup>	1.817	1.844	1.844	1.9420
$\zeta^c$	0.10	0.10	0.10	0.10

<sup>a</sup>  $D_e = D_0^{298} + \text{ZPE}$ . <sup>b</sup> Morse parameter;  $\beta = 1.2177 \times 10^7 \times \bar{\nu}_3 \times (\mu/D_e)^{1/2}$ ,  $\mu = (m_H m_C)/(m_H + m_C)$ , and  $D_e$  in cm<sup>-1</sup> unit. <sup>c</sup> Sato parameter. <sup>d</sup> Reference 25. <sup>e</sup> C-H stretching frequency, C-D stretching frequency in parentheses. Pinchas, S.; Lailicht, I. "Infrared Spectra of Labeled Compounds"; Academic Press: London, 1971; pp 78 and 79. <sup>f</sup> Jacob, E. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1967**, *47*, 3736-3753. <sup>g</sup> Reference 10. <sup>h</sup> Lifson, S.; Stern, P. S. *J. Chem. Phys.* **1982**, *77*, 4542-4550.



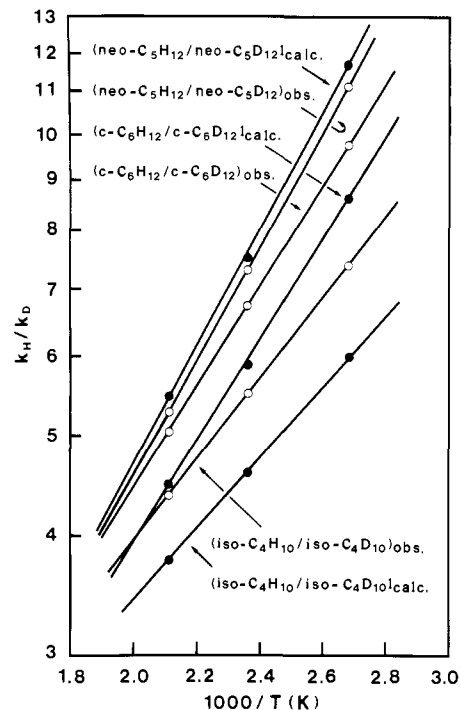
**Figure 4.** Potential energy contour map for the collinear reaction  $\text{H} + \text{neo-C}_5\text{H}_{12} \rightarrow \text{H}_2 + \text{neo-C}_5\text{H}_{11}$ , calculated according to the LEPS method. The solid lines are equipotentials, and the dashed line shows the reaction path. The contour lines are at 1.0-kJ/mol intervals.



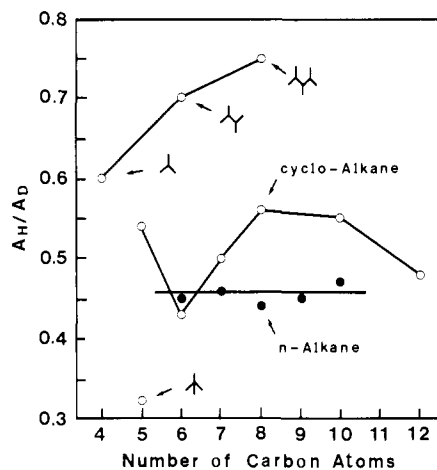
**Figure 5.** LEPS potential energy profiles as a function of distance  $\chi$  along the reaction path from the saddle point of the surface.

distance  $r_0$ . As an example we illustrated in Figure 4 the potential energy surface for the reaction of a hydrogen atom with neopentane calculated by the LEPS method. Table IV lists the properties of the activated complexes which were obtained by the standard analyses<sup>1c,10</sup> of the LEPS surfaces.

The tunnel correction factors  $\Gamma^*$  were calculated by the procedures described in a previous work.<sup>10</sup> In brief, the LEPS potential energy profiles along the reaction path were first delineated as shown in Figure 5. Then, the LEPS profiles were substituted



**Figure 6.** Observed and theoretically calculated kinetic isotope effects vs. the reciprocal of the absolute temperature.



**Figure 7.**  $A_H/A_D$  ratios vs. the number of carbon atoms in the alkanes.

by idealized Eckart potentials<sup>29</sup> for which the transmission coefficients can be computed exactly. Throughout the tunnel calculations, we use the relationship

$$V_1 = V^\ddagger + \text{ZPE}(\text{activated complex}) - \text{ZPE}(\text{reactant})$$

where  $V^\ddagger$  is the so-called electronic potential energy of activation<sup>1c</sup> and

$$V_2 = V^\ddagger + \Delta D_e + \text{ZPE}(\text{activated complex}) - \text{ZPE}(\text{product})$$

where  $\Delta D_e = D_e(\text{product}) - D_e(\text{reactant})$ . The tunnel correction  $\Gamma^*$  is very sensitive to the imaginary frequency  $\nu_i$  and the potential barrier height  $V^\ddagger$ . The tunnel correction contribution increases with increasing  $\nu_i$  and  $V^\ddagger$ . As seen in Table IV, the imaginary frequencies are always much higher for protiated than for deuterated activated complexes. This indicates qualitatively that the tunnel correction is more important in the hydrogen than in the deuterium abstraction. Note that we acknowledge the approximate nature of our calculation of the tunnel corrections. In the three-atom model we are apt to overestimate the tunnel effects. If the CH<sub>2</sub> bending, wagging, and twisting frequencies in the

**Table IV.** Properties of the Activated Complexes for the Collinear Three-Atom Model  $A + BC \rightarrow AB + C^a$ 

property	H $\cdots$ H $\cdots$ neo-C <sub>5</sub> H <sub>11</sub>	H $\cdots$ D $\cdots$ neo-C <sub>5</sub> D <sub>11</sub>	H $\cdots$ H $\cdots$ c-C <sub>6</sub> H <sub>11</sub>	H $\cdots$ D $\cdots$ c-C <sub>6</sub> D <sub>11</sub>	H $\cdots$ H $\cdots$ <i>i</i> -C <sub>4</sub> H <sub>9</sub>	H $\cdots$ D $\cdots$ <i>i</i> -C <sub>4</sub> D <sub>9</sub>
$V^\ddagger$ , kJ mol <sup>-1</sup>	49.231	49.231	38.014	38.014	31.709	31.709
$r_{AB}^\ddagger$ , Å	0.9968	0.9968	1.0479	1.0479	1.0932	1.0932
$r_{BC}^\ddagger$ , Å	1.2916	1.2916	1.2563	1.2563	1.2356	1.2356
$F_{AB}^\ddagger$ , mdyne/Å	0.306	0.306	0.081	0.081	-0.043	-0.043
$F_{BC}^\ddagger$ , mdyne/Å	0.981	0.981	1.433	1.433	1.742	1.742
$F_{AC}^\ddagger$ , mdyne/Å	1.640	1.640	1.492	1.492	1.334	1.334
$F_{\phi}^\ddagger$ , 10 <sup>11</sup> erg/rad <sup>2</sup>	0.081	0.081	0.073	0.073	0.067	0.067
$\bar{\nu}_s$ , cm <sup>-1</sup>	1329	1268	1334	1239	1361	1233
$\bar{\nu}_b$ , cm <sup>-1</sup>	756	598	704	554	659	517
$\bar{\nu}_i$ , cm <sup>-1</sup>	2113i	1622i	1978i	1560i	1819i	1470i

<sup>a</sup> Calculated by using the LEPS potential energy surfaces with  $\zeta = 0.10$ .

**Table V.** Experimental and Theoretically Calculated Kinetic Isotope Effects

<i>T</i> , K	$(k_H/k_D)_{\text{exptl}}$	$(k_H/k_D)_{\text{calcd}}^a$	$(k_H/k_D)_{\text{calcd}}^b$
	H + neo-C <sub>5</sub> H <sub>12</sub> /neo-C <sub>5</sub> D <sub>12</sub>		
373	11.11	11.70	2.99
423	7.30	7.51	2.69
473	5.25	5.47	2.46
	H + <i>c</i> -C <sub>6</sub> H <sub>12</sub> / <i>c</i> -C <sub>6</sub> D <sub>12</sub>		
373	9.72	8.62	2.80
423	6.72	5.87	2.53
473	5.03	4.46	2.33
	H + <i>i</i> -C <sub>4</sub> H <sub>10</sub> / <i>i</i> -C <sub>4</sub> D <sub>10</sub>		
373	7.37	5.97	3.03
423	5.48	4.58	2.69
473	4.34	3.75	2.44

<sup>a</sup> Calculated including the tunnel correction terms  $\Gamma_H^*/\Gamma_D^*$ .

<sup>b</sup> Calculated excluding the tunnel correction terms  $\Gamma_H^*/\Gamma_D^*$ .

reactant alkanes appreciably decrease in forming the activated complexes, it also tends to make  $k_H/k_D$  values larger. Then, the observed large KIEs have to be rationalized in part by the decreases in the vibrational frequencies for bending, wagging, and twisting in going from reactant to transition state.

Table V summarizes the temperature dependence of the theoretical  $k_H/k_D$  values. The  $k_H/k_D$  values calculated by omitting the tunnel corrections are too small compared to the experimental values, and the characteristic magnitudes of the  $k_H/k_D$  values for H abstraction from the primary, secondary, and tertiary C-H bonds are not reflected at all. In Figure 6 the experimental results are compared with the theoretical values calculated by including the tunnel correction terms. Agreement between the experimental and theoretical values is satisfactory, although appreciable discrepancy exists between the experimental and calculated values in the case of isobutane. An important conclusion in the present work is that the good agreement between the experimental and theoretical values is attained only when the tunnel corrections are taken into consideration. It is worth mentioning that the Sato parameter  $\zeta$  is kept constant in going from neopentane through

cyclohexane to isobutane. If we were to adjust the Sato parameter from reaction to reaction, the predictive value of the semiempirical LEPS method is largely diminished.

The electronic activation energies  $V^\ddagger$  calculated with  $\zeta = 0.10$  are 49.2, 38.0, and 31.7 kJ/mol for the reaction of H atoms with neopentane, cyclohexane, and isobutane, respectively, as shown in Table IV. These calculated activation energies are higher than the experimental Arrhenius activation energies<sup>27</sup> by 5~10 kJ/mol. However, the electronic activation energy  $V^\ddagger$  is connected to the Arrhenius activation energy through a complicated equation.<sup>1a,10</sup> Thus, we do not necessarily have a one-to-one correspondence between them. It is still hard work to theoretically elucidate the relationship between the electronic and the Arrhenius activation energy, especially when the tunnel effects play important roles. In our calculations the Sato parameters were chosen in such a way that the experimental and theoretical  $k_H/k_D$  values for neopentane agree well with each other.

Figure 7 shows the variation in  $A_H/A_D$  values with the molecular structures. The  $A_H/A_D$  values are mirror images of the  $E_D - E_H$  values shown in Figure 2a. That is, the larger is the  $E_D - E_H$  value the smaller is the  $A_H/A_D$  ratio. This trend also supports the occurrence of tunnelling, since the tunnel effects tend to make the values of  $E_D - E_H$  greater and the ratios  $A_H/A_D$  smaller.<sup>11</sup> A ratio of  $A_H/A_D$  smaller than 1/2 is frequently cited as a criterion for the occurrence of the tunnel effect. As a matter of fact, many of the  $A_H/A_D$  ratios listed in Table I are less than 1/2 and satisfy the above criterion. Further quantitative discussion of the  $A_H/A_D$  ratio is possible<sup>1a</sup> but beyond the scope of the present work.

**Acknowledgment.** The authors thank M. Goël for analyses of isotopic hydrogens. They also acknowledge H. Öz and A. Heusler for synthesizing the perdeuterated compounds. This work was supported by a grant from the Swiss National Science Foundation.

**Registry No.** neo-C<sub>5</sub>H<sub>12</sub>, 463-82-1; *c*-C<sub>5</sub>H<sub>10</sub>, 287-92-3; *c*-C<sub>6</sub>H<sub>12</sub>, 110-82-7; *c*-C<sub>7</sub>H<sub>14</sub>, 291-64-5; *c*-C<sub>8</sub>H<sub>16</sub>, 292-64-8; *c*-C<sub>10</sub>H<sub>20</sub>, 293-96-9; *c*-C<sub>12</sub>H<sub>24</sub>, 294-62-2; *n*-C<sub>6</sub>H<sub>14</sub>, 110-54-3; *n*-C<sub>7</sub>H<sub>16</sub>, 142-82-5; *n*-C<sub>8</sub>H<sub>18</sub>, 111-65-9; *n*-C<sub>9</sub>H<sub>20</sub>, 111-84-2; *n*-C<sub>10</sub>H<sub>22</sub>, 124-18-5; *i*-C<sub>4</sub>H<sub>10</sub>, 75-28-5; (C-H<sub>3</sub>)<sub>2</sub>CHCH(CH<sub>3</sub>)<sub>2</sub>, 79-29-8; (CH<sub>3</sub>)<sub>2</sub>CHCH(CH<sub>3</sub>)CH(CH<sub>3</sub>)<sub>2</sub>, 565-75-3; H<sub>2</sub>, 1333-74-0; D<sub>2</sub>, 7782-39-0; H<sub>2</sub>O, 7732-18-5; H, 12385-13-6.