Absolute Rate Constants for the Addition of Atomic Hydrogen to Monosubstituted and Trisubstituted Olefins

Dennis D. Tanner,* Liying Zhang,¹ and Pramod Kandanarachchi²

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received: January 22, 1996[®]

A mechanism is established for the formation of the products resulting from the solution phase regioselective addition of atomic hydrogen to 1-methylcyclohexene. From this data and new data for the reactions of 1-octene, the absolute rates and activation parameters for the addition of hydrogen atom to an olefin can be extracted. A method was established to determine the absolute rate of addition of a hydrogen atom to a terminal olefin in the solution phase. The addition rate constants, k_a (25 °C), to 1-octene [$k_a = (4.2 \pm 3.6) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$] and 1-methylcyclohexene [$k_a = (4.6 \pm 0.8) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, -78 °C] are found to be in reasonable agreement with the published values for the vapor phase rate of addition to ethylene. The large rate constants are supported by the observation that the activation parameters ($E_a = 5.3 \pm 2.9 \text{ kcal/mol and } \log A = 14 \pm 3.5 \text{ M}^{-1} \text{ s}^{-1}$ for 1-octene) are consistent with the values expected for this fast reaction.

Introduction

Recently we published the results of a study of the mechanism of formation of the products resulting from the addition of atomic hydrogen to 1-octene.³ One of the products, octane, was formed from the reaction of hydrogen with the 1-methylheptyl radical:

$$+ H \cdot (H_2) \xrightarrow{k_c} + (H \cdot)$$
 (1)

The capping reaction, eq 1, was only ambiguously defined since the concentration of atomic hydrogen in this bimolecular reaction was estimated to be too low to account for the formation of the products, and the activation energy for the reaction of a secondary radical with molecular hydrogen defined a rate that was also prohibitively slow.³

The concentration of atomic hydrogen was estimated by using the values of the absolute rate constant, k_a (10⁹ M⁻¹ s⁻¹), reported for the addition of hydrogen to an olefin in both the vapor phase⁴ and in aqueous solution.⁵ Since the velocity of the reaction of neat 1-octene [7.05 M, -78 °C, with atomic hydrogen, ($\Delta P/\Delta t$)_{total} = 3.36 × 10⁻⁴ M s⁻¹] was determined, the concentration of atomic hydrogen could be estimated by using the reported rate constant for the addition of atomic hydrogen to an olefin.^{4,5}

$$(\Delta P/\Delta t)_{\text{total}} = k_{a}[1\text{-octene}][\text{H}^{\bullet}]$$

$$[\text{H}^{\bullet}] = (\Delta P/\Delta t)/(k_{a}[1\text{-octene}]) = 4.8 \times 10^{-14} \text{ M}$$
(2)

At these concentrations, a bimolecular reaction, k_c , between an alkyl radical ($\sim 10^{-7}$ M)⁶ and an atom of hydrogen reacting with a diffusion-controlled rate constant, $\sim 10^9$ M⁻¹ s⁻¹, would have achieved a rate of conversion of only 4.8×10^{-12} M s⁻¹. The preceding kinetic analysis will be correct only if the reaction describes a homogeneous process between freely diffusing species; however, with very fast reactions between a vapor and a solution, reaction can take place at the surface of the solution and will deplete the concentration of the initial substrate (*i.e.*, olefin) in that region and increase the concentration of the radicals formed.

The establishment of a rate constant for the addition of a hydrogen atom to an olefin is an important undertaking since most of the solution phase rate constants for the reactions of atomic hydrogen have been determined from the relative rates of reaction with a large variety of structurally different substrates compared to the known absolute rate of the solution phase reaction of hydrogen with ethylene.⁵

The rate of formation of the total products resulting from the initial addition of a hydrogen atom to an olefin in a given time, $(\Delta P/\Delta t)_{\text{total}}$, is proportional to the concentration of the reactants. In the case of a nonhomogeneous reaction, only the first molecules that react obey these kinetics. Under nonhomogeneous conditions reaction occurs only upon the encounter of the reactants in the volume of the reaction zone, *i.e.*, the true concentration is achieved only when the initial concentration of olefin, [olefin]⁰, approaches zero. Under these conditions, an estimate of k_a can be obtained:

$$(\Delta P/\Delta t)_{\text{total}} = k_a [\text{H}^{\bullet}] [\text{olefin}]^0$$
(3)

Since the products of combination (C) and disproportionation (D) are diffusion controlled, the concentration of radicals formed from addition can be calculated from those products if one determines the time dependence of the products formed from their reactions:

$$(\Delta P/\Delta t)_{\rm CD} = k_{\rm R} \cdot [{\rm R}^{\bullet}]^2 \tag{4}$$

The diffusion rate constant, k_{R^*} , can be estimated using the Stokes–Einstein equation by assuming slip conditions and applying a spin statistic correction:⁶

$$k_{\rm R.} = \frac{(8RT)10^3}{3\eta} 3 \tag{5}$$

The concentration of R[•] can then be calculated from eq 4.

The products from the reaction of hydrogen atoms with the alkyl radicals, the capping reaction (eq 1), can be determined from the products resulting from 1,2-addition:

$$(\Delta P/\Delta t)_{\rm RH_2} = K_{\rm H^{\bullet}}[\rm R^{\bullet}][\rm H^{\bullet}]$$
(6)

Since this radical-radical coupling will also be diffusion controlled, an estimation of the hydrogen atom concentration can be made. As the hydrogen atom concentration has now been determined, the addition of hydrogen to a primary olefin can likewise be determined, eq 3, if the time dependent concentrations of the reactants and the products formed in the reaction zone, $(\Delta n/V/\Delta t)^{RZ}$ are known. Since the volume of the reaction zone is only a fraction, *f*, of the bulk volume, the kinetic expressions listed, eqs 2, 4, and 6, are valid only at

S0022-3654(96)00189-X CCC: \$12.00 © 1996 American Chemical Society

[®] Abstract published in Advance ACS Abstracts, June 1, 1996.

reaction time (min)	4-25	9	33	2.2	2.2	2.0	0.75 - 3.0	17	15.2	13.5	5.7	9.5	4.1	2.8	1.3
$\sum_{i=1}^{i}$	1.2	1.3	0.9	1.3			0.08	1.3	1.0	1.1	1.2	0.9	1.2		2.9
	12.6	12.9	12.9	13.9	14.0	11.8	14.0	14.5	14.5	15.1	15.6	13.0	15.3	18.1	14.9
	3.1	3.3	5.5	4.3	3.4	3.3	2.4	5.7	3.6	3.5	2.6	2.3	2.1		2.9
°	11.8	10.4	19.2	12.9	11.3	13.9	13.3	14.3	12.6	11.8	9.2	9.0	9.7	7.8	12.2
C,d	32.3	32.9	32.6	35.4	35.5	29.0	34.3	35.5	35.5	36.9	38.2	32.0	37.5	23.4	36.5
a	22.8	20.0	20.9	14.0	14.9	30.2	17.2	13.1	13.4	10.1	7.0	22.2	8.4	35.0	9.1
C,d	16.4	19.2	7.9	18.2	20.9	11.8	18.0	15.5	19.3	21.6	26.3	20.6	25.7	15.6	21.4
$[1-octene]^b$ \gg	7.05	3.38	1.69	0.57	0.11	0.011	0.0055	1.10	1.10	1.10	1.10	0.075	0.075	0.029	0.029
reaction %	1.1 - 7.0(6)	1.7	2.7	1.4	2.5	20.3	9.32 - 25.4(5)	5.3	6.7	8.5	2.3	12.8	23.5	4.1	11.4
reaction ^a	1 - 6	7	8	6	10	11	12	13	14	15	16	17	18	19	20

TABLE 1: Product Distribution of the Addition of Atomic Hydrogen or Deuterium to 1-Octene (-78 °C)

out without stirring and with stirring speeds of 1200-1400, 1500-2000, and 2500-2800 rpm, respectively. Reactions 17 and 18 were carried out without stirring and at speeds of 2400-3000 rpm, and reactions 19 and 20 were run without stirring and at 2400-3000 rpm, respectively. The volume of the solutions was 10 mL, except those run with mechanical stirring in which case 50 mL aliquots were used. ^b All Reactions 13-20 were carried out in a cell equipped with a variable speed mechanical stirrer. Reactions 13-16 were carried solutions were neat octene (7.05 M) or acetone solutions. Concentrations were corrected for -78 °C.^d Values for k_d/k_c were determined from the reactions with D₂ and used to calculate the product distributions for H₂ reactions. ^e Product from 1,2-addition of hydrogen to 1-octene. f A = 1/1 mixture of $d_i l_i$ and meso-isomers. ^{*a*} Reactions 1-5 were taken from ref 3, and reaction 5 was carried out with D_2 .

	reaction time (min)	5-25	5 - 25	ŝ	4	4.3	2.0	5 - 30
		0.9	0.8	3.1		0.8		0.5
	₹ ↓	11.3	8.6	7.8	11.2	11.2	9.4	6.9
	3	2.6	3.2	6.0	3.6	1.9	2.3	1.9
		<i>T.T</i>	10.4	17.4	10.0	9.0	14.5	6.9
O-T ON HIMITANNAT L	c,d	31.7	27.8	24.8	35.4	35.5	29.6	3.2
	a	24.5	35.0	39.4	17.9	17.1	19.0	46.2
	c,d	21.5	14.0	1.5	21.8	24.6	25.3	14.3
	[1-octene] ^b <	7.10	7.13	5.65	0.57	0.12	0.058	7.19
T TOTAL	reaction %	1.8-11.9(4)	2.7 - 3.0(4)	0.8	1.6	0.6	1.2 - 11.6(3)	1.5 - 4.2(4)
	reaction ^a	21-24	25 - 28	29	30	31 1	32 1	33 - 36

ŝ
66-
and
-91,
(-85,
-Octene
0
Deuterium t
or
Hydrogen
ic.
Atom
J.
he Addition
from t
distribution
Product
ä
ABLE
H

The concentrations were corrected for temperature. c Products from disproportionation. d Values for $k_{d}k_{e}$ were determined from the reactions with D_{2} and used to calculate product distributions for H_{2} reactions. e Product from 1,2-addition of hydrogen ^a Reactions 21-24, 25-32, and 33-36 were carried out at -85, -91, and -99 °C, respectively. ^b Solutions were neat 1-octene or acetone solutions of 1-octene. to 1-octene. f A 1/1 mixture of $d_i l_i$ and meso-isomers.

TABLE 3: Absolute Rate Constants $(f^{1/2}k_a)$ for the Addition of Hydrogen Atoms to 1-Octene at $-78 \,^{\circ}C^a$

reaction	$10^4 (\Delta P / \Delta t)^{\text{bulk}}_{\text{total}} (\text{mol } \mathrm{L}^{-1} \mathrm{s}^{-1})^b$	$(\Delta P/\Delta t)_{\rm C,D}$	$10^{7}[R^{\bullet}]^{c}$	$(\Delta P/\Delta t)_{\mathrm{RH}_2}$	$10^7 [\mathrm{H}^{\bullet}]^d$	$f^{1/2}k_a^{\ e} (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$
1-6	3.36	2.61	5.90 (±0.7)	0.75	$1.80(\pm 0.5)$	0.24 (±0.05)
7	1.58	1.26	4.54	0.32	1.13	0.41
8	2.53	1.99	5.71	0.53	1.52	0.99
9	0.61	0.52	2.93	0.08	0.48	2.2
10	0.21	0.18	1.71	0.03	0.30	6.3
11	0.16	0.11	1.26	0.05	0.54	28.1
12	0.09	0.07	1.10	0.02	0.25	70.2
13	0.57	0.49	2.59	0.08	0.39	1.34
14	0.81	0.70	3.08	0.11	0.48	1.54
15	1.16	1.04	3.76	0.12	0.42	2.5
16	0.74	0.69	3.06	0.05	0.23	2.9
17	0.18	0.14	1.32	0.04	0.56	4.3
18	0.71	0.65	2.98	0.06	0.27	34.9
19	0.072	0.55	0.794	0.02	0.43	5.7
20	0.44	0.39	2.33	2.33	0.23	65.2

^{*a*} Calculated by using data in Table 2. ^{*b*} Experimentally measured as the change in the concentration of 1-octene with time. ^{*c*} Calculated by using eq 4. ^{*d*} Calculated by using eq 7.

TABLE 4: Absolute Rate Constants ($f^{1/2}k_a$) for the Addition of Hydrogen Atoms to 1-Octene at -91 °C^a

reaction	$10^4 (\Delta P / \Delta t)^{\text{bulk}}_{\text{total}} (\text{mol } \mathrm{L}^{-1} \mathrm{s}^{-1})^b$	$(\Delta P/\Delta t)_{\rm C,D}$	$10^7 [R^{\bullet}]^c$	$(\Delta P / \Delta t)_{\mathrm{RH}_2}$	$10^7 [H^{\bullet}]^d$	$f^{1/2}k_a{}^e$ (×10 ³ M ⁻¹ s ⁻¹)
25-28	2.59	1.95	5.40 (±0.8)	0.63	3.1 (±0.9)	$0.10(\pm 0.01)$
29	2.59	1.57	5.10	1.02	3.71	0.12
30	0.38	0.31	2.51	0.07	0.54	1.23
31	0.51	0.42	2.43	0.09	0.72	5.90
32	0.06	0.05	0.99	0.01	0.24	45.7

^{*a*} Calculated by using data from Table 3. ^{*b*} Experimentally measured as the change in the concentration of 1-octene with time. ^{*c*} Calculated by using eq 4. ^{*d*} Calculated by using eq 7.

extremely low concentrations where

$$\left(\frac{\Delta n/V}{\Delta t}\right)^{\text{RZ}} \simeq \left(\frac{\Delta n/V}{\Delta t}\right)^{\text{bulk}}$$

An expression (eq 7) that defines the rate constant for addition, k_a , can be derived by combining eqs 2–6:

$$k_{\rm a} = f^{-1/2} \left[\frac{(\Delta P / \Delta t)_{\rm total} (k_{\rm diff} (\Delta P / \Delta t)_{\rm C,D})^{1/2}}{[{\rm olefin}] (\Delta P / \Delta t)_{\rm RH_2}} \right]$$
(7)

Results and Discussion

Hydrogen Atom Addition to 1-Octene. To determine an accurate value for the absolute rate constant for the solution phase reactions of a hydrogen atom with an olefin, the data reported previously for the hydrogen atom addition to 1-octene³ (-78 °C) were expanded to include varying concentrations of olefin at several temperatures (see Tables 1 and 2).

Absolute Rate of Addition of H[•] **to 1-Octene.** The experimental data (Tables 1 and 2) were used to calculate the concentrations of the reactants ([olefin], [R[•]], [H[•]]) and the rate constants for each reaction at each concentration of olefin. The apparent rate constants ($f^{1/2}k_a$) of the substrates in their reaction zone are listed in Tables 3 and 4. By using the data in Tables 3 and 4, a plot of the calculated values of $f^{1/2}k_a$ vs their olefin concentration was constructed (Figure 1).

The data were fit to an equation of the form $\log f^{1/2}k_a = a[\text{olefin}]^b + c$. The function is monotonic and steeply dependent upon concentration. An approximation of the rate constant [upper limits = $(1.4 \pm 0.4) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, -78 °C], $f^{1/2}k_a$, where *f* equals unity, was obtained from the intercept of a plot of $\log f^{1/2}k_a$ (the apparent rate constant) *vs* [1-octene] (see Figure 1). The value of *f* can be calculated for the reactions of neat octene using $f^{1/2}k_a$ at -78 °C [$f = (3.0 \pm 1.5) \times 10^{-12}$]. The reaction volume ($2.8 \times 10^{-11} \text{ mL}$) for neat 1-octene (-78 °C) can be estimated as a fraction of the total volume of the solution ($3.0 \times 10^{-12} \times 9.0 \text{ mL}$). Since the surface area of the cell (54.1 cm²) contains approximately 2.8×10^{15} molecules of 1-octene⁷ and the reaction zone contains only 1.1×10^{11}



Figure 1. Variation in observed rate constant $\log(f^{1/2}k_a) vs [1-octene]^0$ at $-78 \,^{\circ}\text{C}$, $\bigcirc (a, -5.02; b, 0.07; c, 8.14)$, and $-91 \,^{\circ}\text{C}$, $\triangle (a, -4.79; b, 0.09; c, 7.69)$. The extrapolated rate constants, $\log k_a$, for $-78 \,(\textcircled{\bullet})$ and $-91 \,^{\circ}\text{C}$ (\bigstar) are also shown.

cell), the reaction is limited to only a fraction of the molecules on the surface of the cell. By using the same method, the value of k_a [(4.9 ± 1.1) × 10⁷ M⁻¹ s⁻¹] was obtained at another temperature, -91 °C (Figure 1). A plot of log $k_a vs 1/T$ gave Arrhenius parameters ($E_a = 5.3 \pm 2.9$ kcal/mol, log $A = 14 \pm$ 3.5 M s⁻¹) that allowed the calculation of $k_a = (4.2 \pm 3.6) \times$ 10^9 M⁻¹ s⁻¹ at 25 °C. The calculated values of the rate constants and activation parameters are in excellent agreement with the previously reported rate constants, which ranged over $k_a = (0.88 - 8.19) \times 10^8 \text{ M}^{-1} \text{ s}^{-1} (25 \text{ °C})^{4,8,9}$ for the addition of atomic hydrogen to ethylene. The previously reported activation energies ranged from 0.5 to 3.3 kcal/mol,⁴ while a value of E_a = 3.18 kcal/mol was calculated by Baldwin *et al.*⁹ on the basis of a combination of the results of Yang¹⁰ and Jennings and Cvetanovic.^{8b} The observed decrease in both concentrations of the 1,2-addition product (Tables 1 and 2) and the [H[•]]^{calc} (Tables 3 and 4) as the concentration of 1-octene is decreased is compatible with the proposed reaction model since as the [olefin] decreases, the reaction volume increases and $(\Delta n/V)^{RZ}$ approaches $(\Delta n/V)^{\text{bulk}}$ and limits the formation of the 1,2addition product. Rapid stirring of the reaction mixture, entries

TABLE 5: Product Distribution of the Addition of Hydrogen Atoms to 1-Methylcyclohexene at -78 °C

reaction	reaction %	[1-methylcyclohexene] ^a	time (min)	p	μ	c	P	μ		others ^d
1-2	9.8-15.9	9.24	10-20	15.4	9.0	19.2	39.1	14.6	1.4	1.2
3	5.4	1.14	4	15.2	8.6	7.8	44.8	21.0	1.6	1.0
4	8.8	0.23	2	19.1	10.8	3.2	47.1	17.2	1.7	0.9
5	6.2	0.12	1	18.3	10.4	3.8	46.7	17.9	1.7	1.2
6	5.3	0.044	0.75	20.6	11.7	3.8	46.7	14.4	1.7	1.1
7	8.6	0.011	0.75	20.5	11.6	4.3	47.0	144.8	1.7	
8	18.7	0.006	1.5	20.8	11.8	4.0	47.2	14.5	1.7	

^{*a*} Reactions 1 and 2 were carried out with neat 1-methylcyclohexene; reactions 3-8 were acetone solutions. The concentrations were corrected for -78 °C. ^{*b*} Products from disproportionation reactions. Calculated by using the product distributions obtained from the experiments carried out with deuterium (see Table 6). k_d/k_c (-78 °C) was taken as 27.8 and ρ_{MDO}/ρ_{MDA} was taken as 1. ^{*c*} Product from the 1,2-addition of hydrogen to 1-methylcyclohexene. ^{*d*} Four unidentified dimers formed in a ratio of 1/0.6/0.6/1 (<1.2%).



Figure 2. Plot of $\log(f^{4/2}k_a)$ vs [1-methylcyclohexene]⁰ (a, -2.76; b, 0.19; c, 6.64). The extrapolated rate constant, $\log k_a$, at -78 °C (O) is shown.

13–20 of Table 1, represents experiments in which the "apparent volume" is increased. Presumably if stirring is rapid enough and competitive with diffusion, $f^{1/2}k_a$ will equal k_a . Unfortunately, although $f^{1/2}k_a$ is increased with stirring, only a 11-fold increase in $f^{1/2}k_a$ could be achieved by stirring (0–4000 rpm).

Regioselective Addition of Atomic Hydrogen to 1-Methylcyclohexene. When atomic hydrogen (0.70–4.44 mmol) is passed over neat 1-methylcyclohexene or acetone solutions of 1-methylcyclohexene at two temperatures (-78 and -91 °C), the products of the reaction are methylcyclohexane, methylenecyclohexane, two isomers of 1,1'-dimethylbicyclohexyl, and four other minor dimeric products (see Table 5).

Some insight into the mechanism of the formation of these products is obtained by carrying out the reduction with deuterium atoms (-78 and -91 °C). The distribution of the products from these reactions is listed in Table 6. By comparing the mass and ¹H and ²H NMR spectra of the protiated and deuterated products, it was obvious that in each of the products, whether monomer or dimer, at least one deuterium is attached to a secondary position attributable to the original olefin (see Table 6). The mass spectra (GC/MS) of the deuterated products showed 1-methylcyclohexene (d₁, A and B), methylcyclohexane (d₂, C; d₁, D), methylenecyclohexane (d₁, E), 1,1'-dimethylbicyclohexyl (d₂, F), and four other minor dimeric products (see Table 5). If the assumption is correct that the initial addition to the secondary position of 1-methylcyclohexene is regiospecific, then the deuterated products are those listed in Table 6. The ²H NMR (see Figure 2) showed absorption with intensity, I_n : δ 0.83, axial 2-deuterium of methylcyclohexane (I_1); 1.25, tertiary deuterium of methylcyclohexane and 1,2-dideuteriocyclohexane (I₂); 1.55-1.60, equatorial 2-deuterium of methylcyclohexane (I_3); 1.82, 6-deuterium of 1-methylcyclohexene (I_4);

2.05, 2-deuterium of methylenecyclohexane (I_5); and 5.33, 2-deuterium of 1-methylcyclohexene, (I_6).

The ratio of dideuterated (C) and monodeuterated methylcyclohexane (D) was obtained from an examination of their GC/ MS spectra. From the concentrations of the products (GC analysis) and the ²H NMR intensity ratios, the concentrations of the deuterated products listed in Table 6 are calculated by using the following relationship: $[E] = \gamma I_5$, $[A] = \gamma I_4$, $[B] = \gamma I_6$, and $[C] + [D] = \gamma I_2$. The proportionality constant $\gamma =$ $[E]/I_5$ was used to calibrate the ²H NMR concentrations. The consistency of the analysis can be checked since the concentrations of monodeuterated alkenes and the monodeuterated alkane will be formed from disproportionation in a 1/1 ratio $\Sigma([A] +$ [B] + [E]/[D]) = 1. The disproportionation products are formed, within experimental error, in the predicted ratio (see Table 6).

The first step in the addition of a H atom to 1-methylcyclohexene no doubt is addition to the secondary position of the double bond to give a tertiary radical:

$$+ D^* \longrightarrow D$$
(8)

When the tertiary radical encounters another deuterium atom, 1,2-dideuterio-1-methylcyclohexane is formed:

$$\underbrace{ \begin{array}{c} & & \\ & & \\ & & \\ & & \\ \end{array}}^{D} + D^{*} \longrightarrow \underbrace{ \begin{array}{c} & & \\ & & \\ & & \\ \end{array}}^{D} D$$
 (9)

In the original report³ on the hydrogenation of 1-octene, the capping reaction could not be definitely attributed to the reaction of a second hydrogen atom, as depicted in eq 9. However, it is now clear that the mode of formation of the 1,2-dideuterated alkanes follows this sequence of reactions.

The major saturated or unsaturated hydrocarbons, however, contain only one deuterium atom. The incorporation of protium into methylcyclohexane can be attributed to disproportionation (eq 10) or allylic abstraction (eq 11).



Since disproportionation gives equal amounts of monodeuterated methylcyclohexane (ρ_{MDA}) and monodeuterated olefin (ρ_{MDO}),

 TABLE 6:
 Product Distribution from the Addition of Deuterium Atoms to Neat 1-Methylcyclohexene

	reaction	temn	time	D			D	D				
reaction	%	(°C)	(min)	(A) ^a	(B) ^a	(C) ^{<i>b</i>}	(D) ^a	(E) ^a	(F)	other	$ ho_{ m MDO}/ ho_{ m MDA}$	$k_{\rm d}/k_{ m c}$
9	2.0	-78	3	15.3	7.9	20.2	39.4	15.3	1.5	0.5	1.0	26.2
10	2.2		3	13.8	9.9	22.0	38.0	14.2	1.4	0.7	1.0	27.1
11	5.0		5	14.8	6.2	20.8	40.7	15.6	1.4	0.6	1.1	29.0
12	5.3		5	15.1	9.5	18.2	37.9	17.0	1.3	1.0	1.1	$\frac{29.2}{\text{ave }27.9\pm1.2}$
13	3.1	-91	5	18.2	8.0	25.4	36.4	10.5	0.9	0.5	1.0	40.6
14	2.1		5	11.9	5.2	17.1	37.6	26.2	1.2	0.9	1.2	$\frac{33.7}{\text{ave } 37.2 \pm 3.4}$

^{*a*} Products from disproportionation reactions, $\rho_{\text{MDO}}/\rho_{\text{MDA}} = 1$. ^{*b*} Products from the 1,2-addition of hydrogen. ^{*c*} Four unidentified dimers (each with two H²) formed in a ratio of 1/0.6/0.6/1.



Figure 3. ²H NMR spectrum of the product mixture obtained from the addition of deuterium atoms to 1-methylcyclohexene.

the monodeuterated products are formed primarily by disproportionation (see Table 6). If a detectable amount of allylic abstraction takes place, then the products from the reactions of the allylic radicals would also be observed (eqs 12–14). Since the products ratio, $\rho_{\text{MDA}}/\rho_{\text{MDO}}$, is approximately unity, and since no diene products are formed [only 1-methylcyclohexane, methylenecyclohexane (monomers), and five saturated dimeric products are formed], it is unlikely that any appreciable allylic abstraction takes place (see Table 5). One of the four unidentified dimeric products (<1% of the total products) are formed in a ratio of approximately 0.3/0.2/0.2/0.3 (see Table 5).



Since the products of disproportionation can be identified, the disproportionation to combination ratio is easily determined. The value determined for the reaction carried out to low conversion (2–5% reaction) is 27.9 \pm 1.2 (–78 °C). When the reaction is carried out at two temperatures, –91 and –78 °C, a plot of ln $k_d/k_c vs 1/T$ gives a slope, $E_{a(dis)}-E_{a(comb)}$, equal to –1.5 kcal/mol (see Figure 3). The ratio of rate constants, k_d/k_c , calculated from the plot at 25 °C is 6.8 and is within experimental error of the value ($k_d/k_c = 7.2$) reported for the *tert*-butyl radical.¹¹



Figure 4. Variation in $\log(k_d/k_c)$ with 1/T. The dashed line represents the extrapolation to 25 °C.

Since the disproportionation to combination ratio for the products from the addition of protium or deuterium atoms will be approximately the same,³ the ratio k_d/k_c determined from the reactions with deuterium was used to calculate the yields of methylcyclohexane and 1-methylcyclohexene formed from disproportionation when the reaction of 1-methylcyclohexene and atomic hydrogen was carried out (see Table 5, footnote b). The yields of the unidentified dimeric addition products were shown to be dependent upon the initial concentration of olefin (see Table 5).

The concentration dependence of the yield of addition products (P_A) is consistent with its formation from a bimolecular reaction and must be due to addition of the 1-methylcyclohexyl radical to 1-methylcyclohexene (eq 13) followed by subsequent disproportionation or addition of a hydrogen atom to the new tertiary radical.



Absolute Rate of Addition of H[•] to 1-Methylcyclohexene (-78 °C). The same kinetic method that was used to calculate the absolute rate of addition of H[•] to 1-octene was used to treat the data collected for 1-methylcyclohexene. The products of the H[•] reaction with varying concentrations of olefin (Tables 5 and 6) yielded the kinetic data listed in Table 7. A plot of log $f^{1/2}k_a$ vs [olefin]⁰ at -78 °C, when extrapolated to zero concentration, yielded the absolute rate constant $k_a = (4.6 \pm 0.8) \times 10^6 \, \text{M}^{-1} \, \text{s}^{-1}$ (Figure 4). If a model reaction,⁴ the vapor

 TABLE 7: Absolute Rate Constants ($f^{1/2}k_a$) for the Addition of Atomic Hydrogen to 1-Methylcyclohexene at -78 °C^a

reaction	$\frac{10^4 (\Delta P / \Delta t)_{\text{total}}^{\text{bulk}}}{(\text{mol } \text{L}^{-1} \text{ s}^{-1})^p}$	$10^7 [\mathbf{R}^{\bullet}]^c$	$10^7 [\text{H}^{\bullet}]^d$	$(\times 10^{-3} \mathrm{M}^{-1} \mathrm{s}^{-1})$
1-2, 9-12		19.1 (±2)	4.7 (±0.4)	0.29 (±0.4)
3	2.47	5.55	0.47	4.77
4	1.62	4.61	0.15	48.3
5	1.14	3.85	0.15	68.1
6	0.52	2.60	0.10	115
7	0.21	1.65	0.07	259
8	0.11	1.22	0.05	412

^{*a*} Calculated by using data from Table 5. ^{*b*} Experimentally measured as the change in the concentration of 1-methylcyclohexene with time. ^{*c*} Calculated by using eq 4. ^{*d*} Calculated by using eq 6. ^{*e*} Calculated by using eq 7.

phase addition of H[•] to cyclohexene⁴ vs 1-octene, is chosen as a comparison reaction for the solution phase reaction of 1-methylcyclohexene vs 1-octene (I, 25 °C),¹² the value of the relative rate (0.46) illustrates that the cyclic olefin reacts more slowly than the terminal olefin. At -78 °C the relative rate of the more highly substituted olefin, 1-methylcyclohexene (II), is even lower, $k_a^{II}/k_a^{I} = 0.03 \pm 0.01$.

Conclusion. The solution phase reaction rate constants of an olefin (1-octene or 1-methylcyclohexene) with atomic hydrogen are the same order of magnitude as the rate constants for the diffusion of their reactants. The addition of hydrogen takes place in a limited volume that contains the first encountered molecules of olefin. When the concentration of olefin approaches zero, the true rate of addition, k_a , can be estimated since the reaction volume is approximately equal to the volume of the reaction cell.

Experimental Section

The apparatus used for the generation of atomic $H^{\bullet}(D^{\bullet})$ and its reaction with 1-octene and 1-methylcyclohexene was identical to that previously reported for the reaction of 1-octene.³

Materials. Additional materials not reported previously:³ The purity of 1-methylcyclohexene (FLUKA, +99%) was varified by GC prior to use. The values used to calculate the viscosities of acetone or 1-octene were taken from the temperature dependent literature values.¹³ The values of the mixture viscosities were measured by using an Ostwald viscometer.¹⁴ The viscosity of 1-methylcyclohexene at -78 and -91 °C was measured as a relative value using methylcyclohexane as a standard.¹³

Identification of the Reaction Products. The products (methylcyclohexane and methylenecyclohexane) were identified by a comparison of their GC retention times, GC/IR spectra, and GC/MS spectra with those of authentic samples.

1,1'-Dimethyl-1,1'-bicyclohexyl was isolated from the reaction product mixture of atomic hydrogen with 1-methylcyclohexene. The structure of the dimer was identified by analysis of its GC/MS, GC/IR, ¹H NMR, ¹³C NMR, and APT: ¹H NMR (300 MHz, CDCl₃) δ 0.85 (s, 6H), 1.20–1.80 (m, 20H); ¹³C NMR (300 MHz, CDCl₃) δ 16.61 (q, 2), 30.34, 26.61, 30.34 (t, 5), 38.15 (s, 2); IR (gas phase) ν 2937, 2872, 1455, 1382, 1302 cm⁻¹; EI⁺ (GC/MS, VG-70) *m*/*z* 194 (M⁺), 97, 96, 81, 69, 68, 67, 55, 41.

General Procedure for the Atomic Hydrogen Reaction. An aliquot solution was placed in the U-shaped reactor. The reactor was cooled to the desired temperature, and a stream of hydrogen or deuterium was passed into the system at a flow rate of 4 mL/min. The reaction system pressure was controlled at 3-4 torr by a make-up gas (helium). The microwave generator was activated and the reaction allowed to proceed for the desired time. After the reaction, the product mixture was analyzed by GC. For each reaction, the products were

identified by comparison of their GC retention times, GC/MS, and GC/IR with those of authentic samples. ²H NMR spectra were also obtained for products of the reactions with deuterium (see Figure 2).

Instrumentation. The ¹H, ²H, and ¹³C NMR spectra were obtained using either a Bruker AM-400 (400 MHz), Bruker AM-300 (300 MHz), or Bruker WH-200 (200 MHz) NMR spectrometer. Unless otherwise noted, the ¹H NMR spectra are referenced to TMS as an internal standard at 0.00 ppm or to CHCl₃ as an internal standard at 7.26 ppm. The ¹³C NMR chemical shifts are reported in δ relative to chloroform (δ CDCl₃ = 77.0).

The ¹³C absorption spectra were examined by APT (an attached proton test) to assign the absorptions obtained from the ¹H NMR spectra.

GC/IR data was obtained by using an HP 5965A IRD GC/FTIR interfaced to an HP 5890 gas chromatograph fitted with a DB-5 (30 m \times 0.25 mm) glass capillary column.

GC/MS data were obtained by using a VG-70E EI⁺ spectrometer fitted with a Varian Vista 6000 gas chromatograph having a glass capillary column (DB-5 30 m \times 0.25 mm, J. & W. Scientific) and interfaced to a 1125 data system.

GC analyses were carried out by using a Varian Vista 6000 FID gas chromatograph fitted with a glass capillary column (PONA, 30 m \times 0.25 mm, Hewlett-Packard) and interfaced to a Varian Vista CDS 401 chromatographic data system. The yield of the reaction products was determined by GC analysis using a standard calibration solution of known concentrations of the authentic materials and an added internal standard (1-chlorooctane or *o*-dichlorobenzene).³

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for their generous support of this work. The authors also thank Professor M. Newcomb for his helpful discussions concerning several points in the manuscript.

References and Notes

(1) Taken in part from the Ph.D. dissertation of Living Zhang, University of Alberta, Edmonton, Alberta, 1994.

(2) Postdoctoral Fellow, University of Alberta, 1994–1995.

(3) Tanner, D. D.; Zhang, L. J. Am. Chem. Soc. 1994, 116, 6683.

(4) Jones, W. E.; Macknight, S. D.; Teng, L. Chem. Rev. 1973, 73, 407.

(5) Neta, P. Chem. Rev. 1972, 72, 533.

(6) (a) Calculated from the rate of combination and disproportionation by using the diffusion rate constant. (b) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: 1973; New York, NY, Vol. 1, Chapter 2.

(7) The number of molecules on the surface of the reaction cell were estimated from the MM2-generated surface area (193 Å²) of a rod-shaped molecule of 1-octene using a closest packing arrangement.

(8) (a) Cvetanovic, R. J.; Doyle, J. C. J. Chem. Phys. 1969, 50, 4705.
(b) Jenning, K. R.; Cvetanovic, R. J. J. Chem. Phys. 1961, 35, 1233.

(9) Baldwin, R. R.; Simmons, R. F.; Walker, R. W. Trans. Faraday Soc. 1966, 62, 2486.

(10) Yang, K. J. Am. Chem. Soc. 1962, 84, 719.

(11) Tanner, D. D.; Rahimi, P. M. J. Am. Chem. Soc. 1982, 104, 225.(12) This work.

(13) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals*; Hemisphere Publishing Corp.: New York, 1989; Vol. 3.

(14) Tanner, D. D.; Mahamat, H. O.; Meintzer, C. P.; Tsai, E. C.; Lu, T. T.; Yang, D. J. Am. Chem. Soc. **1991**, 113, 5397.

JP960189U