Absolute Rate Constants for Allylic Abstraction of Hydrogen by Atomic Hydrogen

Dennis D. Tanner,* Liying Zhang,[1] and Pramod Kandanarachchi[2]

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

Received: April 25, 1997; In Final Form: September 22, 1997[⊗]

The solution-phase absolute rate constants (23 °C) for the abstraction by atomic hydrogen of 1°, 2°, and 3° allylic hydrogens have been calculated by determining the relative rates of abstraction vs addition, since the absolute rate constants for addition is known. The absolute rate constant for benzylic abstraction by deuterium has also been determined. The rate ratios for 1°, 2°, and 3° allylic abstraction are remarkably similar to those reported for the ratio of rate constants for methyl radical abstraction. The determinations of the rate constants were based on the values for the relative rates of abstraction/addition using atomic deuterium, k_{ab}^{D}/k_{add}^{D}, the absolute rate constant for the addition of hydrogen to an olefin, k_{add}^{H}, and the deuterium isotope effects for both addition, k_{add}^{H}/k_{add}^{D}, and abstraction, k_{ab}^{H}/k_{ab}^{D}.

Introduction

Recently we published the results of a study of the mechanism of formation of the products from the addition of atomic hydrogen to 1-octene.[3] No evidence was obtained for competitive allylic abstraction of hydrogen relative to addition. After the initial report the absolute rate constants for the addition of atomic hydrogen to both 1-octene and 1-methylcyclohexene were reported.[4]

Since it was obvious from the first study (−78 °C) that allylic abstraction from a straight chain terminal olefin was not competitive with addition at these low temperatures a series of more reactive allylic olefins was studied. More highly substituted olefins should be less amenable to addition and allylic abstraction should be more favored.

Several competitive complicating factors, steric inhibition to allylic abstraction as well as increased stabilization of the radical formed from both addition to and abstraction from the more highly substituted olefins, make the analysis of the structural factors governing the kinetics of the reactions more difficult.

The relative rates of reaction of atomic hydrogen (k_{add}/k_{ab}) with several of the olefins chosen in this study have been previously reported. As these studies had been carried out at 23 °C (radiolysis of hexane solutions) in the presence of olefins and both allylic abstraction and addition were observed, it appeared that at higher temperatures the rates of allylic abstraction were competitive with those of addition.[5] Furthermore, one of the olefins studied was a 1,2-disubstituted ethylene and another was a tetrasubstituted ethylene; these reports enabled us to compare the results of the two kinetic methods and to determine the absolute rates of hydrogen atom addition to the more highly substituted olefins.

Results and Discussion

The model olefins chosen are listed in Table 1. All values reported for k_{ab}/k_{add} have been corrected for the number of hydrogens statistically available for abstraction.

The data given in Table 1 are experimentally determined from two or more experiments. The average values of these determinations is used to construct the temperature dependence of the ratio, k_{ab}/k_{add}, see Figure 1. The Arrhenius parameters for these reactions are used to determine, after extrapolation, the values of k_{ab}^{D}/k_{add}^{D} at 23 °C.

TABLE 1: Relative Rate of Allylic Abstraction vs Addition (k_{ab}/k_{Add}) for Atomic Deuterium with a Number of Model Compounds
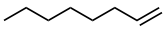
olefin	temp (°C)	(k_{abs}/k_{add})
	−23	0.045
		0.037
	−42	0.029
		0.026
	−51	0.082
		0.072
	−63	0.074
		0.066
	−72	0.068
		0.058
		0.066
	−63	0.157
		0.143
	−72	0.163
		0.149
		0.165
	−94	0.176
		0.164
	−42	0.440
		0.420
	−63	0.375
		0.357
	−72	0.301
		0.276
		0.296
	−94	0.241
		0.225
Ph	−23	0.0935
		0.0775
	−42	0.044
		0.038
	−72	0.022
		0.018

Table 2 lists the calculated values of $E_{ab}^{D} - E^{D}$ kcal/mol taken from Figure 1, the extrapolated values of k_{ab}^{D}/k_{add}^{D} at 23 °C, and the calculated values of k_{ab}^{H} s^{-1} M^{-1} which are derived by multiplying the ratio of rate constants by the previously reported determinations of k_{add}^{H}.

Analysis of the Products that Determine the Ratio of Rate Constants. The genesis of the products formed was determined in the same manner as previously reported for the reaction of 1-octene.[3] By the use of deuterium the observation can be made that the products formed from disproportionation yield a 1:1 ratio of monodeuterated alkanes to monodeuterated olefins. Due to the deuterium isotope effect the amount of deuterium

9328 *J. Phys. Chem. A, Vol. 101, No. 49, 1997*
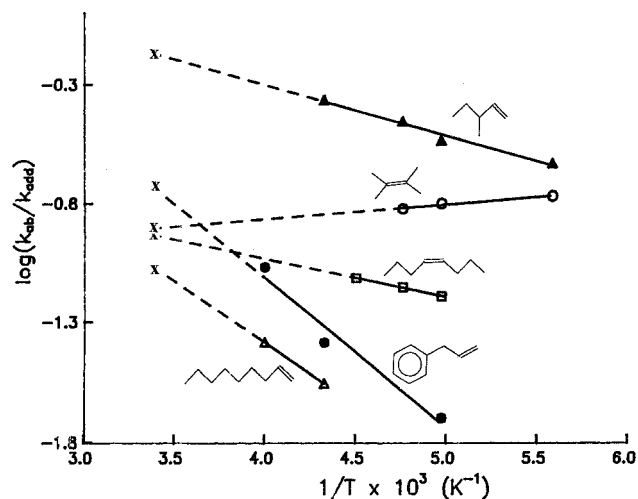
Tanner et al.

Figure 1. Variation in $\log(k_{ab}/k_{add})$ with $1/T$. The dashed line is the extrapolated value of ($\times$) k_{ab}/k_{add} at 23 °C.

transferred during the bimolecular disproportionation reactions appeared to be negligible, since the results using protium appeared to be the same as those obtained when deuterium was used. The method used to calculate the rates of abstraction is listed in Tables 3−7. The values quoted are average values obtained from two or more independent experiments.

Allylic Abstraction from 1-Octene. The products of allylic abstraction were not competitive with addition at −72 °C, but at higher temperatures, −23 °C and −42 °C, the relative rates of abstraction/addition, k_{ab}/k_{add}, could be determined, see Tables 1 and 3.

Allylic Abstraction from 2-Ethylbutene. Due to the volatility of this substrate only one temperature −72 °C, was attempted. No 3-deuterio-2-ethylbutene could be detected; see Table 2.

Allylic Abstraction from cis-4-Octene. From the products resulting from the competitive reactions of atomic deuterium with *cis*-4-octene the relative rates of reaction, k_{ab}/k_{add}, can be determined, see Tables 1 and 4. Since the rate constant for the addition to a 1,2-disubstituted olefin had previously been reported[6] this value allowed us to calculate the rate constant for abstraction, 3.1×10^7 s^{-1} M^{-1}, at 23 °C. A comparison with the previously reported abstraction rate constant,[6] 6.3×10^7 s^{-1} M^{-1}, showed that the present rate constant was approximately 2 times slower.

Allylic Abstraction from 2,3-Dimethyl-2-butene. The absolute rate constant for addition of atomic hydrogen has previously been reported.[6] The ratio of rate constants, k_{ab}^H/k_{add}^H, had been estimated as $<2.5 \times 10^{-4}$. Using the rate ratio obtained from the present study k_{ab}^D/k_{add}^D, (Tables 1 and 5), combined with the previously reported addition rate constant, $k_{add} = 2.25 \times 10^8$ s^{-1} M^{-1}, the value for the abstraction rate constant for a primary allylic hydrogen could be determined, see Table 2.

Allylic Abstraction from 3-Methyl-1-pentene. The abstraction rate constant for a tertiary hydrogen was determined from analysis of the products from the reaction of 3-methyl-1-pentene with atomic hydrogen or deuterium, see Tables 1 and 6. The relative rates of addition vs abstraction, k_{ab}/k_{add}, (23 °C) can be determined from the product yields and since the rate constant for addition to a terminal olefin is known,[4] the absolute rate constant, k_{ab} s^{-1} M^{-1} = 2.7×10^9 (23 °C) is determined (Tables 2).

Allylic Benzylic Abstraction. The rate of abstraction for a benzylic hydrogen was found, as expected, to be competitive with addition to a terminal olefin, k_{ab}^D/k_{add}^D = 1.9×10^{-1} (23 °C), and the abstraction rate for deuterium was determined to

be, 7.9×10^8 s^{-1} M^{-1}, 3.6 times slower than the rate constant for abstraction of a tertiary hydrogen by deuterium (Tables 2 and 7). The rate constant for benzylic abstraction was made even more favorable when tetrabenzylethylene was used as the substrate. The products from addition could not be detected ($<5\%$) by ^{2}H NMR, only allylic abstraction and aromatic substitution takes place, see experimental for the reactions of tetrabenzylethylene.

Calculation of the Absolute Rates, k_{ab}^H of Allylic Abstraction. The absolute rate constant for addition has previously been reported for the reaction of atomic hydrogen with 1-octene.[4] In the present work the ratio of k_{ab}^D/k_{add}^D for 1-octene (Tables 1 and 2) was determined using atomic deuterium. A probable error in the determination of k_{ab}^H was introduced by ignoring the deuterium isotope effect. Fortunately, the vapor phase value for the total reaction of 1-butene with both atomic hydrogen and atomic deuterium has been reported,[5] $[(k_{add}^H + k_{ab}^H)/(k_{add}^D + k_{ab}^D)] = 1$ at 25 °C. Since the ratio of rate constants do not show an isotope effect and since abstraction is only a minor reaction ($<10\%$),[4,8c] it appears to be justifiable to use the value of k_{add}^D for k_{add}^H.
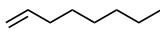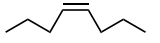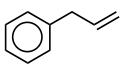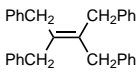
The rates of radical addition to 2,2-disubstituted ethylenes are usually not much different than the addition rates to a monosubstituted olefin;[5,6] however, even in the case of 2-ethylbutene (Table 2, entry 2) where 4 secondary allylic hydrogens were available for abstraction, no allylic abstraction could be detected at −72 °C. The observation that allylic abstraction was not competitive with addition was consistent with the results reported at 65 °C for the vapor phase rate ratios observed for the reactions of methyl radicals (an intermediate of similar reactivity) with propylene or isobutylene ((k_{add}/k_{ab}) 22; and 36).[7] In the case of addition of a radical to a 1,2-disubstituted ethylene the rate of addition will be much slower than for a terminal olefin. With *cis*-4-octene (Table 2, entry 3) where four allylic hydrogens are present, allylic hydrogen abstraction was observed ($k_{ab}^D/k_{add}^D = 6.4 \times 10^{-2}$) at −72 °C.

To obtain more useful values of the rate constants for allylic abstraction the activation parameters ($E_{ab}^D - E_{add}^D$) were determined for a number of the olefinic substrates. The rate ratios could then be calculated for reaction at a more useful temperature, 23 °C. Because of the volatility of the model compounds the rate constants were determined at several lower temperatures and the Arrhenius parameters allowed the rate constants for abstraction to be determined at 23 °C, see Tables 1 and 2 and Figure 1.

Previously k_{ab}^H and k_{add}^H had both been reported for the solution phase reactions (23 °C) of atomic hydrogen with 2-heptene.[6] Since we have now determined k_{ab}^H for the abstraction of a secondary allylic hydrogen from 1-octene a comparison of the two determinations for $(k_{ab}^H)2°$ can be made; both values differ by a factor of 10. The discrepancy in these values and our preference for the use of our experimental values is addressed when the $1°/2°/3°$ selectivities is examined.
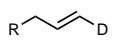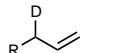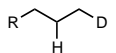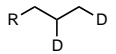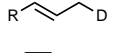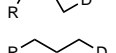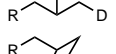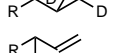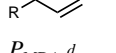
Our value, k_{ab}^D/k_{add}^D, determined for the reaction of *cis*-4-octene (see Table 1) can be used to calculate k_{ab}^H by recognizing that $(k_{add}^H + k_{ab}^H)/(k_{add}^D + k_{ab}^D) = 1$ had been reported[5] for the vapor phase reactions of 1-butene and that abstraction from 1-octene ($<8\%$) and from *cis*-4-octene ($<11\%$) can be neglected, see Table 2. The negligible amount of abstraction was in agreement with the previously reported vapor phase reaction of 1- and 2-pentene with atomic hydrogen.[4,8c] Since we have experimentally determined k_{add}^D/k_{ab}^D for *cis*-4-octene the value of k_{ab}^D can be used to calculate k_{ab}^H if the kinetic isotope effect for abstraction is known. The kinetic isotope effect for the total reactions of a number of model compounds have been reported.[5]

Allylic Abstraction of Hydrogen

J. Phys. Chem. A, Vol. 101, No. 49, 1997 **9329**

TABLE 2: Absolute Rate Constants for Allylic Abstraction and Addition at 23 °C

	olefin	structure feature	allylic abstraction, −72 °C	$(k_{ab}^D/k_{add}^D \times 10^2)$ °C	$(k_{add}^H \times 10^9$ s^{-1} M$^{-1})$ °C	$E_{ab}^D - E_{add}^D$, kcal/mol	$(k_{ab}^H/$s^{-1} M$^{-1})$
1		monosubstituted ethylene 2 × secondary allylic C−H	no (yes, 23 °C)	$(8.6 \pm 0.8)^a{}_{23}$	$(4.2)^a{}_{23}$	2.34	$(3.6 \pm 3.3) \times 10^8$
2		1,1-disubstituted ethylene 4 × secondary allylic C−H	no	$(0)_{-78}$			
3		disubstituted ethylene 4 × secondary allylic C−H	yes	$(12 \pm 0.3)^b{}_{23}$	$(0.26)^b{}_{23}$	0.74	$(3.1 \pm 0.2) \times 10^7)^c$
4		tetrasubstituted ethylene 12 × primary C−H	yes	$(12 \pm 0.5)_{23}$	$(0.23)^d{}_{23}$	−0.28	$(4.1 \times 10^7)^{d,e}$
5		monosubstituted ethylene tertiary C−H	yes	$(68 \pm 0.7)_{23}$	$(4.2)^a{}_{23}$	0.97	$(2.7 \pm 2.5) \times 10^9$
6		monosubstituted ethylene 2 × benzylic C−H	yes	$(19 \pm 4)_{23}$	$(4.2)_{23}$	2.83	$(7.9 \pm 8.3) \times 10^8$
7	PhCH₂ / CH₂Ph / PhCH₂ / CH₂Ph	tetrasubstituted ethylene 8 × benzylic C−H	yes	$(\infty)_{-78}$			

[a] Reference 4. [b] Reference 6 at 23 °C, $(k_{ab}^H/k_{add}^H) = 2.4 \times 10^{-1}$. [c] $k_{ab}^H = 6.2 \times 10^7$ s^{-1} M^{-1} taken from ref 6. [d] Reference 6 at 23 °C $(k_{ab}^H/k_{add}^H) = <0.303 \times 10^{-2}$. [e] Calculated using the addition rate constant from ref 6; no error limits are reported.

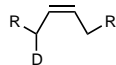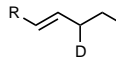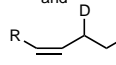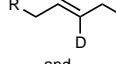**TABLE 3: Product Distribution from the Reaction of Atomic Deuterium with 1-Octene**[a]
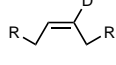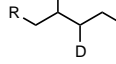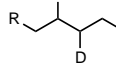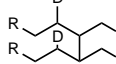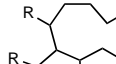
products R = C₅H₁₁	yield (%)[b] −23 °C	yield (%)[c] −42 °C
R‒‒D (A)	5.03	8.46
(B)	2.99	1.73
(C)	12.6	18.0
(D)	64.8	43.1
(E)	6.95	7.91
(F)	3.47	2.58
(G)	2.88	15.6
(H)	0.31	1.41
(I)	1.24	1.18
$\dfrac{P_{MDA}}{P_{MDO}}$ [d]	0.88	0.95

[a] Since the amount of monodeuterated alkane (C) formed from disproportionation must equal the monodeuterated olefins formed from disproportionation, $C/f(E + F) + A = 1$, where $(1 - f)$ equals the fraction of (E + F) that is formed by allylic abstraction, the k_{ab}/k_{add} was calculated by $k_{ab}/k_{add} = [2I + (1 - f)(E + F) + B]/[A + C + D + f(E + F) + 2G + H]$. [b] The total percentage conversion of 1-octene was 11.2. [c] The total percentage conversion of 1-octene was 9.2. [d] The ratio of products formed from disproportionation: P_{MDA}, monodeuterated alkanes; P_{MDO}, monodeuterated olefins.

The ratio, k_{total}^H/k_{total}^D appears to decrease, as expected, for reactions which involve abstraction of either 1°:2°:3° hydrogen. If we assume that addition to a disubstituted or monosubstituted ethylene does not show an isotope effect for addition then the values reported are due to allylic abstraction. They range from 1.17 (*cis*-2-butene):1 (1-butene):0.97 (3-methyl-1-butene).

A tetrasubstituted olefin, 2,3-dimethyl-2-butene, whose abstraction/addition rate constant ratio has been estimated using pulsed radiolysis (23 °C) was compared with our data. The reported ratio of rate constants at 23 °C (k_{ab}^H/k_{add}^H) was $<2.5 \times 10^{-4}$ (Table 2, entry 4). A comparison with our relative rate
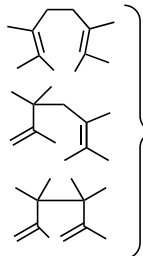
TABLE 4: Product Distribution from the Reaction of Atomic Deuterium with *cis*-4-Octene[a,b]

products R = C₂H₅	yield (%) −72 °C	yield (%) −63 °C	yield (%) −51 °C
(A)	10.2	6.98	7.74
(B)	2.32	1.68	2.05
(C)	5.15	3.95	3.86
(D)	7.47	5.48	5.92
(E)	58.6	66.8	69.4
(F)	13.5	12.3	8.89
(G)	2.7	2.74	2.13
$\dfrac{P_{MDA}}{P_{MDO}}$ [c]	1.0	0.97	1.0

[a] Since the monodeuterated alkane (D) formed from disproportionation must equal the monodeuterated olefins formed from disproportionation, $D/f(B) + C = 1$, where $(1 - f)$ equals the fraction of (B), which is formed by allylic abstraction. The relative rate constant k_{ab}/k_{add} was calculated as $k_{ab}/k_{add} = [A + (1 - f)B + G]/[D + E + 2F + C + f(B)]$. [b] The total percentage conversion of *cis*-4-octene was 20.5, 9.2, and 25.0 at −72, −63, and −51 °C, respectively. [c] The ratio of products formed from disproportionation: P_{MDO}, monodeuterated alkanes; P_{MDO}, monodeuterated olefins.

data $(k_{ab}^D/k_{add}^D = 1.2 \times 10^{-1})$ at 23 °C, however, unlike the data obtained for entries 1 and 3, was not in agreement (Table 2,

9330 *J. Phys. Chem. A, Vol. 101, No. 49, 1997*

Tanner et al.

TABLE 5: Product Distributions from the Reactions of Atomic Deuterium 2,3-Dimethyl-2-butene[a,b]

products	yield (%) −63 °C	yield (%) −72 °C	yield (%) −94 °C
(A)	21.7	16.5	11.5
(B)	7.22	4.89	3.14
(C)	22.7	21.4	15.2
(D)	19.4	27.2	35.9
(E)	22.7	21.4	15.2
(F)	2.15	7.54	18.2
(G)	3.61	0.85	0.64
(H)	0.51	0.11	0.20

[a] The total percentage conversions of 2,3-dimethyl-2-butene were 13.9, 16.6, and 15.0 at −63, −72, and −94 °C, respectively. [b] The amount of monodeuterated alkane (E) from the addition, disproportionation pathway was estimated by determining the amount of monodeuterated alkene (C), since their ratio should be equal to 1. The relative rate k_{ab}/k_{add} was calculated by the following equation k_{ab}/k_{add} = [A + B + D + 2H]/[C + E + F + 2G].

entry 4) with the published values (see Table 2). To calculate both k_{ab}^H and k_{add}^H from our data it was necessary to estimate the isotope effects for both abstraction and addition. Although the isotope effect for addition to ethylene,[9] mono or disubstituted ethylene[5] is 1, the isotope effect for the reaction of the tetrasubstituted ethylene does not appear to be the same. An attempt to calculate this isotope effect can be made using the known total isotope effect ($k_{total}^H/k_{total}^D = 0.82$) previously reported[5] for the vapor phase reactions of 2,3-dimethyl-2-butene in combination with the value of ($k_{ab}^H/k_{ab}^D = 1.17$) for the kinetic isotope effect for the abstraction of the primary hydrogens of 2-butene,[5] see eq 1 and Table 2.

$$k_{ab}^H = \frac{1.17(k_{add}^H)}{0.82\left[\left(\dfrac{k_{add}^D}{k_{ab}^D}\right) + 1\right] - \left(\dfrac{k_{ab}^H}{k_{ab}^D}\right)} = 4.06 \times 10^7 \text{ s}^{-1} \text{ M}^{-1} \quad (1)$$

The calculated value for abstraction of a primary hydrogen is only 1.5 times slower than the value (6.2×10^7 M^{-1} s^{-1}) found[6] for abstraction of a secondary hydrogen (23 °C). However, if the abstraction rate for a secondary hydrogen, obtained for the reaction of 1-octene (this work) is used to calculate the 1°/2° abstraction rate ratio, a more reasonable value (1:9) is obtained.

The reaction of atomic deuterium with an allylic hydrocarbon having a terminal olefin and a tertiary hydrogen was carried

TABLE 6: Product Distributions from the Reactions of Atomic Deuterium with 3-Methyl-1-pentene[a,b]

products	yield (%) −72 °C	yield (%) −63 °C	yield (%) −51 °C
(A)	1.04	4.36	11.8
(B)	13.9	4.45	8.23
(C)	21.7	22.5	21.6
(D)	33.2	18.0	27.5
(E)	17.5	18.2	14.9
(F)	4.05	6.52	4.64
(G)	3.32	11.5	9.02
(H)	2.47	6.67	0.92
(I)	2.26	6.86	1.13
(J)	0.43	0.82	0.21
$\dfrac{P_{MDA}}{P_{MDO}}$ [c]	1.02	1.00	0.98
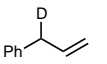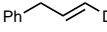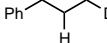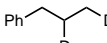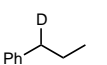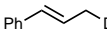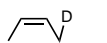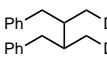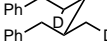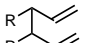
[a] The total percentage conversions of 2-methyl-1-pentene were 7.40, 4.89, and 22.6 at −92, −72, and −63 °C, respectively. [b] Since the amount of monodeuterated alkane (C) formed from disproportionation must equal that of monodeuterated olefins formed from disproportionation, $1/[f(F + G) + B] = 1$, where $(1 − f)$ equals to the fraction of (F + G), which is formed by allylic abstraction. The relative rate constant k_{ab}/k_{add} was calculated by k_{ab}/k_{add} = [A + E + (1 − f)(F + G) + 2J]/[B + f(F + G) + C + D + 2H + I]. [c] The rates of products formed from disproportionation: P_{MDA}, monodeuterated alkanes; P_{MDO}, monodeuterated olefins.

out with 3-methyl-1-pentene (Table 2, entry 5). Competitive addition/allylic abstraction takes place at 23 °C, (k_{ab}^D/k_{add}^D) = 6.8×10^{-1}. Using the temperature dependence determined for a terminal olefin[4] the rate constant for allylic abstraction of a tertiary hydrogen atom can be calculated at 23 °C, $k_{ab}^D = 2.8 \times 10^9$ s^{-1} M^{-1}. Since the total kinetic isotope effect for the vapor phase reaction of 3-methyl-1-butene has been reported[5] as $k_{total}^H/k_{total}^D = 0.97$, and the isotope effect for addition to a terminal olefin is approximately 1, then the isotope effect for abstraction is $k_{ab}^H/k_{ab}^D = 0.97$ and $k_{ab}^H = 2.7 \times 10^9$ s^{-1} M^{-1}. The abstraction rate at 23 °C, k_{ab}^H, when compared with those obtained for 1° and 2° hydrogen abstraction (3°:2°:1°), was 66:9:1 (at 65 °C 3°:2° is 5:1). The rate ratios were in excellent agreement with those found for allylic abstraction by methyl radicals (43:11:1) at 65 °C.[7]

Experimental Section

Materials. 1-Octene, allylbenzene, 2,3-dimethyl-2-butene, 3-methyl-1-pentene, *cis*-4-octene, 2,3-dimethylbutane, 2,3-dimethyl-1-butene, 2-methyl pentane, and 3-methyl-2-pentene

Allylic Abstraction of Hydrogen

J. Phys. Chem. A, Vol. 101, No. 49, 1997 **9331**

TABLE 7: Product Distribution from the Reaction of 3-Phenyl-1-propene with Atomic Deuterium[a,b]

products	yield (%) −23 °C	yield (%) −42 °C	yield (%) −72 °C
(A)	0.23	0.71	0.41
(B)	9.55	11.0	17.5
(C)	14.8	24.4	29.7
(D)	52.7	20.5	19.3
(E)	5.31	4.09	1.32
(F)	9.72	11.4	9.32
(G)	4.86	3.79	2.92
(H)	2.21	20.4	16.9
(I)	0.25	1.85	1.19
(J)	0.33	1.72	1.39

[a] The total conversions of 3-phenyl-1-propene were 4.9, 5.0, and 9.5 at −23, −42, and −72 °C, respectively. [b] Since the monodeuterated alkane (C) should be equal to the monodeuterated alkenes B, F, and G from disproportionation (C/[B + f(F + G)] = 1), where (1 − f) is the fraction of F + G arising from the allylic abstraction the relative rate constant was calculated as the following equation $k_{ab}/k_{add} = [A + E + (1 − f)(F + G) + 2J]/[B + C + D + f(F + G) + 2H + I]$.

(Aldrich) were checked for purity by GC and used as received. Samples of *cis*- and *trans*-propenyl benzene and propyl benzene (99%) were purchased from chemical samples company, Columbus, Ohio and used as received.

Tetrabenzylethylene was prepared according to the literature procedure.[10] 1,3-Diphenylacetone (Aldrich) was allowed to react with anhydrous titanium trichloride and lithium in 1,2-dimethoxyethane. The resulting product was recrystallized from methanol and purified by flash chromatography to yield 73% of tetrabenzylethylene as a crystalline solid: mp 121−122 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.61 (s, 8 H), 7.2−7.4 (m, 20 H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 37.23, 126.13, 128.52, 128.71, 134.37, 140.35; IR 3030 (benzene ring CH), 1600 cm^{-1} (C=C). Anal. Calcd for C$_{30}$H$_{28}$: C, 92.74; H, 7.26. Found: C, 92.44; H, 7.26.

Identification and Characterization of the Reaction Products. Propyl benzene, *cis*- and *trans*-propenyl benzene, 2,3-dimethyl-1-butene, 2,3-dimethyl butane, 3-methyl-2-pentene, 2-methylpentane, octane, and *cis*- and *trans*-2-octene were identified by comparison of their GC/IR and GC/MS with authentic samples. The dimeric products were separated from the reaction mixture and identified by GC/IR, GC/MS and GC/AED.

Determination of the Relative Rates between Hydrogen (Deuterium) Atom Addition and Allylic Abstraction. An aliquot (5 mL, 1−3 M) of a substrate in acetone was placed in a U-shaped reactor[3] and allowed to react with the atoms produced by a D$_2$/He or H$_2$/He plasma (D$_2$ or H$_2$ flow rate; 6 mL/min, 4−5 Torr, −94 to −23 °C) for 5−15 min. The reaction mixture was analyzed by ^{2}H NMR, GC/MS and GC/IR. The relative rates were calculated from the relative amounts of the products originating from allylic abstraction and addition to the double bond. The relative rates were corrected for the number of abstractable hydrogen atoms. In the case of 2,3-

dimethyl-2-butene and *cis*-4-octene the addition rate was corrected for the two equivalent sites at which the addition of a hydrogen atom can occur.

Reactions with 1-Octene. The products from allylic abstraction were calculated from the ^{2}H NMR integrals for the 3-D absorption of 1-octene (2.15 ppm) and the GC analysis for the diunsaturated dimer. The products for addition were calculated using the ^{2}H NMR integrals for compounds having terminal deuterium. The remaining products were quantitated in the same manner as previously described.[4]

Reactions with 3-Methyl-1-pentene. The products from allylic abstraction were calculated from the ^{2}H NMR integrals for the 3-D absorption of 3-methyl-1-pentene (2.10 ppm), 3-D for 3-methylpentane (1.47 ppm) and by GC analysis for the diunsaturated dimer. The products from the addition were calculated by ^{2}H NMR integrals of the compounds having a terminal deuterium.

Reactions with *cis*-4-Octene. The products from allylic abstraction were calculated from the ^{2}H NMR integrals for the 3-D absorption of *cis*-4-octene (2.11 ppm) and by the GC analysis of the unsaturated dimer. The products from addition were calculated from the ^{2}H NMR integrals for the 4-D absorption of octane (1.36 ppm), the 4-D absorption of 4-octene (5.50 ppm), the 5-D absorption for 3-octene (2.05 ppm) and the 4,7-D absorption of 4,4-dipropyl decane (1.22 ppm).

Reactions with 2,3-Dimethyl-2-butene. The products from the allylic abstraction pathway were calculated from the ^{2}H NMR integrals of the 1-D absorption of 2,3-dimethyl-2-butene (1.64−1.68 ppm), 1-D absorption of 2,3-dimethylbutane (0.84 ppm), 1-D absorption of 2,3-dimethyl-1-butene (4.66 ppm, 4.71 ppm) and from the GC analysis of unsaturated dimers. The products from the addition pathway were calculated from the ^{2}H NMR integrals of the 2-D and 3-D deuterium of 2,3-dimethyl butane (1.39 ppm), the 2-D and 5-D of 2,3,3,4,4,5-hexa methyl hexane (1.39 ppm), and the 3-D of 2,3-dimethyl-1-butene (2.23 ppm). The data were corrected to account of 2,3-dideutero-2,3-dimethyl butane.

Reactions with 3-Methyl-1-pentene. The products from allylic abstraction were calculated from the ^{2}H NMR integrals for the 3-D absorptions for 3-methyl-1-pentene (2.10 ppm), 3-methylpentane (1.47 ppm) and by GC analysis for the diunsaturated dimer. The products from the addition were calculated by ^{2}H NMR integrals of the compounds having a terminal deuterium.

Reactions with Allylbenzene. The products from allylic (benzylic) abstraction was calculated from the ^{2}H NMR integrals for benzylic allylic deuterium in allyl benzene (3.44 ppm), benzylic deuterium in propyl benzene (2.64 ppm) and the unsaturated dimer by GC analysis of the product mixture. The products from the addition were calculated by ^{2}H NMR integrals of the compounds having terminal deuterium.

Reaction of Atomic Hydrogen with Tetrabenzylethylene. A solution of tetrabenzylethylene (1 M in DMSO, Freon-11 or Fluorolube) was allowed to react with atomic hydrogen or deuterium produced with a H$_2$/He or D$_2$/He plasma. The products were analyzed both by TLC and by HPLC. HPLC analyses were carried out on a Perkin-Elmer Series 2 liquid chromatograph with a Perkin-Elmer LC-55B spectrophotometric detector interfaced with a Varian Vista CDS 401 chromatograph data system. An S$_1$-normal phase Radial-PAK liquid chromatography cartridge column was used for the HPLC analysis. Hexane was used as eluant. No 1,2-addition product was detected. When the tetrabenzylated ethylene was allowed to react with a D$_2$/He plasma and the reaction mixture was subjected to ^{2}H NMR analysis a 12:1 ratio of aromatic

substituted deuterium:benzylic substituted deuterium was (δ 7.3):(δ 1.5), was observed. When the reaction was carried out with H_2 in Freon 11 and -100 °C and in Fluorolube at 70 °C no reduction products could be found.

References and Notes

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

(2) Postdoctoral Fellow, University of Alberta 1994−1996.

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

(4) Tanner, D. D.; Zhang, L.; Kandanarachchi, P. *J. Phys. Chem.* **1996**, *100*, 11319.

(5) Daby, E. E.; Niki, H.; Weinstock, B. *J. Phys. Chem.* **1971**, *75*, 1601.

(6) Hardwick, T. J. *J. Phys. Chem.* **1962**, *66*, 291.

(7) Buckley, R. P.; Szwarc, M. *Proc. R. Soc. London*, **1957**, *A240*, 396.

(8) (a) Marcoux, L. S.; Adams, R. N.; Feldberg, S. W. *J. Phys. Chem*. **1969**, *73*, 2611. (b) Nelson, R. F.; Feldberg, S. W. *Ibid*. **1969**, *73*, 2623. (c) Cvetanovic, R. J.; Doyle, L. C. *J. Chem. Phys.* **1969**, *50*, 4705.

(9) (a) Toby, S.; Schiff, H. I. *Can. J. Chem*. **1956**, *34*, 1061. (b) Melville, H. W. *J. Chem. Soc*. **1934**, 1243.

(10) (a) Fleming, M. P.; McMurry, J. E. In *Organic Synthesis*; Chapman, O. L., Ed.; John Wiley and Sons: New York, 1982; Vol. 60, p 113. (b) Fleming, M. P.; McMurry, J. E. *J. Am. Chem. Soc*. **1974**, *96*, 4708.