

Arrhenius Parameters for the Reactions of Hydrogen and Deuterium Atoms with Four Butenes

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The absolute rate constants of the H and D atom addition to 1-butene, *cis*- and *trans*-2-butenes, and isobutene have been measured over the temperature range 200–500 K at the total pressure of about 600 Torr (1 Torr = 133.3 Pa). The rate constants obtained were well expressed by the Arrhenius equations: $k(\text{H} + 1\text{-butene}) = (2.48 \pm 0.43) \exp[-(1492 \pm 94)/RT]$, $k(\text{H} + \textit{cis}\text{-2-butene}) = (2.67 \pm 0.39) \exp[-(1918 \pm 83)/RT]$, $k(\text{H} + \textit{trans}\text{-2-butene}) = (3.96 \pm 0.27) \exp[-(2096 \pm 37)/RT]$, $k(\text{H} + \textit{isobutene}) = (2.08 \pm 0.16) \exp[-(860 \pm 49)/RT]$, $k(\text{D} + 1\text{-butene}) = (2.42 \pm 0.72) \exp[-(1642 \pm 169)/RT]$, $k(\text{D} + \textit{cis}\text{-2-butene}) = (2.25 \pm 0.19) \exp[-(2082 \pm 48)/RT]$, $k(\text{D} + \textit{trans}\text{-2-butene}) = (2.33 \pm 0.23) \exp[-(2036 \pm 55)/RT]$, and $k(\text{D} + \textit{isobutene}) = (1.54 \pm 0.19) \exp[-(879 \pm 81)/RT]$ in units of $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The isotope effects due to the difference between H and D atoms can simply be explained by the difference in collision frequency. The difference between *cis*- and *trans*-2-butenes in reactivity may be explained in terms of the pre-exponential factors.

The reactions of hydrogen atoms with olefins have long been a subject for chemical kinetics. Twenty years ago, the relative rate constants of addition of hydrogen atoms to a number of simple olefins at room temperature were measured by Jennings and Cvetanović, who used a photochemical competitive technique.¹⁾ Since then, several different experimental approaches were devised for the determination of these relative rate constants, and some disparities in the rate constants were reported.^{2,3)}

In the last decade, new techniques such as flash photolysis,⁴⁾ pulse radiolysis,⁵⁾ and a phase shift method⁶⁾ were introduced for the determination of the absolute rate constants of simple reactions. Consequently, the absolute rate constants as well as their temperature dependence for a number of simple reactions have been accumulated and are awaiting theoretical analysis. Absolute rate constants of hydrogen atom addition to olefins have also been measured.⁷⁾ A few years ago, our laboratory used the pulse radiolysis-resonance absorption technique for the determination of the rate constants of these reactions⁸⁾ and confirmed that the relative rate constants reported by Jennings and Cvetanović are the most reliable among earlier measurements.

The temperature dependence for these rate constants, however, has not been reported except for the reaction $\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$. In the preceding paper,⁹⁾ we reported the temperature dependence for the reaction $\text{H} + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_7$; therefore, we have extended our measurement to the reactions with four butenes: 1-butene, *cis*- and *trans*-2-butenes, and isobutene.

It is well known that among simple mono-olefins at room temperature isobutene is the most reactive to hydrogen atoms. This is probably because the activation energy for this reaction is the smallest; however, the absolute value has not been reported. On the other hand, in many free radical addition reactions, *trans*-2-butene is often found to be about 10% more reactive than *cis*-2-butene;¹⁰⁾ therefore, it may be worthwhile to know whether this difference in the hydrogen atom addition reaction comes from its activation energy or from the pre-exponential factor.

Experimental

The experimental procedure is the same as described in a previous paper.¹¹⁾ The mixture of about 600 Torr hydrogen or deuterium and a small amount of an olefin (0.01–0.1 Torr) was pulse-irradiated with high energy electrons from a Febetron 706 (Hewlett Packard) and the decay of the concentration of hydrogen or deuterium atoms was followed by the absorption of the Lyman- α radiation.

1-Butene, *cis*- and *trans*-2-butenes, and isobutene were purchased from the Takachiho Shoji Co. and used as supplied. Gas-chromatographic analysis using a 5 m long column packed with dimethyl sulpholane on celite showed that impurities in each butene are less than 1%.

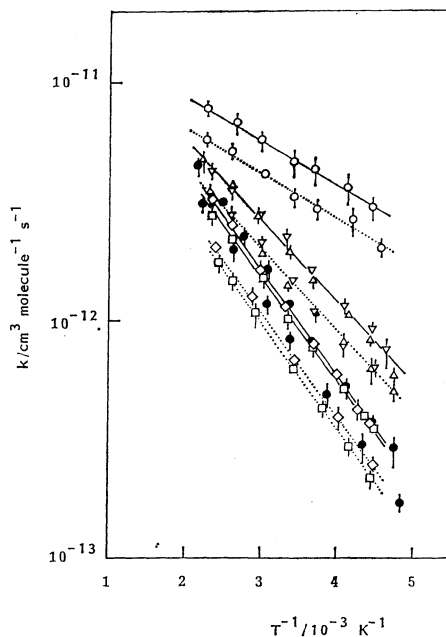


Fig. 1. Arrhenius plots for the reactions of H and D atoms with olefins: (●) ethylene, (△) propylene, (▽) 1-butene, (□) *cis*-2-butene, (◇) *trans*-2-butene, and (○) isobutene. Solid lines for H atom reactions and dotted lines for D atom reactions.

TABLE 1. RATE CONSTANTS OF H OR D ATOM ADDITION TO C₄ OLEFINS
Uncertainties are 2 σ .

Reaction	T/K	$k/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹	Reaction	T/K	$k/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹
H + 1-Butene	426	4.12 \pm 0.32	H + <i>trans</i> -2-Butene	423	3.22 \pm 0.46
	379	3.56 \pm 0.42		379	2.49 \pm 0.26
	331	2.66 \pm 0.36		333	1.65 \pm 0.20
	299	2.19 \pm 0.31		299	1.15 \pm 0.14
	272	1.60 \pm 0.09		269	0.783 \pm 0.066
	244	1.10 \pm 0.06		249	0.585 \pm 0.053
	223	0.914 \pm 0.096		233	0.414 \pm 0.059
	216	0.730 \pm 0.145		225	0.365 \pm 0.035
D + 1-Butene	428	3.10 \pm 0.52	D + <i>trans</i> -2-Butene	421	2.03 \pm 0.13
	383	2.75 \pm 0.41		348	1.26 \pm 0.12
	334	2.13 \pm 0.12		292	0.679 \pm 0.057
	292	1.49 \pm 0.17		248	0.394 \pm 0.051
	272	1.09 \pm 0.08		225	0.244 \pm 0.014
	245	0.778 \pm 0.070	H + Isobutene	438	7.69 \pm 0.44
	222	0.625 \pm 0.055		375	6.69 \pm 0.61
H + <i>cis</i> -2-Butene	423	2.73 \pm 0.37		335	5.64 \pm 0.43
	380	2.16 \pm 0.19		293	4.60 \pm 0.88
	330	1.49 \pm 0.15		270	4.34 \pm 0.46
	297	1.00 \pm 0.05		242	3.53 \pm 0.60
	270	0.764 \pm 0.061		225	2.95 \pm 0.33
	243	0.500 \pm 0.048	D + Isobutene	447	5.78 \pm 0.23
	227	0.390 \pm 0.036		390	5.12 \pm 0.33
	221	0.356 \pm 0.043		333	4.06 \pm 0.06
D + <i>cis</i> -2-Butene	412	1.74 \pm 0.16		295	3.28 \pm 0.37
	382	1.47 \pm 0.13		270	2.95 \pm 0.24
	341	1.05 \pm 0.15		240	2.65 \pm 0.23
	292	0.612 \pm 0.039		221	2.02 \pm 0.35
	262	0.423 \pm 0.030			
	241	0.288 \pm 0.027			
	226	0.215 \pm 0.024			

TABLE 2. ARRHENIUS PARAMETERS FOR THE REACTIONS OF H AND D ATOMS WITH C₄ OLEFINS
 $A/10^{-11}$ cm³ molecule⁻¹ s⁻¹ and $E/\text{cal mol}^{-1}$. Uncertainties are 2 σ .

Olefin	H-Atom addition		D-Atom addition	
	A	E	A	E
1-Butene	2.48 \pm 0.43	1492 \pm 94	2.42 \pm 0.72	1642 \pm 169
<i>cis</i> -2-Butene	2.67 \pm 0.39	1918 \pm 83	2.25 \pm 0.19	2082 \pm 48
<i>trans</i> -2-Butene	3.96 \pm 0.27	2096 \pm 37	2.33 \pm 0.23	2036 \pm 55
Isobutene	2.08 \pm 0.16	860 \pm 49	1.54 \pm 0.19	879 \pm 81

Results

Table 1 summarizes the rate constants obtained at various temperatures. Each rate constant was estimated as the average of four to five measurements. Figure 1 shows the Arrhenius plots. For comparison, the rate constants obtained with ethylene and propylene are also plotted. All data are well expressed by the Arrhenius equations. The Arrhenius parameters calculated by the least squares method¹²⁾ are summarized in Table 2.

Discussion

Isotope Effects Due to the Difference between H and D Atoms and the Tunneling Effect. Figure 1 clearly shows that Arrhenius plots for H and D atom reactions with the same olefin are always parallel and the interval is nearly constant irrespective of the kind of reactant olefin. This fact can simply be explained by the difference in collision frequency as follows:¹³⁾

$$k_{\text{H}}/k_{\text{D}} \approx \left[\frac{m_{\text{D}}m_{\text{olefin}}}{m_{\text{D}} + m_{\text{olefin}}} \right]^{1/2} \left/ \left[\frac{m_{\text{H}}m_{\text{olefin}}}{m_{\text{H}} + m_{\text{olefin}}} \right]^{1/2} \right. \cong \sqrt{2}.$$

Here k_{H} and k_{D} are the rate constants of the H and D atom reactions. m_{H} , m_{D} , and m_{olefin} are the masses

TABLE 3. RELATIVE VALUES OF PRE-EXPONENTIAL FACTORS

Olefin	H-Atom addition	D-Atom addition
Ethylene	(2.0)	(2.0)
Ethylene- d_4	1.94	2.11
<i>cis</i> -2-Butene	1.14	1.34
<i>trans</i> -2-Butene	1.69	1.39
Propylene	1.28	1.18
Propylene- d_6	1.09	1.31
1-Butene	1.05	1.44
Isobutene	0.89	0.92

of H and D atoms and olefin molecules, respectively.

In the hydrogen atom-molecule reaction, $H + H_2 \rightarrow H_2 + H$, the Arrhenius plots deviated from linearity at temperatures lower than 300 K and the deviation showed a strong H/D isotope effect.¹⁴ This result has been attributed to the tunneling effect. In the present reaction systems, however, no such deviation from linearity could be observed within experimental error. Although a slightly concave curve can be realized in the Arrhenius plot for the reaction of $H + C_2H_4 \rightarrow C_2H_5$, this is also found in the reaction of $D + C_2D_4 \rightarrow C_2D_5$; therefore, this curvature cannot be attributed to the isotope effect.

The Number of Reaction Site and the Difference in Reactivity between cis- and trans-2-Butenes. It is now well known that in the reactions of unsymmetric olefins such as propylene, 1-butene, and isobutene, a hydrogen atom adds to the less substituted carbon atom of the double bond. In other words, there is only one reaction site. On the other hand, symmetric olefins such as ethylene and 2-butenes have two identical reaction sites. In the simple collision theory, the difference in the number of reaction sites should appear in the pre-exponential factors. Table 3 compares the relative values for the pre-exponential factors. Although the exact ratio between symmetric and unsymmetric olefins is not clearly determined, the expected trend can be observed.

Another noticeable point in Table 3 is the difference between *cis*- and *trans*-2-butenes. Although the experimental errors prevent us from estimating the quantitative ratio, the difference in reactivity between *cis*- and *trans*-2-butenes may be attributed to the difference in the pre-exponential factors. If methyl radical substitution restricts the reaction zone for an attacking hydrogen atom, unrestricted spaces on two carbons at both sides of the double bond may overlap with each other in the case of *cis*-2-butene, but not in the case of *trans*-2-butene. This difference probably corresponds to the difference in the pre-exponential factors.

Atom Localization Energies. When Jennings and Cvetanović measured the relative rate constants of H atom addition to a series of simple olefins, they compared the logarithms of the rate constants with the

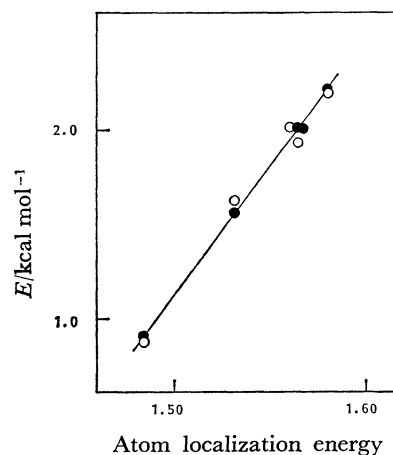


Fig. 2. Correlation between activation energies (\circ for H atom reactions and \bullet for D atom reactions) and atom localization energies of olefins.

atom localization energies of the olefins, which were calculated by the simple Hückel method on the assumption of hyperconjugation, and obtained a linearity.¹ However, it is obvious that the atom localization energies should be compared with the activation energies. Figure 2 shows this comparison. A linear relation has been obtained as expected.

The atom localization energy is a very rough concept. A more sophisticated treatment is highly desirable.

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