Isomerization of Chemically Activated 1-Buten-1-yl and 1-Buten-4-yl Radicals

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Chemically activated 1-buten-1-yl radicals were generated by the addition of ethyl radicals produced by the photolysis of diethyl ketone to acetylene at 75 and 123°. The unimolecular rate constant for the isomerization of the excited 1-buten-1-yl to 1-buten-4-yl radicals through 1,4-hydrogen atom migration was measured. In addition, it was found that the 1-buten-4-yl formed can isomerize to methylallyl radicals via 1,2-H atom shift. The average rate constants for isomerization were found to be 1.00×10^9 and 1.05×10^9 sec⁻¹ for 1-buten-1-yl and 3.47×10^7 and $6.20 \times 10^7 \text{ sec}^{-1}$ for 1-buten-4-yl radicals at 75 and 123°, respectively. The best agreement between the rate constants as calculated by the RRKM theory and the experimental results was found when the threshold energies, E_0 , were chosen as 17.1 and 33.0 kcal/mol for 1,4-and 1,2-H atom shifts, respectively. It is shown that these values satisfy the expression, $E_0 = E_{ab} + E_s$, where E_{ab} is the activation energy for a bimolecular H atom abstraction and E_s is the ring strain energy.

Introduction

Isomerization of vibrationally excited radicals via intramolecular hydrogen atom migration forms an important class of the reactions of alkyl¹⁻⁹ and alkenyl radicals¹⁰⁻¹⁴ both in thermal⁶⁻⁹ and chemical activation systems.^{1-5,10-14} Especially 1,4- and 1,5-hydrogen atom migrations which occur via five- and six-membered cyclic transition states have been well studied, the activation energies of which have been found to be in the range $15-21^{1-4,6,7,10,13}$ and $8-11 \text{ kcal/mol},^{3,8,9}$ respectively. Study of the isomerization of nonyl-2 to nonyl-3 radical through 1,6-H atom shift has given the value of 16.0 kcal/mol as the threshold energy.³ Recently, 1,2- and 1,3-H atom shifts have been substantiated in chemical activation systems and they have high threshold energies, $30-34.5 \text{ kcal/mol}.^{5,13,14}$

In the calculation of the RRKM specific reaction rate, two factors are required; one is the vibrational frequency assignments of the radical and H-atom transfer activated complex, and the other is the critical energy for isomerization. The former can be obtained by using the formulation developed by Rabinovitch and coworkers.^{3,15} For the latter we proposed in a previous paper¹⁴ that the critical energy can be approximately estimated by the expression, $E_0 = E_{ab} + E_s$, where E_0 is the critical energy, E_{ab} the activation energy for a bimolecular H atom abstraction, and E_s the ring strain energy.

In previous work,⁵ the rate constant for a 1,2-H atom shift was measured by the relative yields of the decomposition products. The object of this work is to substantiate 1,2-H atom shift by measuring the relative yields of stabilized isomers and to ascertain the above expression in the case of isomerization of vibrationally excited 1-buten-1-yl and 1-buten-4-yl radicals.

Experimental Section

The experimental details were the same as described previously.¹⁴ 1-Buten-1-yl radicals were generated by the vapor phase photolysis of diethyl ketone in the presence of acetylene. A quartz reactor of 206 cm³ was used. The cell was illuminated with the output from a 500-W high-pressure mercury lamp with a Matsuda UV-27 filter interposed to cut off radiation of wavelength shorter than 2500 Å. Analyses were carried out by gas chromatography using a 2.25-m phenylisocyanate-Porasil C (Waters Associates Inc.,) and a 2.25-m Porapak Q columns. Reaction products were identified by the retention time of authentic substances and also by means of Shimadzu Model LKB-9000 gas chromatograph-mass spectrometer.

Results

Reaction of Excited 1-Buten-1-yl Radicals. The products measured were ethane, ethylene, n-butane, 1-butene, 1,3-butadiene, 3-methyl-1-pentene, cis- and trans-3-hexene (and/or cis- and trans-2-hexene), cis- and trans-1,3hexadiene, and benzene. Despite efforts to detect further products, none could be found (i.e., no substantial chromatographic peaks eluted after benzene). The peaks were well resolved except cis and trans isomers and 3-hexene overlapped completely with 2-hexene. The rate of formation of each product is given in Tables I and II.

The addition of ethyl radicals to acetylene at 75 and 123° produces a 1-buten-1-yl radicals with about 33 kcal/mol in average (see Discussion section). The excited radical can either react or be stabilized by collisional energy transfer. The presence of 1-hexene and 3-methyl-1-pentene seems to be an evidence for the existence of 1-buten-4-yl and methylallyl radicals, respectively.

Stabilized 1-buten-1-yl radicals abstract a H atom from diethyl ketone to yield 1-butene. Combination of 1-buten-1-yl with ethyl radicals produces 3-hexene. Cross disproportionation products may be 1-butyne and ethane. However, the amount of 1-butyne was too small to be measured. Subsequent addition of 1-buten-1-yl to acetylene results in 1,3-hexadiene and benzene which appear in the steps of typical free-radical-initiated polymerization of acetylene.¹⁶ Methylallyl radicals may react with ethyl radicals to produce 2-hexene, 2-butene, and 1,2-butadiene in addition to 3-methyl-1-pentene. However, 2-hexene could not be resolved and cross disproportionation products were also too small to be measured in the present conditions.

A reaction scheme which can explain the products distribution shown in Tables I and II and their dependence on pressure is given as

$$C_2H_5COC_2H_5 + h\nu \rightarrow 2C_2H_5 + CO \tag{1}$$

TABL	E I: Exper	imental Re	sults at 75°	C Q									-		
No.	DEK pressure ^a	C_2H_2 pressure	Total pressure	Temp, °C	t,b sec	C_2H_6c	C_2H_4	n - C_4H_{10}	$1-C_4H_8$	$1,3-C_4H_6$	3MP1d	1-C ₆ H ₁₂	2-C ₆ H ₁₂ + 3-C ₆ H ₁₂	1,3-C ₆ H ₁₀	C_6H_6
11	34.2	104.0	138.2	74.3	300	12.2	7.73	58.3	8.37	0.335	0.0321	3.14	0.213	1.14	0.233
12	30.6	68.1	98.7	75.7	300	11.8	7.00	56.3	5.64	0.290	0.0325	2.69	0.164	0.666	0.122
13	34.6	42.4	77.0	75.8	300	12.7	7.67	63.9	3.87	0.201	0.0275	2.02	0.121	0.232	0.0451
14	14.2	41.8	56.0	74.3	300	5.66	3.88	32.5	1.69	0.203	0.0369	1.79	0.112	0.212	0.0555
15	9.8	45.4	55.2	74.1	300	3.80	2.70	21.5	1.19	0.194	0.0354	1.64	0.108	0.186	0.0868
16	26.6	28.0	54.6	74.7	360	10.3	6.75	57.1	2.10	0.161	0.0284	1.60	0.0947	0.130	0.0326
17	11.4	43.0	54.4	75.7	300	4.38	3.14	25.3	1.41	0.208	0.0352	1.72	0.110	0.208	0.0709
18	18.0	36.1	54.1	75.1	300	7.07	4.83	40.4	1.92	0.207	0.0353	1.83	0.112	0.184	0.0367
19	35.7	18.0	53.7	75.2	300	13.8	8.31	73.4	1.80	0.113	0.0173	1.16	0.0619	0.0535	0~
20	13.9	38.3	52.2	74.7	300	5.26	3.84	31.5	1.57	0.216	0.0369	1.74	0.103	0.195	0.0399
21	9.1	37.6	46.7	74.1	300	3.40	2.46	20.5	1.01	0.192	0.0341	1.50	0.0962	0.166	0.0646
22	14.9	22.7	37.6	74.0	300	5.94	4.29	34.8	0.992	0.147	0.0288	1.26	0.0819	0.0736	~0
23	20.5	11.3	31.8	74.9	300	8.51	5.75	49.9	0.596	0.0751	0.0155	0.722	0.0407	0~	0~
24	7.0	22.7	29.7	75.0	300	2.52	1.86	14.6	0.396	0.139	0.0310	0.963	0.0662	0.0467	0.0310
25	10.9	12.1	23.0	75.9	300	3.89	2.83	23.6	0.333	0.0876	0.0236	0.653	0.0500	0.0220	0.0103
<i>a</i> Pre	ssures are (expressed i	n Torr. b Pł	10tolysis t	ime. ^c Pro	ducts are e	xpressed	in terms of	their rates	of formation	n in mol cm	$^3 \text{ sec}^{-1} \times 10$	112. d 3-Meth	yl-1-pentene.	

TABLE II: Experimental Results at 123° Ca

	DEK	C.H.	Total	Temp.	t.								2-C,H,, +		
No.	pressure	pressure	pressure	°.	sec	C_2H_6	C_2H_4	n-C ₄ H ₁₀	$1-C_4H_8$	$1,3-C_4H_6$	3MP1	$1-C_6H_{12}$	3-C ₆ H ₁₂	1,3-C ₆ H ₁₀	C_6H_6
31	33.5	100.0	133.5	123.9	180	14.0	6.06	28.2	19.3	1.42	0.158	6.51	0.478	3.32	1.41
32	32.0	66.2	98.2	122.1	180	15.2	6.63	36.2	14.5	1.29	0.179	6.99	0.458	2.11	0.634
33	35.7	36.4	72.1	122.5	60	38.2	17.0	103.4	20.9	2.07	0.306	11.9	0.554	1.00	0.480
34	29.0	29.8	58.8	123.3	60	14.8	6.92	42.5	7.12	0.975	0.164	5.12	0.334	0.588	0.135
35	13.6	44.9	58.5	123.0	300	6.09	3.65	19.8	4.49	1.10	0.211	5.03	0.425	0.755	0.553
36	14.3	43.9	58.2	123.0	180	5.85	3.36	18.7	4.25	1.03	0.186	4.38	0.379	0.702	0.501
37	18.0	39.6	57.6	121.3	180	8.56	4.62	28.1	5.25	1.06	0.200	5.44	0.438	0.744	0.335
38	9.3	48.3	57.6	122.5	300	4.01	2.65	13.2	3.03	1.01	0.195	4.25	0.409	0.645	0.898
39	11.3	45.7	57.0	123.2	300	4.05	2.67	13.0	3.08	0.993	0.187	4.04	0.373	0.592	0.713
40	20.4	36.0	56.4	122.2	300	10.2	5.23	33.0	6.06	0.988	0.222	5.74	0.508	0.679	0.279
41	25.0	30.3	55.3	124.1	180	13.1	6.09	41.0	6.70	0.991	0.211	5.88	0.449	0.610	0.156
42	33.1	21.5	54.6	122.2	180	19.4	7.98	61.2	6.54	0.712	0.161	5.36	0.356	0.358	0.0376
43	15.9	31.1	47.0	122.5	180	7.54	3.99	26.1	3.86	0.882	0.183	4.24	0.353	0.372	0.198
44	21.0	23.4	44.4	122.0	60	10.6	5.20	33.5	3.93	0.772	0.155	3.96	0.297	0.303	0~
45	13.5	24.1	37.6	121.8	180	6.43	3.65	23.4	2.52	0.785	0.185	3.65	0.340	0.272	0.130
46	20.0	11.5	31.5	122.5	180	10.9	5.24	41.9	2.07	0.450	0.135	2.98	0.257	0.110	0~
47	14.7	15.8	30.5	121.4	60	8.67	4.25	27.8	1.92	0.638	0.154	3.04	0.271	0.166	0~
48	6.4	19.5	25.9	123.0	180	2.61	1.96	10.7	0.842	0.722	0.168	2.16	0.277	0.112	0.189
a Set	: Table I fo	or units.													

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$$C_2H_5 + C_2H_5 \rightarrow n \cdot C_4H_{10} \tag{2}$$

$$\rightarrow C_2 H_6 + C_2 H_4 \tag{3}$$

 $C_2H_5 + RH \rightarrow C_2H_6 + R$ (4)

$$C_2H_5 + C_2H_2 \rightarrow CH_3CH_2CH = CH^*$$
(5)

$$CH_3CH_2CH = CH^* \xrightarrow{\sim} CH_3CH_2CH = CH$$
(6)

$$\xrightarrow{\text{A}_a}$$
 CH₂CH₂CH=CH₂* (7)

$$CH_3CH_2CH = CH + RH \rightarrow 1 - C_4H_8 + R \tag{8}$$

$$CH_3CH_2CH = CH + C_2H_5 \rightarrow 3 - C_6H_{12}$$
(9)

→ $1 - C_4 H_8 + C_2 H_4$ (10)

$$\rightarrow 1 - C_4 H_6 + C_2 H_6$$
 (11)

(12)

$$CH_3CH_2CH = CH + C_2H_2 \rightarrow C_6H_9^* (1,3-hexadien-1-yl)$$

$$C_e H_0^* \xrightarrow{\omega} C_e H_0$$
 (13)

$$C_6H_9 + RH \rightarrow 1.3 - C_6H_{10} + R$$
 (14)

$$C_6H_9 + C_2H_2 \rightarrow C_8H_{11}*(1,3,5\text{-octatrien-1-yl})$$
 (15)

$$C_8H_{11}* \xrightarrow{\omega} C_8H_{11} \tag{16}$$

$$\longrightarrow C_6 H_6 + C_2 \dot{H}_5 \tag{17}$$

$$C_8H_{11} + n - C_2H_2 \rightarrow \text{polymer}$$
 (18)

(19) CH₂CH₂CH=CH₂* - \rightarrow CH₂CH₂CH=CH₂

$$\xrightarrow{R_{a'}} CH_3 CH \xrightarrow{==} CH \xrightarrow{==} CH_2^* (20)$$

$$CH_2CH_2CH = CH_2 + C_2H_5 \rightarrow 1 - C_6H_{12}$$
(21)

$$\rightarrow 1 \cdot C_4 H_8 + C_2 H_4 \qquad (22)$$

 $+1,3-C_4H_6+C_2H_6$ (23)

$$CH_3CH \longrightarrow CH_2 CH_2 CH_3CH \longrightarrow CH_3CH \longrightarrow CH_2 (24)$$

 $CH_3CH=CH=CH_2 + C_2H_5 \rightarrow C_2H_5CH(CH_3)CH=CH_2$ (25)

→
$$1 - C_4 H_8 + C_2 H_4$$
 (26)

$$\rightarrow 1.3 \cdot C_4 H_6 + \dot{C}_2 H_6 \qquad (27)$$

$$\rightarrow 2 - C_6 H_{12}$$
 (28)

►
$$2 - C_4 H_8 + C_2 H_4$$
 (29)

$$\rightarrow 1.2 - C_4 H_6 + C_2 H_6$$
 (30)

where RH and R represent the $(C_2H_5)_2CO$ molecule and the $C_2H_5COC_2H_4$ radical, respectively.

Kinetic Treatments. In order to obtain rate constants for isomerization, it is required to estimate the portion of stabilized 1-buten-1-yl radicals which are consumed in polymerization reactions and the rate of formation of 2-hexene produced by the cross combination reaction of isomerized methylally with ethyl radicals.

For reactions 1-30, steady-state treatments are applied, which lead to the following equation

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$$R^{1/2}(n - C_4H_{10})[C_2H_2]/R_8(1 - C_4H_8) = {(\omega + k_a)/\omega}(k_2^{1/2}/k_5)\{(k_{12}/k_8)[C_2H_2]/[DEK] + 1 + (k_9 + k_{10} + k_{11})/k_8[C_2H_2]/[DEK]\}$$

where $R_8(1-C_4H_8)$ is the rate of 1-butene formation via reaction 8, DEK diethyl ketone, and ω the effective stabilization rate constant.

Since $R(3-C_6H_{12}) < 0.05R(1-C_4H_8)$ in every run (3-hexene formation see the next section), the above equation is rewritten as

$$R^{1/2}(n \cdot C_4 H_{10}) [C_2 H_2] / R_8 (1 \cdot C_4 H_8) = {(\omega + k_a) / \omega} (k_2^{1/2} / k_5) [(k_{12} / k_8) [C_2 H_2] / [DEK] + 1 \}$$
(A)

Although 1-butene is formed by reactions 8, 10, 22, and 26, the fraction formed by reactions 10 and 26 can be neglected because formation of 3-hexene and 3-methyl-1-pentene was very small as compared with other products.

The rate constant ratios of k_{22}/k_{21} and k_{23}/k_{21} were estimated to be 0.06 and 0.08, respectively, in accord with the known disproportionation to combination ratios of *n*-alkyl and ethyl radicals.¹⁷ Thus

$$R_8(1-C_4H_8) = R(1-C_4H_8) - 0.06R(1-C_6H_{12})$$

On the condition that the ratio of $(\omega + k_a)/\omega$ is constant (i.e., total pressure are kept approximately constant), plots of $R^{1/2}(n-C_4H_{10})[C_2H_2]/\{R(1-C_4H_8) - 0.06R(1-C_6H_{12})\}$ vs. [acetylene]/[diethyl ketone] from the data in Table I (runs 14-20) and Table II (runs 34-42) gave values of k_{12}/k_8 as 0.311 and 0.382 at 75 and 123°, respectively. Then the portions of 1-buten-1-yl radicals consumed in polymerization are calculated by the following equation:

$$R_{12}(\text{polymerization})/[R(1-C_4H_8) - 0.06R(1-C_6H_{12})] = (k_{12}/k_8)[C_2H_2]/[\text{DEK}] \quad (B)$$

The value of k_{28}/k_{25} can be obtained from the equation

$$R(2-C_{6}H_{12} + 3-C_{6}H_{12})/R(3MP1) = (k_{9}/k_{2}^{1/2}k_{8})R^{1/2}(n-C_{4}H_{10})R_{8}(1-C_{4}H_{8})/R(3MP1)[DEK] + k_{28}/k_{25} (C)$$

where 3MP1 is 3-methyl-1-pentene. Figure 1 shows the plots of eq C by using the experimental data from Tables I and II. A least-squares treatment gave a slope of 3.91 \times 10^{-3} , and $k_{28}/k_{25} = 1.67$ at 75°; and a slope of 3.05×10^{-3} , and $k_{28}/k_{25} = 1.55$ at 123°. In the case of reactions of mutual interaction of radicals, the activation energies are considered to be small.¹⁸ Then the value of k_{28}/k_{25} should show temperature independence. Accordingly the mean value 1.61 was used in the following calculations.

Isomerization of Chemically Activated 1-Buten-1-yl Radicals. In a chemically activated system the average rate constant k_a for a unimolecular reaction is given by $k_a =$ $\omega(I/S)$,¹⁹ where ω is the specific collision frequency of the excited radical, I is the total rate of formation of the isomerized products, and S is the total rate of formation of the stabilized products. In the present case I and S are given by

I = R(1-buten-4-yl products) + R(methylallyl products)

S = R(1-buten-1-yl products)

Concerning methylallyl products, the ratios of disproportionation to combination were estimated to be $(k_{25} + k_{26} +$ $(k_{27})/k_{25} = (k_{28} + k_{29} + k_{30})/k_{28} = 1.18$ assuming that the ratios are equal to that of allyl and ethyl radicals.²⁰ Then I



Figure 1. Experimental plot of eq C: O, 75°; D, 123°.

is rewritten as below by using the obtained value $k_{28}/k_{25} = 1.61$

$$\begin{split} I &= R(1\text{-}C_6\text{H}_{12}) + R_{22}(1\text{-}C_4\text{H}_8) + R(1,3\text{-}C_4\text{H}_6) + \\ &\quad 1.18R(3\text{MP1}) + 1.18R(2\text{-}C_6\text{H}_{12}) = \\ &\quad 1.06R(1\text{-}C_6\text{H}_{12}) + R(1,3\text{-}C_4\text{H}_6) + 3.08R(3\text{MP1}) \end{split}$$

x060On the other hand S was calculated by using eq B

$$\begin{split} S &= R_8(1\text{-}C_4\text{H}_8) + R(3\text{-}C_6\text{H}_{12}) + R_{12}(\text{polymerization}) = \\ &\{1 + (k_{12}/k_8)[\text{C}_2\text{H}_2]/[\text{DEK}]\}\{R(1\text{-}C_4\text{H}_8) - \\ & 0.06R(1\text{-}C_6\text{H}_{12})\} + \\ & R(2\text{-}C_6\text{H}_{12} + 3\text{-}C_6\text{H}_{12}) - 1.61R(3\text{MP1}) \end{split}$$

A plot of I/S vs. $1/\omega$ from the data in Table I is shown in Figure 2. The calculation of collision rates is given in Appendix. The values 1.00×10^9 and $1.05 \times 10^9 \text{ sec}^{-1}$ were obtained as k_a at 75 and 123°, respectively.

Isomerization of Chemically Activated 1-Buten-4-yl Radicals. The rate constant for isomerization of chemically activated 1-buten-4-yl radicals k_a' is given by

$$k_a' = \omega(I'/S') = \omega R$$
(methylallyl products)/ R (1-buten-4-yl products)

As mentioned in the previous sections, the rates of formation of methylallyl and 1-buten-4-yl products are

$$R$$
(methylallyl products) = 1.18 R (3MP1) +
1.18 R (2-C₆H₁₂) = 3.08 R (3MP1)

$$R(1-\text{buten-4-yl products}) = 1.14R(1-C_6H_{12})$$

A plot of I'/S' vs. $1/\omega$ (Figure 3) and a least-squares treatment gave values of $k_a' = 3.47 \times 10^7$ and $6.20 \times 10^7 \text{ sec}^{-1}$ at 75 and 123°, respectively.

Discussion

If isomerized methylallyl radicals can be formed by direct isomerization of chemically activated 1-buten-1-yl radicals, the possible course is formation through a four-membered cyclic transition state

In this case, we can see easily that the ratio, I'/S = R (methylallyl products)/R(1-buten-1-yl products), should be in direct proportion to ω^{-1} , i.e.

$$I'/S = k/\omega \tag{D}$$



Figure 2. Plots of I/S vs. 1/w at 75°.



Figure 3. Plots of I'/S' vs. 1/ω: O, 75°; □, 123°.

On the other hand, when the proposed reaction scheme in which isomerized 1-buten-4-yl radicals are assumed to isomerize successively to the methylallyl radicals is correct, a plot of I'/S vs. ω^{-1} should give a parabolic curve. That is, using the relations $k_a = \omega(I/S)$, $k_a' = \omega(I'/S')$, and I = I' + S', one can obtain

$$I'/S = k_{a}k_{a}'/\omega(\omega + k_{a}')$$

where $k_{a'}$ is negligibly small as compared with ω (see Results section). Thus we can write

$$I'/S = k_{\rm a}k_{\rm a}'/\omega^2 \tag{E}$$

or

$$(I'/S)^{1/2} = (k_a k_a')^{1/2} / \omega$$
 (F)

Figure 4 shows plots of I'/S vs. ω^{-1} and of $(I'/S)^{1/2}$ vs. ω^{-1} at 75° (similar curves are also obtained at 123° runs). From this figure it is clear that the data are well described by eq E and F, but not by eq D. The slope of the straight line in Figure 4 gives values of $k_a k_a' = 3.40 \times 10^{16}$ and 5.09 $\times 10^{16}$ sec⁻² at 75 and 123°, respectively, which agree with those obtained separately in the Results section, i.e., 3.47×10^{16} and 6.51×10^{16} sec⁻².

In addition, the critical energy for the isomerization of 1-buten-1-yl to methylallyl radicals via 1,3-H atom shift is estimated to be in the range 34–37 kcal/mol both by using eq G (see the following discussion section) and by analogy with the critical energy for the isomerization of chemically activated propenyl to allyl radicals,¹⁴ $E_0(4pp) = 34.5$ kcal/

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Figure 4. Plots of l'/S and $(l'/S)^{1/2}$ vs. $1/\omega$ at 75° : \blacktriangle , l'/S vs. $1/\omega$; O, $(l'/S)^{1/2}$ vs. $1/\omega$.



Figure 5. Schematic potential energy diagram.

TABLE III: Comparison of Calculated and Experimental Results

°C	\overline{E} , kcal/mol	$k_{a}(obsd), sec^{-1}$	$E_{o},$ kcal/mol	$k_{a}(calcd),$ sec ⁻¹
		1,4-H Atom	Shift	
75	33.1	1.00×10^{9}	17.1	$0.99 imes10^{9}$
123	33.5	1.05×10^{9}	17.1	$1.06 imes 10^{9}$
		1,2-H Atom	Shift	
75	43.3	$3.47 imes10^7$	33.0	$3.64 imes 10^{7}$
123	43.7	$6.20 imes10^{7}$	33.0	4.68×10^{7}

mol, which undergoes a similar 1,3-H atom shift. The 1buten-1-yl radicals isomerize to 1-buten-4-yl via 1,4-H atom shift by reaction 7 with a low critical energy, 17.1 kcal/mol (see the following RRKM calculation section). Thus the ratio of the rate constant for the 1,3-H atom shift isomerization of the 1-buten-1-yl radicals to that of reaction 7 results in smaller than 10^{-10} . This implies that the formation of methylallyl radicals by 1,3-H atom shift of 1buten-1-yl is negligible under the present conditions.

Therefore, it is concluded that the methylallyl radicals

TABLE IV: Parameters Used in Collision Calculations^a

Species	σ, Å	ε/k, K
C,H,	4.11	212
C,H,COC,H,	5.91	413
CH,CH,CH=CH	5.20	319
CH ₂ CH ₂ CH=CH ₂	5.20	319
" Defense of D7 never story	for radicals ar	a accumed to be

^a Reference 27, parameters for radicals are assumed to be equal to those for 1-butene.

are formed by the succeeding isomerization of the 1-buten-4-yl radicals. The only energetically possible process is the isomerization through a three-membered cyclic activated complex

$$CH_2CH_2CH \longrightarrow CH_2^* \longrightarrow H \\ CH_2 \longrightarrow CH$$

CH₃CH---CH---CH₂*

In order to obtain estimates of isomerization critical energies of 1,4- and 1,2-H atom shifts, RRKM calculations were carried out.¹⁹ Calculational procedures were described in detail previously when data for the addition of methyl radicals to acetylene were reported.¹⁴ Figure 5 is a schematic potential energy diagram starting with $C_2H_5 + C_2H_2$ and leading to the observed products. Energy parameters for isomerization are given in the Appendix. Details of frequency assignments of the radicals, association complex, and isomerization complexes are also given in the Appendix.

The best agreement between the theoretical and experimental rate constants was obtained when the threshold energies were chosen as 17.1 and 33.0 kcal/mol for 1,4- and 1,2-H atom shifts, respectively. The calculated average rate constants k_a are shown in Table III.

The nonzero intercept in Figure 2 has about a 25% increasing effect on the value of k_a , and in Figure 3 about a 40% decreasing effect on k_a' as compared with those obtained on the assumption that the straight lines in the figures would have a zero intercept. However, the uncertainty caused by the nonzero intercept does not cause an uncertainty in the critical energies greater than 0.5 kcal/mol.

The critical energy for 1,4-H atom shift, $E_0 = 17.1$ kcal/ mol, agrees well with the values reported in exothermic reactions.^{2-4,10,11,13} Stabilized isomers of 1,2-H atom shift have not been found hitherto. The only evidence for 1,2-H atom shift is the work of Tardy⁵ in which the decomposition products in H + 1-pentene system were analyzed, and the value of approximately $E_0(3s) = 33 \pm 1$ kcal/mol has been proposed as its critical energy, which agrees with that obtained in the present work $E_0(3sp) = 33.0$ kcal/mol.

Abnormally low critical energies have been found when the so-called homoallylic rearrangement is included in the cyclic transition states.¹¹⁻¹³ The above agreement in 1,2-H atom shift suggests that the activation complex for the isomerization of 1-buten-4-yl to methylallyl radicals has very little or no stabilization by allylic conjugation, though the isomerized methylallyl radicals are stabilized. The same matter was observed in the isomerization of chemically activated propenyl to allyl radicals.¹⁴

Estimation of critical energies E_0 for isomerization of alkyl and alkenyl radicals is given by

$$E_0 = E_{ab} + E_s - Q$$
, if any (for endothermic reaction)
(G)

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TABLE V: En	thalpies of	Formation and	Bond	Energy	at 0]	K (kcal	i/mol)
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$\Delta H_{f}^{\circ}(C_{2}H_{\epsilon})$	28.86^{a}	$D^{\circ}(\text{vinylic C-H})$	106.5	
$\Delta H_{f}^{\circ}(C_{2}H_{2})$	54.33^{b}	D° (primary C-H)	96.2	
$\Delta H_{f}^{\circ}(1-C_{A}H_{s})$	4.96^{a}	D° (secondary C–H)	92.8	
$\Delta H_{f}^{\circ}(\mathbf{H})$	51.62^{a}	D° (secondary allylic C-H)	81.5	
ΔH_{f}° (CH ₂ CH ₂ CH ₂ CH=CH)	59.8			
$\Delta H_{f}^{\circ}(CH, CH, CH=CH)$	49.5			
$\Delta H_{f}^{\circ}(CH_{3}CH \rightarrow CH \rightarrow CH_{2})$	34.8			
^a Reference 19. ^b Reference 11.				

TAB	LE	VI:	Frequency	Changes for	Radical \rightarrow	Activated	Complex
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			(A) Associatio	on Complex		
C–C stretch	Sl	eletal bend or C=CC	C = C stretch $\rightarrow C = C \text{ stretch}$	Libration	Frequencies lowering	Torsion for forming C==C
826 → 0	4	169 → 234	1649 → 1811	102 → 51	$\begin{array}{c} 1445 \to 722 \\ 1333 \to 666 \\ 301 \to 150 \end{array}$	995 → 1200
			(B) 1,4- and 1,2-H ato	m Shifts Complexes		
		Frequencies del radical assig	eted from inments	-	Replaced deformatio	l ring on modes
	Mode		CC-C=C	Ċ—C—C=C	CC($C = \dot{C}^{b}$
	CCCH3C=CC=CC	tors tors twist bend	102 237 995 469	237	1623 937 (2 1116 386)
	CCC CC =CC C=C	bend str str str	$301 \\ 1046 \\ 826 \\ 1649$	1046	$662 \\ 1100 (3) \\ C - C - C - C \\ 850 (2)$) C=C
	CH CH	str	2972 967	2982	1100	, ,
	CH	bend	007	1333		

^a Frequencies are in units of cm⁻¹. ^b Taken from C. W. Bekett, N. K. Freeman, and K. S. Pitzer, J. Am. Chem. Soc., 70, 4227 (1948).

where E_{ab} and E_s are already stated and Q is the "thermal effect"²¹ which is the difference between the zero-point energies of the initial and final states (Q is negative when the reaction is endothermic). Although accurate critical energies for isomerization of radicals have not been obtained in endothermic reactions, 1,5-H atom shifts of the 6ps type show somewhat higher critical energies than those expected.³ This seems to correspond to the thermal effect.

In the present case, we can adopt for a 1,4-H atom shift $E_{\rm ab} = 9.1 \, \rm kcal/mol^{22}$ and $E_{\rm s} = 8.5 \, \rm kcal/mol$, the strain energy for cyclopentene;²³ and for 1,2-H atom shift $E_{\rm ab} = 7.6 \, \rm kcal/mol^{24}$ and $E_{\rm s} = 28.7 \, \rm kcal/mol$, the strain energy for cyclopropane,²³ where the values of $E_{\rm s}$ are corrected to 0 K.

The difference between the experimental and calculated critical energies by means of eq G is approximately $\pm 10\%$ through three-, four-,^{13,14} five-,^{2-4,10,11,13} six-,⁹ and seven-membered³ ring activated complexes. The errors do not have large effects on the value of k_a when the activation energies of the activated complexes (E^+ in Figure 5) are large (five-, six-, and seven-membered ring), but when they are small, k_a is affected considerably. In the present case, when the calculated $E_0 = 36.3$ kcal/mol and the same calculational procedures are adopted, the rate constant for the 1,2-H atom shift becomes approximately 10% of that when $E_0 = 33.0$ kcal/mol.

There is an allowance of more than ± 1 kcal/mol in choosing the values E_{ab}^{25} and $E_s.^{23,26}$ Therefore it seems natural that there are approximatley $\pm 10\%$ errors between the calculated and experimental critical energies. Nevertheless eq G is considered convenient in order to estimate

the activation energies for isomerization of alkyl and alkenyl radicals via ring complexes.

Appendix

Calculation of Collision Rates. Collision rates were calculated by the standard kinetic relationship

$$\omega = \{(s_{\rm a}+s_{\rm b})/2\}^2 \{(M_{\rm a}+M_{\rm b})/M_{\rm a}M_{\rm b}\}^{1/2} (8\pi kT)^{1/2} N_{\rm b}$$

where s is the effective collision diameter, M the molecular weight, and N_b the concentration of B molecules. The s values were derived from the Lennard-Jones parameters σ and ϵ/k .

$$s_{ab}^2 = \sigma_{ab}^2 [\Omega^{(2,2)}(T^*)]$$

where

$$T^* = T[\epsilon/k)_{\rm a}(\epsilon/k)_{\rm h}]^{-1/2}$$

and the collision integrals $\Omega^{(2,2)}(T^*)$ were obtained from standard tables.²⁷ The values used are given in Table IV.

Thermochemical Parameters. Heats of formation of radicals are obtained from the appropriate bond dissociation energies and the 0 K heat of formation of 1-butene (Table V). C-H bond dissociation energies used are 96.2 and 92.8 kcal/mol for primary and secondary bonds, respectively,²⁸ 106.5 kcal/mol for the vinylic bond,²³ and 81.5 kcal/mol for the secondary allylic C-H bond.²⁹ The activation energy for the addition of ethyl radicals to acetylene $E_{C_2H_5}$ has been found to be 7.0 kcal/mol.³⁰

Frequency Assignments. The frequency assignments for

1-buten-1-yl and 1-buten-4-yl radicals were taken from 1butene,³¹ in which the torsional mode about the central C-C bond was lowered to 102 cm^{-1} as pointed out by Pearson and Rabinovitch,¹⁵ and the following three frequencies were removed: CH stretch, 3011 cm⁻¹, and two HCH bends, 1443 and 913 cm⁻¹, for 1-buten-1-yl; 2972, 1045, and 1470 cm^{-1} for 1-buten-4-yl radicals.

For the calculation of k_a , the association complex was specified as

and the isomerization complexes as

$$CH_2$$

 CH_2 H and H
 $HC \longrightarrow CH$ CH_2 — $CHCH \longrightarrow CH_2$

and modifications of their frequency assignments were made according to those by Rabinovitch and coworkers.^{3,15} The modified frequencies are given in Table VI. These frequencies give log $A(\sec^{-1}) = 12.11$ and log $A(\sec^{-1}) =$ 12.68 for 1,4- and 1,2-H atom shifts, respectively.

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Direct Identification of Reactive Routes and Measurement of Rate Constants in the Reactions of Oxygen Atoms with the Fluoroethylenes

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The room temperature reactions between oxygen atoms and monofluoro-, difluoro (1,1 and 1,2)-, trifluoro-, and tetrafluoroethylene have been studied in crossed jets to directly identify their reactive routes. Free radical and stable products were detected using photoionization mass spectrometry and were assigned to reactive routes. The routes identified were of three types: :0 + WXC=CYZ \rightarrow WXC: + CYZO, :0 + WXC=CYZ \rightarrow WXYC + ·CZO (or Z + CO), :0 + WXC=CYZ \rightarrow WX + C₂YZO, where W, X, Y, and Z are either H or F atoms. Individual O + fluoroethylene reactions were found to proceed by either one, two, or three of these distinctly different kinds of routes. The results of this study are interpreted using an expanded version of a mechanism proposed by Cvetanović for O + olefin reactions. Overall rate constants for several of these reactions were also measured at 300 K and are reported.

Introduction

The reactions of oxygen atoms with unsaturated organic molecules proceed via the formation of extremely energy rich adducts which are capable of decomposing or undergoing rapid internal rearrangements.¹ These reactions have long been recognized as important steps in thermal and photochemical combustion mechanisms and are now receiving new attention as potential chemical lasers.² Although today there is considerable information on the overall rate constants for many of these reactions, knowledge of the products they produce is still quite sparse.^{3,4} We are