Isomerization of Allene \rightleftharpoons Propyne in Shock Waves and ab Initio Calculations

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The isomerization allene \Rightarrow propyne has been studied behind shock waves over the temperature range between 1300 and 2100 K and the total density range of $(0.6-2.4) \times 10^{-5}$ mol/cm³. The isomerization rate was monitored by means of the IR emission from allene and propyne. It was found that the process proceeded in the fall-off region, and the high-pressure limit rate constants were determined as $k_1 = 10^{14.34} \exp[-68.1 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$, for the isomerization of allene to propyne, and $k_{-1} = 10^{14.14} \exp[-69.7 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$, for the isomerization of propyne to allene, using the equilibrium constants. Ab initio molecular orbital calculations have also been performed for the isomerization. It was found that the isomerization proceeded in a series of successive reactions via cyclopropene, which has been suggested by Honjou et al. (Honjou, N.; Pacansky, J.; Yoshimine, M. J. Am. Chem. Soc. 1984, 106, 5361). The rate constants estimated in terms of the transition-state theory, $k_1 = 10^{14.23} \exp[-66.6 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$ and $k_{-1} = 10^{14.12} \exp[-67.0 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$, are consistent with the experimental results.

Introduction

There have been reported several experimental investigations on the isomerization allene \Rightarrow propyne. Sakakibara^{1,2} mentioned in a series of his papers that the structural isomerization was considerably faster than the decomposition, although he did not evaluate the rate constants. Using a flow system, Levush et al.³ determined the first-order rate constants of the isomerization over the temperature range 900–1150 K. They obtained $k_1 = 10^{11.64}$ $\exp[-54.7 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$ for the isomerization of allene to propyne and $k_{-1} = 10^{11.32} \exp[-55.2 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$ for the isomerization of propyne to allene. They did not, however, look at the effect of the total pressure on the isomerization, nor did they try to study the mechanism of the reaction. The shock-tube study has been carried out with the single-pulse shock-tube technique by Lifshitz et al.⁴ and Bradley and West.⁵ Lifshitz et al.⁴ studied the allene \rightarrow propyne isomerization over the temperature range 1030-1220 K and pressure range 1.2-6 atm. Only 0.17% of the decomposition products was found after 30% of the allene had isomerized. The isomerization was first order with respect to allene and very slightly dependent on the total pressure. Around 5 atm the first-order rate constant was $k_1 = 10^{13.17} \exp[-60.4 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$, with an overall power dependence of 0.2 on the total pressure. In addition, several shock runs in the propyne \rightarrow allene direction gave rate constants that were smaller than those for the allene \rightarrow propyne direction by a factor of ~2.3. Bradley and West⁵ reported $k_1 = 10^{14.48}$ exp- $[-92.7 \text{ kcal mol}^{-1}/(RT)]$ s⁻¹ over the temperature range 1440–1700 K and the pressure range 3.9-5.3 atm. From the experimental results with deuteriated allenes, combined with the absence of side products, they concluded that below 1700 K the mechanism was a predominantly (>95%) molecular process. Recently Hidaka et al.⁶ studied the isomerization of propyne to allene over the temperature range 1170-1440 K and the pressure range 1.4-2.3 atm behind reflected shock waves. They followed the absorption at 225 nm and determined the rate constant $k_{-1} = 10^{11.89} \exp[-55.7]$ kcal mol⁻¹/(RT)] s⁻¹; however, they did not mention the mechanism of the isomerization.

From the previous papers reviewed above, it is likely that the mechanism of the isomerization is a unimolecular process; however, there still remain arguments about the first-order rate constant;

 (2) Sakakibara, Y. Bull. Chem. Soc. Jpn. 1964, 37, 1268.
 (3) Levush, S. S.; Abadzhev, S. S.; Shevchuk, V. U. Neftekhimiya 1969. 9. 215.

that is, the reported values for k_1 are separated widely and there is a large difference in the activation energy, about 30 kcal/mol between Lifshitz et al.⁴ and Bradley and West.⁵ Thus far it has been believed the allene \rightarrow propyne isomerization takes place by the removal of a hydrogen from one carbon and the attachment of the hydrogen to another carbon in the molecule.^{4,5} A single bond and a triple bond are thus formed in place of two double bonds as $CH_2 \rightarrow CH_2 \rightarrow CH_3 \rightarrow CH_3$. This process can take place by a unimolecular migration of the hydrogen atom from one end of the molecule to the other end (1,3-hydrogen shift). Recently Honjou et al.^{7,8} studied the detailed C_3H_4 surface by ab initio calculations. According to their results, the isomerization of allene to propyne by the direct 1,3-hydrogen shift has the potential barrier of 94.9 kcal/mol. They found the other reaction path with a series of successive reactions via cyclopropene. The highest barrier of this reaction path is 68.4 kcal/mol. This is thought to be a strong suggestion for the thermal isomerization mechanism and for the explanation of the experimental results because there is a large difference in the potential barriers between the two probable reaction paths.

In this work, we have studied the isomerization allene \Rightarrow propyne behind shock waves by monitoring time-resolved concentrations of the reactant and the product. We have also tried to evaluate the geometry, the potential energy, and the vibrational frequencies for probable transition states of the isomerization by ab initio molecular orbital methods and then compare the experimental results and the calculated results in terms of transition-state theory.

Experimental Section

The experiments have been performed in a shock tube made of stainless steel, which was used in a previous study.9 All experiments were performed behind reflected shock waves. The isomerization of allene \Rightarrow propyne was monitored by observing time-resolved IR radiations from allene and propyne. IR emission from the shock-heated gas was taken out through a CaF_2 window mounted on the tube walls 2 cm upstream from the end plate. The radiation from the window was passed through a gas cell (10 cm long), into which was admitted about 300 Torr of allene or propyne, and through a band-pass filter $(3.37 \pm 0.13 \,\mu\text{m})$ and then focused on an InSb detector maintained at 77 K. Although both allene and propyne have an emission band around 3.4 μ m, the CH₂ stretch of allene (3.24, 3.32, and 3.33 μ m) and the CH₃

⁽¹⁾ Sakakibara, Y. Bull. Chem. Soc. Jpn. 1964, 37, 1262.

⁽⁴⁾ Lifshitz, A.; Flenklach, M.; Burcat, A. J. Phys. Chem. 1975, 79, 1148.
(5) Bradley, J. N.; West, K. O. J. Chem. Soc., Faraday Trans. 1 1975, 71, 967.

⁽⁶⁾ Hidaka, Y.; Chimori, T.; Suga, M. Chem. Phys. Lett. 1985, 119, 435.

⁽⁷⁾ Honjou, N.; Pacansky, J.; Yoshimine, M. J. Am. Chem. Soc. 1984, 106. 5361.

⁽⁸⁾ Honjou, N.; Pacansky, J.; Yoshimine, M. J. Am. Chem. Soc. 1985, 107. 5332.

⁽⁹⁾ Kakumoto, T.; Saito, K.; Imamura, I. J. Phys. Chem. 1985, 89, 2286.



Figure 1. Typical emission profiles at 3.4 μ m using the propyne cell (A) and at 5.3 μ m without the gas cell (B). IS denotes the incident shock front. (A) corresponds to the increase of allene by the isomerization of propyne \rightarrow allene and (B) corresponds to the decrease of allene by the isomerization allene \rightarrow propyne.

stretch of propyne (3.32 and 3.43 μ m), the radiation from propyne could be removed through the gas cell admitted propyne and vice versa. The IR radiations at 4.63 ± 0.09 μ m, the C=C stretch of propyne, and at 5.34 ± 0.20 μ m, the C=C stretch of allene, were also monitored. The output signal was fed into a preamplifier (Iwatsu Electric, DA-2A) and a digital wave memory (Kawasaki Electronica, M-50Es) and then analyzed to obtain kinetic data. The resultant time constant of the electrical and the optical system was about 10 μ s, enough for the present purposes.

The allene and the propyne used for the experiments were commercially available: allene, Takachiho Kagaku Kogyo, 97% purity; propyne, Tokyo Kasei Kogyo, >98% purity. After trapto-trap distillation, these samples were stored in glass flasks as mixtures of 0.1-1.0% allene or propyne in Ar (99.999% purity). The experimental conditions behind the reflected shock waves were as follows: temperature 1300–2100 K; total density (0.61–2.39) $\times 10^{-5}$ mol/cm³.

Experimental Results

Figure 1A shows a typical emission trace at 3.4 μ m for the mixture of 0.25% propyne in Ar using the gas cell admitted propyne. This profile corresponds to an increase of allene concentration by the reaction propyne \rightarrow allene. The emission intensity begins to increase just behind the reflected shock front and seems to approach a constant value as the isomerization proceeds. It was ascertained that the contribution of propyne to the emission profile is negligible. Figure 1B shows a typical emission trace at 5.3 μ m for the mixture of 0.15% allene in Ar without the gas cell. This profile corresponds to a decrease of allene concentration by the reaction allene \rightarrow propyne. The emission trace decaved exponentially after an initial rapid rise, immediately following the reflected shock front, and reached a steady value, which is the emission from the allene at equilibrium. The first-order rate constants obtained from these profiles correspond to the sum of the rate constants for the forward and the reverse directions, because the isomerization proceeds in both directions, simultaneously. Here we consider the reversible reaction, allene \rightleftharpoons propyne; k_1 and k_{-1} are the rate constants in the forward and the reverse directions. If the experiment is started with pure allene of concentration a_0 and if after the time t the concentration of propyne is x, then that of allene is $a_0 - x$. The net rate for the production of propyne is given by $dx/dt = k_1(a_0 - x) - k_{-1}x$, since propyne is being produced by the forward reaction (first term)



Figure 2. Arrhenius plot of the first-order rate constants for the allene \Rightarrow propyne isomerization, k, for various mixtures and for a constant total density, $[M] = (1.13-1.34) \times 10^5 \text{ mol/cm}^3$.

and removed by the reverse reaction (second term). If x_e is the concentration of propyne at equilibrium, when the net rate of the reaction is zero, $a_0 = (k_1 + k_{-1})x_e/k_1$. Substitution of this expression into the above equation and integration using the fact that x = 0 when t = 0 give $\ln [x_e/(x_e - x)] = (k_1 + k_{-1})t$. The first-order rate constant, k, obtained from the experiment is, therefore, $k_1 + k_{-1}$. The individual rate constants k_1 and k_{-1} can be found on the basis of the equilibrium constant, $K = k_1/k_{-1}$.

Figure 2 shows an Arrhenius plot of the first-order rate constants, k, against T^{-1} for different concentriions of allene or propyne and for a constant total density, $[M] = (1.13-1.34) \times 10^{-5} \text{ mol/cm}^3$. There exists no difference in the rate constants evaluated from the allene-Ar and the propyne-Ar mixtures and at three different wavelengths. There is no systematic change in the rate constants with variation of the reactant concentration, 0.2-1.0%, within experimental error. Thus, the isomerization rate is first order with respect to the reactant, being consistent with previous results.³⁻⁶ An Arrhenius plot of k for different total densities is shown in Figure 3. This figure shows a marked tendency for k to increase with increasing total density, although the data points show some scatter. Thus it seems that the isomerization proceeds in the fall-off region under the present experimental conditions.

Troe et al.^{10,11} published a method for obtaining a reduced fall-off curve including the weak-collision effect. According to this method, the reduced form rate constant, k/k_{∞} , is written by the product of three factors as

$$k/k_{\infty} = F^{\text{LH}}(k_0/k_{\infty})F^{\text{SC}}(k_0/k_{\infty})F^{\text{WC}}(k_0/k_{\infty})$$

where k_{∞} is the limiting high-pressure rate coefficient and k_0 the limiting low-pressure rate coefficient at the bath gas concentration [M] under consideration. The first factor on the right-hand side corresponds to the Lindemann-Hinshelwood factor

$$F^{\text{LH}} = (k_0/k_\infty)/(1+k_0/k_\infty)$$

 $F^{SC}(k_0/k_{\infty})$ corresponds to the strong collision broadening factor

⁽¹⁰⁾ Troe, J. Ber. Bunsen-Ges. Phys. Chem. 1983, 87, 161.

⁽¹¹⁾ Gilbert, R. G.; Luther, K.; Troe, J. Ber. Bunsen-Ges. Phys. Chem. 1983, 87, 169.

 $\log F^{\rm SC} \simeq$

$$\frac{\log F_{\text{cent}}^{\text{sc}}}{1 + [(\log (k_0/k_{\infty}) - 0.12)/(N^{\text{SC}} + \delta(0.1 + 0.6 \log F_{\text{cent}}^{\text{SC}}))]^2}$$

$$N^{\text{SC}} \simeq 0.75 - 1.27 \log F_{\text{cent}}^{\text{SC}}$$

$$\delta = +1 \text{ if } k_0/k_{\infty} > 1, \quad -1 \text{ if } k_0/k_{\infty} < 1$$

where F_{cent}^{SC} is the broadening factor at the center of fall-off curve and depends on the Kassel integral parameters

$$F_{\text{cent}}^{\text{sc}} \simeq F_1 + F_2 \exp(-B_{\text{K}}/19.5) + (1 - F_1 - F_2) \exp(-2.3[B_{\text{K}}/F_3]^{1.5})$$

$$F_1 = 1.32 \exp(-S_{\text{K}}/4.2) - 0.32 \exp(-S_{\text{K}}/1.4)$$

$$F_2 = 1 - \exp(-S_{\text{K}}/30)$$

$$F_3 = 7.5 + 0.43S_{\text{K}}$$

For the Kassel parameters $S_{\rm K}$ and $B_{\rm K}$ the definitions suggested by Troe¹² have been adopted. The last factor, $F^{WC}(k_0/k_{\infty})$, corresponds to the weak collision broadening factor

$$\log F^{\text{WC}} \simeq \frac{\log F^{\text{WC}}_{\text{cent}}}{1 + [\log (k_0/k_{\infty})/N^{\text{WC}}]^2}$$
$$\log F^{\text{WC}}_{\text{cent}} \simeq 0.14 \log \beta_{\text{c}}$$
$$N^{\text{WC}} \simeq 0.7 + 0.3S_{\text{K}} + 0.25 \log \beta_{\text{c}}$$

In the above equations, β_c is the collision efficiency, $\beta_c = k_0/k_0^{SC}$, where k_0^{SC} is the low-pressure limiting strong collision rate constant.¹⁰ The parameters used in the construction of the fall-off curve are listed in Table I, and the fall-off curves fitted to the experimental data points are shown in Figure 4. In general the extrapolation of the fall-off curves causes some arbitrariness in the determination of the limiting rate constants, especially in an experiment with a small range of pressure. The fall-off curves were fitted to the experimental data points in such a way as to meet the following requirements at the same time: (a) the calculated curves fit the experimental data points reasonably well, (b) the high- and low-pressure limit rate constants give temperature-independent activation energies, $E_{a\infty}$ and E_{a0} , in the experimental region, and (c) the difference between $E_{a\infty}$ and E_{a0} , where S_{eff} is the effective number of transition-state oscillators and \bar{T} is the mean temperature of the experiments. The rate constants for the high-pressure limit k_{∞} and for the low-pressure limit $k_0/[Ar]$ were then determined over the temperature range 1300-1800 K as

 $k_{\infty} = 10^{14.54} \exp[-68.5 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$

and

 $k_0/[Ar] = 10^{14.59} \exp[-38.2 \text{ kcal mol}^{-1}/(RT)] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

The individual rate constants for the high-pressure limit of the isomerization, k_1 and k_{-1} , can be easily evaluated from the equilibrium constants. The evaluated rate constant expressions are

 $k_1 = 10^{14.34} \exp[-68.1 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$

for the isomerization of allene to propyne, and

$$k_{-1} = 10^{14.14} \exp[-69.7 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$$

for the isomerization of propyne to allene. The equilibrium constants used in the above evaluation are 2.94, 2.71, and 2.48 at 1300, 1500, and 1800 K, respectively, on the basis of the thermochemical data.¹⁴ In this respect, Lifshitz et al.⁴ reported



Figure 3. Arrhenius plot of the first-order rate constants for the allene rightarrow propyne isomerization, k, for various total densities.



Figure 4. Fall-off curves including the weak-collision effect.^{10,11} Vertical lines indicate experimental errors. k_{∞} and k_0 denote the rate constants for the high-pressure limit and the low-pressure limit, respectively.

the equilibrium constant of ~ 2.3 over the temperature range 1030-1220 K, which was smaller than the thermodynamic equilibrium constant, K_{th} , of 3.45 at 1100 K. Their results were based on the ratio of the rate constants, k_1/k_{-1} , where k_1 and k_{-1} were obtained independently from the experiments for the forward

⁽¹²⁾ Troe, J. Ber. Bunsen-Ges. Phys. Chem. 1974, 78, 478.

⁽¹³⁾ Troe, J.; Wagner, H. Gg. Ber. Bunsen-Ges. Phys. Chem. 1967, 71, 937.

⁽¹⁴⁾ Benson, S. W. Thermochemical Kinetics, 2nd ed.; Wiley: New York, 1976; p 26, 295.

TABLE I: Evaluated Parameters Used for the Construction of the Fall-Off Curves



Figure 5. Optimized geometries for the transition state by the direct 1,3-hydrogen shift. Bond distances are in angstroms and angles in degrees. The structures have the C_s symmetry.

and the reverse reactions. However, their data are limited in the lower temperature region, and particularly the data for k_{-1} give large scatter. In fact, the $K_{\rm th}$ value is within the scatter of their data. Thus, we used K_{th} for the evaluation of k_1 and k_{-1} in our high-temperature region. It was ascertained that the extent of the uncertainty of the equilibrium constants was not serious compared with the present experimental error.

Discussion

From the present experiment by the time-resolved observation, we could evaluate the rate constants for the isomerization allene \Rightarrow propyne. Our results are very close to the previous data except for that of Bradley and West.⁵ From the present results and the previous data, it is likely that the threshold energy of the isomerization is less than 70 kcal/mol and not greater than 90 kcal/mol obtained by Bradley and West.⁵ Values of the preexponential factor, on the other hand, scatter largely from each other. Considering that the absolute rate constants agree with each other, the difference of the kinetic parameters arises from the error factor of the data and the temperature range over which the activation energy is evaluated. It is considered that transition-state theory helps us in the discussion of the isomerization mechanism. First, we try ab initio calculations for the probable reaction paths.

Ab Initio Calculations. The mechanism of the isomerization of allene to propyne has so far been presumed to be the direct 1,3-hydrogen shift.^{4,5} In order to check the isomerization proceeds by this mechanism, we tried to evaluate the geometry, the potential energy, and the vibrational frequencies for allene, propyne, and the probable transition state by ab initio MO methods. We used the Hartree-Fock (HF) method with LCAO approximation using the 3-21G and the 4-31G basis sets with standard parameters to calculate the geometrical and the vibrational structures. The energy gradient technique was employed for the geometry optimization. Correlation effects are known to lower significantly the barrier heights for many unimolecular reactions. Therefore, we applied Møller-Plesset second-order perturbation (MP2), single and double configuration interaction (SD-CI), and symmetryadapted cluster expansion (SAC)¹⁵ calculations at the HF/3-21G and the HF/4-31G optimized geometries.¹⁶ The energy gradient method was also employed to calculate the vibrational frequencies.

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TABLE II: Total Energies (in hartrees) and Relative Energies (in Parentheses in kcal/mol Relative to Allene) for the Isomerization by the Direct 1,3-Hydrogen Shift

method	allene	TS	propyne
HF/3-21G	-115.2199 (0.0)	-115.0227 (123.7)	-115.2254 (-3.4)
SD-CI/ 3-21G ^{a,c}	-115.4839 (0.0)	-115.3028 (113.7)	-115.4900 (-3.8)
SAC/ 3-21G ^{a,c}	-115.5133 (0.0)	-115.3367 (110.8)	-115.5191 (-3.7)
HF/4-31G	-115.6988 (0.0)	-115.5016 (123.8)	-115.7013 (-1.6)
SD-CI/ 4-31G ^{b,c}	-115.9638 (0.0)	-115.7832 (113.3)	-115.9668 (-1.9)
MP2/ 4-31G ^b	-115.9651 (0.0)	-115.8000 (103.6)	-115.9752 (-6.3)
SAC/ 4-31G ^{b,c}	-115.9940 (0.0)	-115.8180 (110.4)	-115.9968 (-1.7)

^aAt HF/3-21G optimized geometries. ^bAt HF/4-31G optimized geometries. c Reference 16.

TABLE III: Observed and Calculated Vibrational Frequencies (in cm⁻¹) for Allene and Propyne

sym		approx type		$\omega_{ m calcd}$	
species		of mode	$\nu_{\rm obsd}^{a}$	3-21G	4-31G
	Allene				
a_1	1	CH ₂ s stretch	3015	3310	3315
	2	CH_2 scis	1443	1645	1648
	3	CC stretch	1073	1198	1202
b 1	4	CH ₂ twist	865	969	967
b ₂	5	CH ₂ s stretch	3007	3309	3314
-	6	CC stretch	1957	2225	2235
	7	CH ₂ scis	1398	1595	1595
e	8	CH_2 a stretch	3086	3383	3391
	9	CH ₂ rock	999	1171	1165
	10	CH ₂ wag	841	1051	1061
	11	CCC deform	355	413	412
Propyne					
a,	1	CH stretch	3334	3668	3672
-	2	CH ₃ stretch	2918	3204	3188
	3	C=C stretch	2142	2433	2413
	4	CH ₃ s deform	1382	1588	1594
	5	CC stretch	931	957	992
е	6	CH ₃ d stretch	3008	3264	3255
	7	CH ₃ d deform	1452	1658	1646
	8	CH ₃ rock	1053	1206	1202
	9	CH bend	633	914	883
	10	CCC bend	328	409	412

^aObserved values are cited from ref 22.

The programs used for the calculations were GAUSSIAN 80,¹⁷ GAUSSIAN 82,18 IMSPAK,19 and GAMESS.20

Allene and propyne have D_{2d} and the C_{3v} symmetries, respectively. Good agreements were obtained between the observed²¹ and calculated valus for the structures of allene and propyne; that is, the differences were within 0.022 Å in bond distances and 2.2° in bond angles. Figure 5 shows the optimized geometries for the transition state of the direct 1,3-hydrogen shift. From the full optimization, the transition state was found to have the C_s symmetry.

In Table II are listed the total energies (in hartrees) and the relative energies (in kcal/mol relative to allene) for allene, propyne, and the transition state. The energy differences between allene

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TABLE IV: Calculated Vibrational Frequencies (in cm⁻¹) for the Transition State of the Direct 1,3-Hydrogen Shift

		ω	alcd	
sym species		3-21G	4-31G	
a'	1	3552	3568	
	2	3336	3337	
	3	2185	2278	
	4	2064	2084	
	5	1598	1605	
	6	1180	1205	
	7	843	854	
	8	583	570	
	9	461	459	
	10	2423 <i>i</i>	2418 <i>i</i>	
a‴	11	3438	3439	
	12	1174	1177	
	13	979	973	
	14	415	430	
	15	324	291	

and propyne are 1.6-6.3 kcal/mol. These values are in good agreement with the thermochemical data of 1.7 kcal/mol.¹⁴ The barrier height of the isomerization from allene to propyne is 104-124 kcal/mol depending on the method of the calculation. Among these calculations, the SAC calculations with the 4-31G basis set¹⁶ are expected to be the most reliable since the SAC calculation gives a total energy that is variationally determined and includes the higher order unlinked terms. This calculated barrier height is, however, expected to be high because of the lack of polarization functions in the calculations.

Table III shows the calculated vibrational frequencies for allene and propyne together with the observed values.²² The calculated vibrational frequencies are overestimated by 3-44% for the 3-21G calculations and 7-39% for the 4-31G calculations relative to the experimental values. The calculated frequencies for the transition state of the direct 1,3-hydrogen shift are listed in Table IV. A knowledge of the vibrational frequencies for the transition state, which is essential to a discussion of the kinetics of a chemical reaction, cannot be inferred from any experiment. There is a single imaginary frequency for transition states, corresponding to motion along the reaction path. It was confirmed that the imaginary vibration clearly indicates the course of the isomerization from allene to propyne. For simplicity, a scaling has been applied to all calculated frequencies by multipling them by a factor of 0.86. These scaled vibrational frequencies for allene and propyne are consistent with experimental values²² within 9% for allene and 20% for propyne. Since a similar situation probably holds for the transition state, the same scaling has been applied to the frequencies for the transition state. Our main concerns are not each vibrational frequency but the zero-point energy correction and the vibrational partition functions for the reactant and the transition state as discussed later.

For the isomerization of allene to propyne, the calculated threshold energy is 105.4 kcal/mol by the SAC/4-31G calculation with the zero-point energy correction. This value cannot be regarded to be the actual barrier height because this energy may be lowered by the use of more sophisticated calculations. However, there is still a large gap between the calculated value and the activation energy of the high-pressure limit rate constant obtained by experiment, 68.1 kcal/mol.

Recently Honjou et al.^{7,8} studied the detailed C_3H_4 surface by ab initio calculations. They stated that in their calculations values of the potential energy height were accurate to within 2 kcal/mol. Figure 6 reproduces their results. According to their calculations, the isomerization of allene to propyne by the direct 1,3-hydrogen shift has the potential barrier of 94.9 kcal/mol, which is still larger than the experimental value. They found that the lowest reaction path is a series of successive reactions via vinylmethylene, cyclopropene, and propenylidene as seen in Figure 6. The highest barrier height in the reaction path is 68.4 kcal/mol. Unfortunately



Figure 6. Reaction paths for the allene \Rightarrow propyne isomerization.⁷ The values in parentheses are with the zero-point energy corrections.



Figure 7. Optimized geometries for the transition state from allene to vinylmethylene, TS1. Bond distances are in angstroms and angles in degrees; dihedral angles, τ , defined as positive clockwise.

TABLE V: Calculated Vibrational Frequencies (in $\rm cm^{-1})$ for the Transition State from Allene to Vinylmethylene, TS1

		ω _{calcd}		
sym species		3-21G	4-31G	
a	1	3432	3441	_
	2	3346	3352	
	.3	3199	3223	
	4	2112	2203	
	5	1992	2018	
	6	1608	1611	
	7	1332	1321	
	8	1188	1187	
	9	1129	1137	
	10	1056	1037	
	11	982	986	
	12	914	915	
	13	501	499	
	14	479	473	
	15	1142 <i>i</i>	1153 <i>i</i>	

TABLE VI: Evaluation of the Rate Constants for Both Directions of the Isomerization in terms of Transition-State Theory

				•		
T/K	tunneling ^a	σ/σ^*	$(I^*/I)^{1/2b}$	$Q^*_{ m vib}/Q_{ m vib}{}^c$	k/s^{-1}	
Allene \rightarrow Propyne $E_0 = 64.8 \text{ kcal/mol}^d$						
300	1.95	4/1	1.06	0.900	2.88×10^{-34}	
1000	1.09	,		0.762	5.02×10^{-1}	
1200	1.06			0.733	1.29×10^{2}	
1400	1.04			0.705	6.94×10^{3}	
1600	1.03			0.677	1.39×10^{5}	
1800	1.03			0.651	1.44×10^{6}	
2000	1.02			0.626	9.34×10^{6}	
Propyne \rightarrow Allene $E_0 = 65.1 \text{ kcal/mol}^d$						
300	1.95	3/1	1.05	0.883	1.28×10^{-34}	
1000	1.09	'		0.742	3.14×10^{-1}	
1200	1.06			0.720	8.38×10^{1}	
1400	1.04			0.698	4.61×10^{3}	
1600	1.03			0.676	9.42×10^{4}	
1800	1.03			0.654	9.91 × 10 ⁵	
2000	1.02			0.632	6.54×10^{6}	

 ${}^{a}\nu_{e} = 994i \text{ cm}^{-1}$, HF/4-31G calculated vibrational frequency decreased by 13.8%. ${}^{b}I_{allene} = 1.05 \times 10^{4} \text{ amu}^{3} \text{ Å}^{6}$; $I_{propyne} = 1.06 \times 10^{4} \text{ amu}^{3} \text{ Å}^{6}$; $I^{*} = 1.17 \times 10^{4} \text{ amu}^{3} \text{ Å}^{6}$; HF/4-31G optimized geometries. c HF/4-31G calculated vibrational frequencies decreased by 13.8%. d Reference 7 with the zero-point energy correction.

they did not report the geometrical structures and the vibrational frequencies for the transition states. We have tried to evaluate the geometry and the vibrational frequencies for TS1, which is considered to be higher than the other TSs as seen in Figure 6. The optimized geometries and the calculated vibrational frequencies are shown in Figure 7 and Table V. It was confirmed that the imaginary vibration clearly indicates the course of the process from allene to vinylmethylene.

Application of Transition-State Theory. A theoretical prediction of the rate constant may be given by the transition-state formula²³

$$k = \kappa (kT/h)(Q^*/Q) \exp[-E_0/(RT)] \text{ s}^{-1}$$

where κ is the transmission coefficient, which is generally treated as unity for a great many reactions and Q and Q^* are the partition functions of the reactant and the activated complex, respectively. E_0 , the threshold energy, is the difference between the total energy corrected by the zero-point energy per mole of the reactant and that of the activated complex. It is difficult to predict the values of Q^* and E_0 experimentally, but the ab initio molecular orbital calculations facilitate the application of the transition-state theory. For unimolecular reactions, if we factorize the total partition function into its translational, rotational, and vibrational contributions, the above equation becomes

$$k = \kappa (kT/h) (\sigma/\sigma^*) (I^*/I)^{1/2} (Q^*_{vib}/Q_{vib}) \exp[-E_0/(RT)] s^{-1}$$

where σ and σ^* are the symmetry numbers, *I* and *I*^{*} the moments of inertia, and Q_{vib} and Q^*_{vib} the vibrational partition functions for the reactant and the transition state, respectively. Quantum mechanical theory admits the possibility that a system having less energy than that required to surmount the barrier may pass from the initial to the final state; it is said to "tunnel" or "leak" through the energy barrier. This tunneling has been allowed for by the inclusion of the formula $1 - (h\nu_e/kT)^2/24$ in the rate expression.²³ The quantity ν_e is the frequency along the reaction coordinate and is related to the curvature of the surface at the col. This effect is 1.95, 1.09, and 1.02 at 300, 1000, and 2000 K, respectively.

Table VI shows the terms that were used to evaluate the rate constants for both directions of the isomerization in the temperature range 300–2000 K. In this evaluation, κ was assumed to be unity, the moments of inertia were estimated in terms of the HF/4-31G optimized geometries, and the vibrational partition functions were estimated with the HF/4-31G calculated vibrational frequencies decreased by 13.8%. The threshold energies,



Figure 8. Comparison of the reported rate constants for the isomerization allene \Rightarrow propyne. k_1 (--) corresponds to the rate constants for the isomerization of allene to propyne and k_{-1} (---) for the isomerization of propyne to allene.

 E_0 , were cited from the results by Honjou et al.⁷ with the zero-point energy corrections. As a result, we have Arrhenius expressions of the rate constants for the reaction path via cyclopropene

$$k_1 = 10^{14.23} \exp[-66.6 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$$

for the isomerization of allene to propyne, and

$$k_{-1} = 10^{14.12} \exp[-67.0 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$$

for the isomerization of propyne to allene in the temperature range 300-2000 K. In a similar manner, the reaction rate constants of the isomerization by the direct 1,3-hydrogen shift were evaluated as follows:

$$k_1^{1,3\text{-H shift}} = 10^{15.08} \exp[-92.4\text{kcal mol}^{-1}/(RT)] \text{ s}^{-1}$$

 $k_{-1}^{1,3\text{-H shift}} = 10^{14.97} \exp[-92.8 \text{ kcal mol}^{-1}/(RT)] \text{ s}^{-1}$

It is found that the calculated rate constants for the reaction path via cyclopropene, k_1 and k_{-1} , are in excellent agreement with the experimental values. On the other hand, those for the direct 1,3-hydrogen shift, $k_1^{1,3\text{-H} \text{ shift}}$ and $k_{-1}^{1,3\text{-H} \text{ shift}}$, are much lower than the observed values. That is, these values are lower than k_1 and k_{-1} by 5 orders of magnitude at 1000 K and 2 orders at 2000 K. These facts lead to a conclusion that the isomerization allene \Rightarrow propyne proceeds mainly by the route via cyclopropene.

Comparison with Other Shock Tube Data. The reported values for the isomerization rate constant of allene to propyne, k_1 , are separated widely as mentioned in the above section. Figure 8 shows an Arrhenius plot of the high-pressure limit rate constants for the allene \rightleftharpoons propyne isomerization for comparison with the previously reported experimental results. The rate constants evaluated in the present experimental study are close to the results of Lifshitz et al.⁴ and Hidaka et al.⁶ The calculated values for the reaction path via cyclopropane are in fair agreement with these experimental results and the results of Levush et al.,³ Lifshitz et al.,⁴ and Hidaka et al.⁶ That is, the calculated rate constants are within a factor of 2 for k_1 and a factor of 3 for k_{-1} respect to these

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experimental results. The results of Bradley and West⁵ seem, on the other hand, too low compared to the other experimental results and the present calculations.

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Registry No. Allene, 463-49-0; propyne, 74-99-7.

Symmetry Selection Rules for Reaction Mechanisms: A Practical Formulation for the Generation of Symmetry-Allowed Mechanisms and Applications

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In a previous paper, the symmetry selection rules for reaction mechanisms were formally developed as a two-stage procedure. The first stage (classical selection rules) determines the mechanisms which are strictly symmetry-allowed, whereas the second stage (state selection rules) determines the relative probabilities of the mechanisms, in the context of a Bader-Pearson analysis of the PE surface, which are allowed in the first stage. In this paper, the classical selection stage is developed in terms of a practical procedure for generating reaction mechanisms, and applied to a range of reactions to highlight the utility of the procedure.

Introduction

U.K.

In the context of simple transition-state theory, given a reactant and a specified product (or intermediate), the determination of the potential concerted pathways from reactant to product may be effected, in principle, by (i) a preliminary determination of the symmetry-allowed pathways and the respective transition-state symmetries (i.e., which reaction coordinates are symmetry-allowed), and (ii) a determination of the quantitative energetics (i.e., the relative probabilities) of the symmetry-allowed pathways. In a previous paper,¹ it was shown that the above two-stage procedure could be given a rigorous theoretical definition in a manner which is philosophically consistent with the generalized selection rule procedure developed for selection rules for spectroscopic processes.² Starting with the quantum description of the potential energy (PE) surface as developed by Bader,³ and Pearson,^{4,5} a set of theorems constituting the basis of the first stage (the classical selection rule (CSR) stage) were derived. The second state selection rule (SSR) stage may be considered the quantum refinement in the sense that it is linked with Bader's explicit state expansion of the PE about a given key point, usually the reactant, in terms of derivatives describing the slope and curvature of the PE surface at that point. The values of the second derivatives (the slope being zero at the key points that were considered by Bader) are directly determined by state-mixing, and the SSR stage effectively determines which states can contribute to the derivatives.

The classical selection rules are most restrictive and require a knowledge only of the reactant (R) and product (P) structures. They are totally independent of the quantitative energetics. They determine the nature of the symmetry-allowed pathways connecting R and P, and the transition-state symmetry (which is uniquely defined for each pathway). This is, in fact, the main difference between our procedure and the results of Stanton and McIver⁶ (discussed below), which are less restrictive in that they enable the elimination of certain postulated transition-state symmetries, but not its unique generation for each path. In this context, it is worth noting that most discussions of reaction mechanisms rely heavily on "intuitive guesses" at possible transition structures, and thus the Stanton and McIver approach of eliminating certain structures, coupled with Murrell and Laidler's work on the one-dimensionality of the reaction coordinate through the

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transition state,7 provided powerful tools based on symmetry arguments consistent with the philosophy of elimination. The CSR approach, however, formally generates and completely specifies (within the context of symmetry specification) the symmetryallowed pathways. This emphasis on the generation of pathways rather than elimination is possible only because the CSR procedure is effectively more restrictive than that based on the earlier work alone and leads to only one possible transition-state symmetry for each symmetry-allowed pathway.

This paper will in fact concentrate exclusively on a practical chemical implementation of the CSR stage and on a range of applications to a set of archetypical reactions in order to illustrate the utility of the approach. In doing so, we note that the second stage of determining the relative probabilities may be addressed exactly (within the Born-Oppenheimer approximation) by an explicit calculation of the energy profile for each symmetry-allowed pathway of stage one. We may, however, differentiate between a number of approximate methods for probing certain portions of the PE surface. We shall use the term "quantum" to refer to Bader's approach of determining the local characteristics of the PE surface in the region of a key point, in particular the reactant, as a Taylor expansion in derivatives (in terms of the electronic excitation manifold determined at the key point) with respect to the reaction coordinate. An alternative procedure is to use "classical" energetics to estimate (either quantitatively or qualitatively) the activation energy directly. This exploits such concepts as bond-breaking/bond strain in a manner analogous to that exploited in molecular dynamics calculations. It is interesting to note that Bader's force constant measure of the curvature of the PE surface at the reactant has a close link with the "classical" description whenever the local curvature at the reactant is a reasonable measure of the activation energy.

As the efforts of this paper are directed principally at the generation of the symmetry-allowed mechanisms, we shall make no attempt to discriminate between the allowed mechanisms other

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