acetylene pyrolysis. We are now in the position to admit that acetylene must be initially converted into an active species, possibly an isomer or an excited state, rather than into free radicals. Since the lowest lying triplet state of C_2H_2 is about 80 kcal/mol above ground state, we have recently advanced the notion that the intermediate is actually singlet vinylidene, the carbene isomer of acetylene.⁶ More specifically, we propose that the mechanism of acetylene dimerization actually takes place via reactions i, -i, and 1':

$$C_2H_2 \rightleftharpoons H_2C = C:$$
 (i, -i)

$$H_2C = C: + C_2H_2 \rightarrow C_4H_4 \tag{1'}$$

with $k_1 = 2k_1K_i$. The initial product of H₂C==C: addition to acetylene, methylenecyclopropene, would rapidly isomerize into vinylacetylene under typical experimental conditions.¹¹ Striking confirmation of this scheme has been recently obtained from a

comparative study of the pyrolyses of neat C_2H_2 and in the presence of excess benzene or toluene, which proceed with similar rate constants, revealing fast addition of a common reactive intermediate.11

Conclusion

The dimerization of acetylene into vinylacetylene takes place in two steps rather than by a free-radical chain mechanism. Acetylene excited at about 40 kcal/mol behaves as a carbene in accordance with ab initio calculations.

Note Added in Proof. After submission of this paper Kiefer et al. (Kiefer, J. H.; Mitchell, K. I.; Kern, R. D.; Yong, J. N. J. Phys. Chem. 1988, 92, 677) have presented similar arguments regarding the nonradical nature of reaction 1. However, their mechanism for the origin of C_4H_2 is different from ours.

Registry No. CH₂=OCC=CH, 63707-54-0; C₂H₂, 74-86-2; C₄H₄, 689-97-4.

Collisional Energy Transfer in Thermal Decomposition Reaction of 1.2-Dichloropropane

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The thermal decomposition reaction of 1,2-dichloropropane (1,2-DCP) was studied at temperatures from 663.2 to 703.2 K over the pressure range 0.04-10.0 Torr. The decomposition modes of 1,2-DCP were monitored via four reaction channels of unimolecular HCl eliminations and a negligible portion of a side radical chain reaction. 3-Chloropropene (3-CP), The theorem is the termination of term mol^{-1}/RT]. The unimolecular thermal decomposition reactions of the four-channel 1,2-DCP system were carried out in the presence of a He bath gas to evaluate intermolecular-energy-transfer parameters. The average energies removed per collision from energized 1,2-DCP by bath gas are as follows: by the substrate, 1200 cm⁻¹ for the stepladder model; by He, 250 cm^{-1} for the exponential model. The effects of active additives, CO₂ and HCl, and the surface condition of the reaction vessel were also studied to ascertain the potential properties of the thermal decomposition reaction of 1,2-DCP.

Introduction

The use of multiple reaction channels has attracted considerable interest in elucidating more reliable and significant information about intermolecular energy transfer in thermal unimolecular reaction systems.¹⁻⁶ Plots of relative rate ratios as a function of pressure have permitted the evaluation of intermolecular-energy-transfer parameters in multichannel unimolecular reactions. Furthermore, the measurements of the ratios of rate constants of competitive reactions have the canceling effect unpredictable experimental errors. Since their usefulness was first recognized by Chow and Wilson,¹ successful utilizations of two- or threechannel systems have been demonstrated for several unimolecular reactions.2-5

The thermal decomposition reactions of 1,2-dichloropropane (1,2-DCP) have been studied in flow and static systems⁶⁻⁸ and in single-pulse shock-tube techniques.9 These early workers reported that the thermal decomposition reaction of 1,2-DCP proceeds via the unimolecular elimination of HCl through four reaction channels. The present work, however, shows that the trace radical chain process is so small that it does not affect the total rate and the rate ratios of the four channels but is accelerated by any catalytic additives. The four channels of the reaction system can be described by

 $CH_3CHClCH_2Cl \rightarrow CH_3CH=CHCl$ (cis or trans) + HCl

$$\rightarrow$$
 CH₃CCl=CH₂ + HCl (i)

$$\rightarrow$$
 CH₂=CHCH₂Cl + HCl

In the present study, the intermolecular-energy-transfer process in the four-channel competitive HCl elimination reaction of 1,2-DCP was investigated. The work was carried out on a neat 1,2-dichloropropane system in the presence of helium. Since helium acts as the weakest collision partner and the substrate molecule as a strong collider, our major aim in this study was to obtain the characteristic energy-transfer profile.

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The effect of additives, CO2 and HCl, was also studied to obtain supplementary information on the induction of the radical chain process as well as autocatalytic effects and thus to describe the system more extensively. The heterogeneous effect in the system was investigated by changing the condition of the reaction vessel surface, and comparisons were made with similar systems, i.e., the pyrolyses of 1,2-dichloroethane^{6,10} and 1,2-dibromopropane.¹¹

Experimental Section

Apparatus. A conventional high-vacuum static system was employed. The initial pressures of 1,2-DCP and additives were measured with a glass spiral gauge and an oil manometer. The reaction vessel was cylindrical quartz tubing with a volume of 1048.4 cm³ and a surface-to-volume ratio (s/v) of ca. 0.6 cm⁻¹. The inner surface of the vessel was coated with carbon film by pyrolyzing allyl bromide or 1,2-dichloropropane at 680-850 K and at 200 Torr for 48 h (see footnote in Table III). Heating of the reactor was done with a three-zone tubular furnace (Electroglas). The temperature of the furnace was controlled, to within ± 1.0 °C along the length of the furnace, by an internal thermocouple. The reaction temperature was calibrated with a digital HP3465B multimeter using a K-type thermocouple and a water-ice junction. Temperature fluctuations in the reaction vessel were kept to less than ± 0.5 °C.

Product analysis was done using a gas chromatographic technique which has been previously described in detail.¹¹ The sample separation was achieved by a 20% OV-17 $^{1}/_{8}$ -in. × 4-m and a 15% SE-30 $^{1}/_{8}$ -in. \times 3-m stainless steel columns at 60 °C with an N₂ flow rate of 20 cm³ min⁻¹.

Materials. 1,2-DCP was obtained from Aldrich Chemicals and purified to better than 99.9% by a gas chromatograph (Perkin-Elmer Sigma 4B), with a 20% SE-30 $^{1}/_{4}$ -in. \times 3-m Ni alloy column. Further purification by the trap-to-trap distillation technique followed. 1-Chloropropene, a mixture of cis and trans isomers, was obtained from Tokyo Chemical. cis-1-Chloropropene was separated from the trans isomer by a gas chromatograph using a 20% OV-17, 1/4-in. × 3-m stainless steel column. 2-Chloropropene, 3-chloropropene, and cyclohexene, also obtained from Aldrich Chemicals with stated purities of 98, 99, and 99%, respectively, were purified by low-temperature trap-to-trap distillation. Propene and hydrogen chloride, with stated purities of 98 and 99%, respectively, were obtained from Matheson and used, after trap-to-trap distillation, at 77 K. Helium, research grade from Takachio Chemical, was used with no further purification. Carbon dioxide, research grade, obtained from Takachio Chemical, was purified by low-temperature trap-to-trap distillation.

Calculation

The collisional-energy-transfer process can be described in terms of the time derivative of the state population at a given energy level, which is here called the master equation.¹² The master equation for the thermal unimolecular reaction is expressed by

$$dn_i/dt = Rf_i + \omega \sum P_{ii}n_i - \omega n_i - k_i n_i$$
(ii)

where n_i is the population of molecules at the energy level *i*, Rf_i the external input into the *i*th level, P_{ij} the collisional transition probability from energy level j to i, k_i the microscopic rate constant, and ω the collisional frequency. Two models, exponential (EXP) and stepladder (SL), were chosen to represent extremes of physical significance as transition probability models. The microscopic rate constant for the unimolecular HCl elimination reaction was calculated by using the harmonic oscillator RRKM formulation¹³ with a four-centered activated complex model.

The solution of the master equation in the steady state was obtained by the iteration method utilizing Tardy and Rabinovitch's algorithm.^{14,15} The steady-state populations were calculated by using the modified transition probabilities with the *i*th column normalized to $\omega/(\omega + k_i)$ and applied repeatedly to a given population distribution until the population output unchanged.¹⁶ The unimolecular rate constant was then calculated by

$$k_{\rm uni} = \sum k_i n_i^{\rm ss} / \sum n_i^{\rm ss}$$
(iii)

where n_i^{ss} is the steady-state population after the *n*th iteration.

When a molecule reacts via competing channels is the falloff region, the energized molecules are depleted by all reaction channels. Each channel, therefore, feels the effect of the drain of energized molecules to other channels. In RRKM theory, the unimolecular rate constant of the *i*th channel for the strong collider system¹⁷ is given by

$$k_{\text{uni}}(i) = \int_{E_{\text{GJ}}}^{\infty} \frac{k(i,E) B(E) dE}{1 + \sum_{m}^{l=1} k(l,E)/\omega}$$
(iv)

where $E_{0,i}$ is the critical energy for the *i*th channel, B(E) the Boltzmann distribution function, m the total number of channels, ω the collision frequency, and k(i,E) the RRKM microscopic rate constants at energy E for the *i*th reaction channel.

The rate constant expression for the lower energy pathway then becomes

$$k(j,E) = 0$$
 for $E_{0,i} < E < E_{0,i}$ (v)

and

$$k_{\text{uni}}(i) = \sum_{j=i}^{m-1} \int_{E_{0,j}}^{E_{0,j+1}} \frac{k(i,E) \ B(E) \ dE}{1 + \sum_{l=1}^{j} k(l,E) / \omega} + \int_{E_{0,m}}^{\infty} \frac{k(i,E) \ B(E) \ dE}{1 + \sum_{l=1}^{m} k(l,E) / \omega}$$
(vi)

where $E_{0,j} < E_{0,j+1}$.

The geometrical parameters of 1,2-DCP were obtained from the literature.¹⁸ Fundamental frequencies of the reactant were assigned from $P_X S_{XH}$ conformation which is the low-energy conformer reported by Crowder.¹⁹ All internal degrees of freedom were taken as active and the overall rotations maintained as adiabatic. The torsional degrees of freedom were treated as simple harmonic vibrations according to Hassler and Setser's representation.²⁰ The model of the four-centered HCl elimination transition state was based upon the previously suggested model for HCl elimination of chloroethanes.²¹ The reaction coordinate was assigned as a low ring bending frequency, and the in-plane ring frequencies were calculated by specifying the bond orders of the breaking and forming bonds. The best representations of the bond orders were found to be 1.8, 0.8, 0.2, and 0.2 for the C-C, C-Cl, Cl-H, and H-C bonds,²² respectively. These values together with the use of Pauling's rule to find bond lengths and Badger's rule relating force constants and bond lengths,²³ were utilized to calculate the fundamental vibrational frequencies of the four-membered ring by Wilson's FG matrix technique. This comprises a systematic way of obtaining the ring vibrational frequencies.

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TABLE I: Group Vibrational Frequencies (cm⁻¹), Principal Moments of Inertia (10^{-39} g cm²), Reaction Degeneracies, and Critical Energies (cm⁻¹) for Molecules and Activated Complexes

	complex for the formation of						
1,2-DCP ^a	cis-1-CP ^b	trans-1-CP	2-CP	3-CP			
2961 (6)	2972 (5)	2972 (5)	2966 (5)	2958 (5)			
1411 (5)	1600 (1)	1600 (1)	1600 (1)	1600 (1)			
1207 (4)	1411 (5)	1411 (5)	1426 (4)	1402 (4)			
1041 (2)	1235 (2)	1235 (2)	1249 (3)	1207 (4)			
907 (1)	1061 (2)	1061 (2)	1061 (3)	1032 (2)			
866 (1)	907 (1)	970 (1)	907 (1)	907 (1)			
739 (1)	861 (2)	907 (1)	861 (2)	861 (2)			
669 (1)	743 (1)	861 (2)	743 (1)	743 (1)			
414 (1)	739 (1)	743 (1)	669 (1)	739 (1)			
353 (1)	700 (1)	739 (1)	414 (1)	418 (1)			
280 (1)	414 (1)	410 (1)	348 (1)	280 (1)			
280 (1) ^c	354 (1)	353 (1)	280 (1)	212 (1)			
212 (1)	290 (1)	280 (1)	180 (1)	205 (1)			
120 (1) ^c	280 (1)	140 (1)	160 (1)	120 (1)			
	170 (1)	134 (1)					
Principal Moments of Inertia							
65.3	51.5	58.9	57.2	59.7			
56.8	45.4	46.9	45.8	48.2			
11.5	13.4	16.5	16.6	14.9			
Reaction Path Degeneracy							
	1	1	1	2			
Critical Energy							
	18758	19372	20542	18946			

^aThorbjørnsrud, J.; Ellestad, O. H.; Klaboe, P.; Torgrimsen, T. J. Mol. Struct. **1973**, 15, 45. ^bCP for chloropropene. ^cTorsional frequency.

The ring-puckering frequency was treated as a parameter and was adjusted to a best fit with the experimental A factor. The critical energies were also calculated from the experimental activation energies and the adjusted vibrational frequency sets. The vibrational frequencies, moments of inertia, critical energy, and reaction path degeneracy of each channel are listed in Table I.

The collisional parameters, σ and ϵ/k , for 1,2-DCP and He molecules were determined by Stiel and Thodes' correlation method of critical properties.^{24,25} The calculated collisional diameters of 1,2-DCP and He were 5.34 and 2.58 Å at 684.4 K, respectively.

Results

Temperature and Pressure Dependence. The reaction products in the first-order thermal decomposition reaction of 1,2-DCP at temperatures from 663.2 to 703.2 K were 3-chloropropene, *cis*-1-chloropropene, *trans*-1-chloropropene, 2-chloropropene, and hydrogen chloride. The reaction vessel with a surface-to-volume ratio (s/v) of <0.6 cm⁻¹ was used after carbonaceous film coating to prevent surface effects. The addition of radical chain inhibitors, e.g., propene, cyclohexene, and nitric oxide, did not reduce the reaction rate and confirmed absence or negligible radical chain processes in the thermal decomposition of 1,2-DCP.

The temperature dependence of the rate constant for 1,2-DCP was studied over the range 663.2–703.2 K. The high-pressure limit rate constant, k_{∞} , was obtained by plotting the first-order rate constants against the reciprocal of the reactant pressure²⁶ at each temperature. The overall first-order rate constant was found to conform to the Arrhenius rate law, $k_{\infty}/s^{-1} = 10^{13.7\pm0.50} \exp[(-54900 \pm 2500)$ cal mol⁻¹/*RT*]. Individual Arrhenius parameters for each reaction product are summarized in Table II.

In Figure 1, the falloff behavior of the reaction is shown for the pressure range 0.04-10.0 Torr at temperatures of 663.2, 684.4, and 703.2 K and compared with the theoretical values calculated by the numerical solution of the master equation. A stepladder

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TABLE II: Comparison of Rate Parameters of 1,2-Dichloropropane

products	$\log A/s^{-1}$	$E_{\rm a}/\rm kcal\ mol^{-1}$	system	ref
cis-1-CP ^a	12.90 ± 0.70	54.26 ± 2.00		this study ^b
trans-1-CP	13.21 ± 0.80	56.07 ± 2.50		•
2-CP	13.05 ± 0.44	59.36 ± 1.50		
3-CP	13.61 ± 0.30	54.96 ± 1.20		
cis-1-CP	13.1	54.5	thermal	8
trans-1-CP	13.3	56.1		
2-CP	8.3	42.8		
3-CP	13.4	54.0		
cis-1-CP	12.98 ± 0.07	53.36 ± 0.27	shock tube	9
trans-1-CP	13.19 ± 0.07	55.35 ± 0.27		
2-CP	13.05 ± 0.15	59.18 ± 0.66		
3-CP	13.48 ± 0.07	54.02 ± 0.27		

^aCP for chloropropene. ^bThe reactor condition for this study was carbon-film-coated vessel (1048.4 cm³, s/v \approx 0.6 cm⁻¹) by 1,2-dichloropropane at 800 K.



Figure 1. Falloff curves at various temperatures as indicated on the curves for the decomposition of 1,2-DCP. Solid lines are SL model calculations for (a) $\langle \Delta E \rangle = 1000 \text{ cm}^{-1}$, (b) $\langle \Delta E \rangle = 1200 \text{ cm}^{-1}$, and (c) $\langle \Delta E \rangle = 1400 \text{ cm}^{-1}$. O represents the experimental values.

model for 1,2-DCP with step sizes of 1000, 1200, and 1400 cm⁻¹ were used in the transition probability calculations. The 1200-cm⁻¹ step size was best fitted to the experimental observation and shown in Figure 1. The reaction times were controlled to less than 10% decomposition of the reactant. The experimental uncertainities of the rate constants were within $\pm 4.5\%$ at 703.2 K, $\pm 6.8\%$ at 684.4 K, and $\pm 6.9\%$ at 663.2 K.

The pressure dependence of the rate ratios of the four channels was also studied in an attempt to obtain information on the collisional energy transfer and the weak collision effect. The experiments were carried out with neat 1,2-DCP in the presence of helium as a weak collider. The pressure of helium was varied from 0 to 10.0 Torr with constant substrate pressure. Some typical results of the ratio of competitive channel rate constants are displayed for k_3 (3-chloropropene) to k_{trans} (trans-1-chloropropene) and $k_{cis}(cis-1$ -chloropropene) to k_{trans} in Figure 2 and for $k_1(cis-1)$ and trans-1-chloropropenes) to k_2 (2-chloropropene) in Figure 3. The corresponding theoretical curves for the best-fitted values of the average energy transferred downward, $\langle \Delta E \rangle_{down}$, per collision are included in the figures for the following conditions: by substrate, 1200 cm⁻¹ for the stepladder model; by He, 250 cm⁻¹ for the exponential model. Different step sizes for He were also tested at 300 cm^{-1} and found to be about 0.025 and 0.014 of the differences in the rate ratios k_3/k_{trans} and $k_{\text{cis}}/k_{\text{trans}}$, respectively; these were compared with that of 250 cm⁻¹ in Figure 2 and 1.45 in Figure 3, at 2.59 Torr. Differences at step size 200 cm⁻¹ for He were also found to fall in the same range of 300 cm⁻¹. The

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Figure 2. The ratio of competitive channel rate constants k_3/k_{trans} and $k_{\text{cis}}/k_{\text{trans}}$ vs log P/Torr for 1,2-DCP at 684.4 K: O, neat system; \bullet , helium bath system. Solid curves are SL model calculations for $\langle \Delta E \rangle$ = 1200 cm⁻¹, and the dashed curves are EXP model calculations for $\langle \Delta E \rangle$ = 250 cm⁻¹.



Figure 3. The ratio of competitive channel rate constants k_1/k_2 vs log *P*/Torr for 1,2-DCP at 703.2 K. The solid curve is the SL model calculating for $\langle \Delta E \rangle = 1200$ cm⁻¹.

substrate pressures were 0.043 ± 0.005 and 0.065 ± 0.005 Torr at 703.2 and 684.4 K, respectively. The formation of 2-chloropropene was found to be minor, and quantitative measurement was impractical when the substrate pressure was less than 0.1 Torr.

The rates and the rate ratios of the four channels over the entire pressure range of this experiment were also not affected by the addition of inhibitors.

Effect of CO_2 . In order to observe the effect of CO_2 , the reaction of 1,2-DCP was carried out at 684.4 K in the presence of CO_2 at constant pressure, i.e., 0.043 ± 0.005 Torr. The major effects found were the changes of the rate constants of 2-chloropropene and 1-chloropropene formations. When the pressure of CO_2 was increased, the formation of 2-chloropropene was rapidly enhanced and that of 1-chloropropene was slightly increased, whereas the formation of 3-chloropropene was hardly affected. These behaviors were not observed when a small amount of propene was added to the system. A typical example of the rate constants as a function of CO_2 pressure is displayed in Figure 4.

Effect of HCl. The autocatalytic effect of HCl was observed from the reaction between various amounts of HCl at a fixed pressure of 1,2-DCP, i.e., 3.50 ± 0.15 Torr. The total rate constants at 684.4 K are displayed as a function of HCl pressure in Figure 5. With increasing HCl, the four products increased, while the relative contribution of each product was unchanged except for a slight increase of 2-chloropropene and trace amounts of allene, which was the secondary decomposition product of 3chloropropene.²⁷ On the other hand, the effect was completely



Figure 4. Rate constants of each product with increasing pressure of CO_2 and log k_i vs log *P*/Torr at constant pressure of 1,2-DCP, 0.043 \pm 0.005 Torr: \bullet , 2-chloropropene; O, 3-chloropropene; \blacktriangle , *cis*-1-chloropropene; \Box , *trans*-1-chloropropene.



Figure 5. Total rate constants of products with increasing pressure of additives: (\odot) 1,2-DCP, 3.50 ± 0.15 Torr, no cyclohexene and HCl; (\odot) 1,2-DCP, 3.50 ± 0.15 Torr, HCl, 1.89 ± 0.10 Torr, and cyclohexene.

TABLE III: Product Distribution, Rate Constants, Surface Conditions, and Inhibitors at 684.4 K

	press./ Torr	ress./ % of products					
		propene	cisa	trans ^a	2-CP ^b	3-CP	$k_{\rm tot} \times 10^4$
1,2-DCP ^c	8.2	3.4	20.0	11.3	11.6	53.8	
1,2-DCP propene	8.6 2.4		18.0	9.8	0.9	71.3	
1, 2-DCP C ₆ H ₁₀	7.1 2.0	5.8	22.1	10.9		61.2	
1,2-DCP ^d	4.5		22.6	12.4	0.5	64.5	1.738
1,2-DCP C ₆ H ₁₀	5.6 3.4		20.1	10.4	0.2	69.3	
1,2-DCP*	10.3	0.2	17.8	9.6	1.7	70.8	1.308
1,2-DCP propene	10.3 10.7		16.7	9.3	0.4	73.6	1.245
1,2-DCP ^f	10.1	1.2	15.8	8.3	4.2	70.5	2.588
1, 2-DCP C ₆ H ₁₀	10.9 0.5	0.2	15.7	8.7	0.4	75.0	1.506
1,2-DCP C ₆ H ₁₀	10.7 10.0	0.2	16.1	8.9	0.4	74.3	1.131

^a1-Chloropropene. ^bCP for chloropropene. ^cCarbon-film-coated vessel (1048.4 cm³, s/v ≈ 0.6 cm⁻¹) by allyl bromide at 680 K. ^dCarbon-film-coated vessel (1048.4 cm³, s/v ≈ 0.6 cm⁻¹) by 1,2-di-chloropropane at 800 K. ^eCarbon-film-coated vessel (1048.4 cm³, s/v ≈ 0.6 cm⁻¹) by allyl bromide at 850 K. ^fClean vessel (222.3 cm³, s/v ≈ 1.0 cm⁻¹).

suppressed by adding a small amount of cyclohexene to the system at constant pressures of 1,2-DCP, 3.50 ± 0.15 Torr, and HCl, 1.89 ± 0.10 Torr, as shown in Figure 5.

Variation of Surface Condition. The reaction rate and the product distribution were considerably altered by the condition of the reaction vessel surface, as shown in Table III. In a clean silica vessel the rate increased by a factor of 1.5; in particular, the formation of propylene and 2-chloropropene depended on the nature of the reactor surface. However, the formation of 2chloropropene was suppressed by the inhibitors cyclohexene and propylene.

Discussion

The radical chain inhibitors did not affect the thermal decomposition reaction of 1,2-DCP even when present in excess. On the other hand, substantial effects were found when additives such as CO₂ and HCl were introduced and the surface conditions of the reaction vessel varied. These findings indicate that the fraction of the radical chain process that is present is negligibly small and the chain length very short. In this study, therefore, we treated the reaction as a homogeneous reaction at selected low surface/volume ratio (ca. 0.6 cm⁻¹) conditions using (1) the carbonaceous film-coated vessel and (2) pyrolysis of 1,2-DCP at 800 K. The kinetics under this condition were then well-described by four parallel unimolecular reactions producing the four different chloropropenes and hydrogen chloride. The experimental rate parameters for the individual reaction channels from this study, as well as the earlier studies, are summarized in Table II. The distribution of the products, i.e., 3-chloropropene, *cis*-1-chloropropene, trans-1-chloropropene, and 2-chloropropene, found in this study are in substantial agreement with the results of earlier thermal⁸ and single-pulse shock-tube studies.⁹ The rate parameters of these products are also in good agreement with the former work. The only disagreement with earlier thermal work is in the rate parameters of 2-chloropropene,8 which were reported to be significantly affected by the surface condition of the vessel. 2-Chloropropene represents a very minor decompositional channel. This study, however, represents the consistency of the rate parameters of 2-chloropropene with those of the shock-type study, in which there is no surface effect.

The relative ratio of 3-chloropropene to 1-chloropropene formed under these conditions was found to be very close to the statistical value. Allene, the secondary decomposition product of 3chloropropene, was not formed at these temperatures. On the other hand, the cis-trans ratio did not follow the statistical estimation. It seems likely that dipole-dipole interactions between $CH_3^{\delta+}$ and $Cl^{\delta-}$ groups, which have been suggested to explain the thermodynamic preference for cis-1-chloropropene over trans-1chloropropene,²⁹ were also applicable in the transition state leading to the formation of the cis isomer. The isomerization between cis- and trans-1-chloropropene was not observed at these temperatures. The activation energy, 59.36 kcal mol⁻¹, for 2chloropropene formation was 4.36 kcal mol⁻¹ higher than that of n-propyl chloride found by Barton,³⁰ and the difference between 3-chloropropene, 54.96 kcal mol⁻¹, and isopropyl chloride,¹ 50.05 kcal mol⁻¹, was 4.91 kcal mol⁻¹.

The measurement of the relative rates by multichannel reaction permitted the evaluation of the amounts of energy transferred downward or upward per collision. The value depended on the assumed form of the collision transition probability, P. Two extreme forms were used here, stepladder (SL) and exponential (EXP) models. They differed in that the EXP model had a higher probability for small jump sizes and a long tail of lower probability for large jump sizes. In the present study, the neat system of 1,2-DCP was treated by the SL model, and the system with the helium bath gas was treated by both EXP and SL models. Sufficiently large polyatomic bath molecules, especially the substrate molecules, have been frequently considered as strong colliders with unit efficiency corresponding to $\langle \Delta E \rangle \ge 3500 \text{ cm}^{-1}$ in thermal systems. In the present system, however, somewhat lower values were obtained, i.e., 1200 cm⁻¹, for the SL model in the temperature range 663.2-703.2 K and were in good agreement with experimental results (within the error range of 100 cm^{-1}). Evidently, this result indicates that 1,2-DCP molecules are no longer Lindemann strong colliders, at least in the temperature range of the present work. By use of this step size for 1,2-DCP, the differences of critical energy, ΔE_0 , between channels were determined from the relative ratio curves, i.e., $k_{\rm cis}/k_{\rm trans}$ or $k_3/k_{\rm trans}$ vs log P as displayed in Figure 2. With the case of 2-chloropropene in a He bath gas, the ratio curves were not properly drawn because of trace amounts of 2-chloropropene. However, the values of $\langle \Delta E \rangle$ for the substrate, deduced from the pressure dependences of k_1/k_2 in Figure 3 and k_3/k_2 in the neat system, are in satisfactory agreement with calculated values. We obtained the collisional energy transfer and transition probability model of helium by variation of the step size of the transition probability model. The step sizes obtained for helium were 300 cm⁻¹ for SL and 250 cm⁻¹ for EXP models. Although the system with the CO_2 additive was studied and CO_2 is known as a much more effective collider than He,⁴ in the present work CO₂ collisional effects were not observed, because of its enhancing capability of 2-chloropropene formation via a nonunimolecular mechanism. The choices of the activated complex models did not affect the calculation as long as the model had an entropy value that satisfied the experimentally determined preexponential A factor.¹³ In other words, the experimental results were well-explained either by the SL model or by the EXP model as if the step size were optimal. Mild falloff to the curve in Figure 1 and the small difference between the weak and strong collision in Figures 2 and 3 indicate the characteristic behavior of molecules with a large complexity.³¹

In the case of the vessel coated carbonaceously by allyl bromide at 680 K, the formations of 2-chloropropene and propene were increased, and the former was completely suppressed by radical chain inhibitors, i.e., propene or cyclohexene. This finding may be intepreted in terms of the radical mechanism activated by the surface. But the formation of propene was not affected by the inhibitors.

Chlorine molecules in this condition may then be produced by direct heterogeneous Cl_2 elimination at the surface as suggested by Holbrook et al.²⁸ for the 1,2-dichloroethane system. Chlorine molecules are then physically absorbed on the carbon-coated vessel surface. The direct heterogeneous elimination of the halide molecules in a vessel, coated with carbon film by pyrolyzing allyl bromide at 620–680 K, allowed observation of the 1,2-DCP, 1,2-dichloroethane,¹⁰ and 1,2-dibromopropane¹¹ systems. This may be described by

$$C_3H_6Cl_2 + S \rightarrow C_3H_6 + (Cl_2)S$$

where S represents the surface of the reaction vessel.

In the case of the carbonaceous-coated vessel with 1,2-DCP, the production of propene was not observed, which may be interpreted as an indication that the vessel surface does not initiate the heterogeneous reaction. Thus, we propose 1,2-DCP as a better surface-coating material than allyl bromide for this system.

The reaction rate of 2-chloropropene was increased by adding CO_2 , and this may due to the induction effect by a radical mechanism. The behavior disappeared by adding small amounts of propene. The reaction was then speeded up by the addition of HCl as shown in Figure 5. Acceleration by HCl may be interpreted as an indication of a change in mechanism at high conversion due to high reaction pressure.

In summary, the formation of propene and 2-chloropropene was affected by the surface conditions of the reaction vessel. Temperature and pressure dependences of the competitive decomposition of 1,2-DCP in selected homogeneous conditions were

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well-explained by the RRKM formulation. Collisional energy transfers by helium were found to be 300 cm^{-1} for the SL and 250 cm^{-1} for the EXP models.

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Diffusion-Controlled Ligand Binding to Multiple Competing Cell-Bound Receptors

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The Brownian dynamics simulation method is employed to numerically calculate the diffusional rate of ligands reacting with circular receptors randomly distributed on a spherical cell surface. The calculation takes complete account of the competition between receptors. Results are compared to an approximate expression due to Berg and Purcell which correctly predicts the rate constant in the limit of low and high density of receptors but which only qualitatively treats the effect of competition between receptor sites for the incoming ligands. This expression is found to deviate somewhat from the correct numerically obtained rate in the intermediate regime in which the density of receptors is sufficiently large that competition effects become important but sufficiently small that the cell has not achieved the hypothetical maximum rate given by the Smoluchowski rate constant.

Introduction

A microorganism can detect the concentration of chemoattractant molecules diffusing in its environment by monitoring the state of occupation of receptors distributed over its surface.¹ A high degree of efficiency may be achieved even when only a small fraction of the cell surface is covered with receptors^{1,2} because of the peculiar volume-filling property of diffusing particle ensembles.³ Further saturation of the cell surface with receptors beyond a certain density will not achieve a commensurate increase of ligand binding efficiency owing to the onset of competition between receptors for incoming ligands. In this paper we will examine the effect of such competition by numerically calculating the diffusional rate of ligand binding to varying numbers of randomly distributed receptors.

The diffusion-controlled bimolecular reaction rate constant k_0 of an incoming ligand with a single isolated circular receptor site of radius *a* lying on an otherwise inert cell surface is given by⁴

$$k_0 = 4Da \tag{1}$$

where D is the translational diffusion coefficient of the ligand. This result has been obtained by assuming that the radius R of the cell is large compared to a, such that the receptor site behaves effectively as a circular disk located on an infinite plane. If Nreceptors are dispersed on the surface sufficiently far apart that they behave independently and are noncompeting, the total rate constant of ligand binding is simply an additive property and can be written as

$$k' = Nk_0 = 4NDa \tag{2}$$

When the number of sites N becomes sufficiently large, the rate constant ultimately reaches its maximum value corresponding to a cell surface which behaves as if it were totally covered with cell receptors and is thus isotropically reactive to incoming ligands. This value is given by the Smoluchowski rate constant⁵

$$k_{\rm D} = 4\pi DR \tag{3}$$

Berg and Purcell,¹ and later Shoup and Szabo by more transparent means,² derived the following approximate expression for the rate constant of this system which connects the limiting results exemplified by eq 2 and 3 through intermediate values of N:

$$k_{\rm BP} = k' k_{\rm D} / (k' + k_{\rm D}) = 4\pi D R N a / (\pi R + N a)$$
(4)

This expression shows that the Berg-Purcell approximate rate constant $k_{\rm BP}$ is always less than the rate constant 4NDa for independent receptor activity and thus at least qualitatively reflects the fact that the receptors compete for the incoming ligands. Furthermore, eq 4 shows that the cell approaches maximum efficiency for binding ligands even when a relatively small fraction of the cell surface is covered by receptors. In other words, the limit $Na \gg \pi R$ (and thus $k_{\rm BP} \approx k_{\rm D}$) can be practically achieved even when the surface coverage fraction $f = N(a/R)^2/4 \ll 1$.

In this paper we will employ a modification of the Brownian dynamics trajectory method developed by Northrup et al. $^{6-14}$ to numerically compute the rate of ligand binding to varying numbers

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