A Gas Phase Kinetic Study of the Energy Transfer by using the High Power CO₂ Laser. II. Decomposition of BrCH₂CH₂CH₂CH₂Cl

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Infrared multiphoton decompositions (IRMPD) of $BrCH_2CH_2CH_2CH_2Cl$ were studied by using the pulsed CO_2 laser. At 0.3 J laser energy the experimentally observed product ratios could be reasonably explained by the RRKM calculation with initial excitation energy of ca. 80 Kcal/mol. The pressure dependence of product yields led us to conclude that the collisional deactivation by the inert gas decreased the yield of low energy dissociation channel more significantly.

Introduction

The infrared multiphoton dissociation (IRMPD) of polyatomic molecules has attracted many scientists because of its potential use for the isotope separation,[1] the mode selective reactions,[2] and the study of energy transfer processes,[3] etc. To initiate the unimolecular dissociation, an intense IR field is required for the absorption of at least 20-30 photons.

The detailed mechanism for the multiphoton absorption process has not been known yet. However, the following facts are universally accepted for the process.[4] The multiphoton process occurs through three regions in the vibrational ladder of the potential energy, In region I (the lower part of the vibrational ladder) the density of state is low, so only the photons in resonance with the vibrational frequency of the mode are possible to be absorbed. In region II, sometimes called 'quasicontinuum' or 'color-blind' region, photons are absorbed without keeping the selection rule because the density of state is very high (almost continuum). Further excited molecules reach the region III, where the energy pumping and the dissociation process compete.

Though much efforts have been delivered for IRMPD of simple molecules, there have been few systematic studies on that of large polyatomic molecules. Large polyatomic molecules have additional distinctive characteristics: The high density of vibrational states in polyatomic molecules allow the sample molecule to be in or nearly in the quasi-continuum after the absorption of only one or two infrared photons. Therefore even when the absorption coefficient is small, polyatomic molecules frequently exhibit high reaction probability. In polyatomic molecules often more than one reaction channels are available, and the collisional quenching by unexcited reactants or bath gas molecules can compete effectively with dissociation channels. Therefore one can study the energy transfer process in competition with the laser pumping.

In this study the IR multiphoton dissociation of 1-Bromo-4-chlorobutane (BCB) is carried out by the intense radiation from the pulsed TEA CO₂ laser. Since the molecule has two very closely located (energetically) dissociation channels, HCl elimination and HBr elimination, the variation of product yields on the experimental parameters, such as the laser power and the system pressures, should give valuable information on the unimolecular dissociation of highly energetic molecules. For comparison purpose a thermal decomposition reaction of BCB was also studied. Arrhenius parameters for
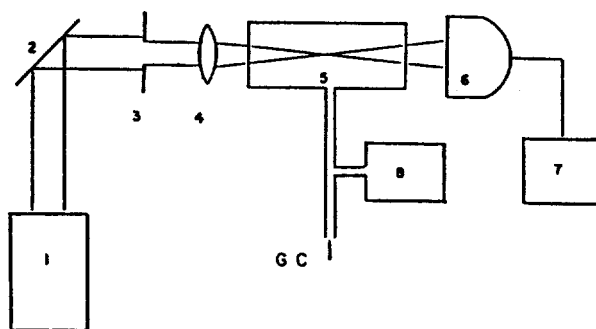

Figure 1. The schematic diagram of IRMPO set up.

1. TEA CO₂ laser
2. Reflector(Cu)
3. Irish diaphrgam
4. ZnSe lens
5. Reaction cell
6. Laser Power meter
7. Power energy meter
8. Electronic Pressure Transducer(MKS Baratron)

the dissociation channels were obtained.

Instrumentation

A thermal decomposition reactions of BCB was carried out with a static gas phase pyrolysis reactor described previously in our laboratory.[5]

Figure 1 shows the schematic diagram for the IRMPD experiments. A Grating tuned TEA CO₂ laser (Tachisto 215G) provides 0.1-0.5J laser pulse at 9 and 10 μm band. The laser output wavelengths were calibrated by using CO₂ spectrum analyzer (Opt. Eng.). The peak intensity of the laser pulse is about 5 megawatt, and each pulse is 40 nsec (FWHM) spike, followed by a weak intensity tail that extends to 500 nsec. A Thermal sensitive paper shows a uniform burning pattern, which is corresponds to TEM OO mode. ZnSe lens (focal length = 15 cm) was used for the focusing of the laser and the output flux was also controlled by a Irish diaphragm. Calorimetric power meter (Scientech 36-2001) with either analog meter (Scientech 36-2002) or storage oscilloscope (Tektronix 5111) was used for the measurement of laser energy.

The reaction cell is a conventional pyrex IR static cell (10 cm long, 2 cm diameter) with polished NaCl end windows. The cell also has a side-arm that can be used for the cold trap of the reaction products. BCB and diluent gases are transfered to the reaction cell through the vacuum line.

All pressure measurements are carried out with MKS Baratron Electronic Pressure Readout System (10 torr, 1000

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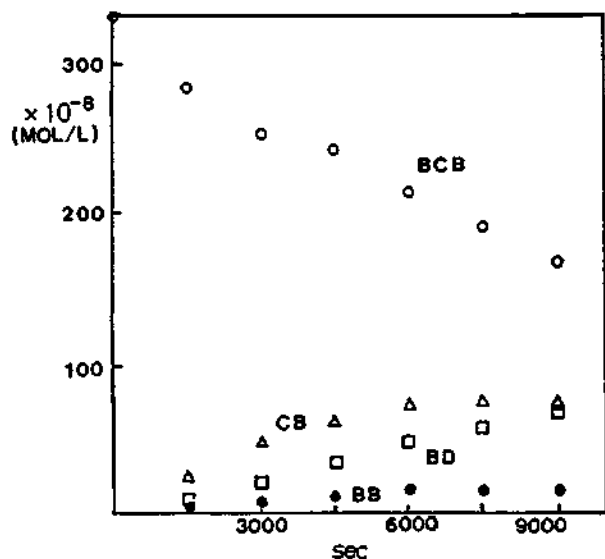
Figure 2. Time dependence of reactant and product concentrations. Initial conditions; [BCB] = 0.10 torr, [Toluene] = 1.6 torr, [Ar] = 469 torr, T = 633 K. BCB[1-Bromo-4-chlorobutane], CB[4-chloro-1-butene], BB[4-Bromo-1-butene], BD[Butadiene].

torr). During the experiments the focusing points of the laser output were moved little by little around the center of the reaction cell. This eliminates the possible polymerization and other heterogeneous surface reactions.

Reagents

1-Bromo-4-chlorobutane (Aldrich), 4-chloro-1-butene (Aldrich), butadiene (Matheson), and Helium (Matheson) were used in this experiments. After several freeze-pump-thaw cycles in the vacuum line all the reagent vapors show no detectable impurities on the gas chromatographic analyses. The maximum vapor pressure of BCB at room temperature is about 0.8 torr. Since BCB is unstable at room temperature and sensitive to light, the purified BCB is kept under dark and cold conditions.

Product analysis

In the pyrolysis experiment the products were sampled directly from the reactor via 6 port GC sampling valve. In the IRMPD study the IR cell was attached to the inlet system of the GC and a fraction of the contents was injected. All the GC analysis were carried out with Yanaco G-180 GC with FID detection.

Result and Discussion

Thermal decomposition of BCB. In the temperature range of 350-380 °C BCB is thermally decomposed to give HCl, HBr, 4-chloro-1-butene, 4-bromo-1-butene, and butadiene in the presence of toluene as a radical scavenger. Since the activation enrgy for HX elimination reaction is expected to be much lower than that for the C-X bond fission reactions, only HX elimination products were found in the presence of radical trap. The radical trap will effectively scavenge any possible radicals (Cl or Br) that may initiate unwanted
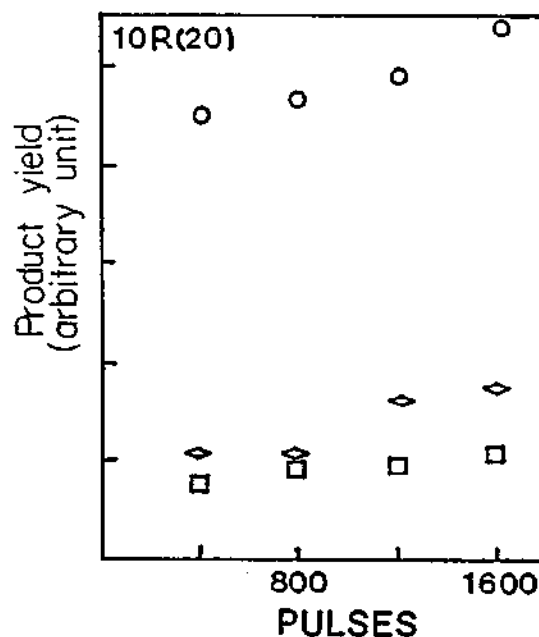
Figure 3. Dependence of the product yields on the number of laser pulses. laser energy: 0.3J. P_{He} = 0 torr. ○: 4-Chloro-1-butene. □: 4-Bromo-1-butene. ◇: Butadiene.

radical chain reaction.

The reaction mechanism for the BCB decomposition must be the followings;

$$BrCH_2CH_2CH_2CH_2Cl \xrightarrow[k_1]{-HCl} BrCH_2CH_2CH = CH_2$$

$$k_2 \downarrow -HBr \qquad\qquad \downarrow -HBr$$

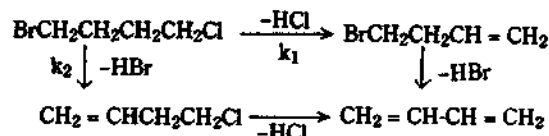$$CH_2 = CHCH_2CH_2Cl \xrightarrow[-HCl]{} CH_2 = CH-CH = CH_2$$

Figure 2 shows the variation of reactant and products concentrations as a function of times. Temperature dependences of the rate constants led us to the following Arrhenius parameters for the HCl and HBr elimination reactions: for k_1; log A = 13.6 sec^{-1}, E_a = 55.2 kcal/mole and for k_2; log A = 13.2 sec^{-1}, E_a = 50.9 kcal/mole.[6] Therefore, in the temperature range of 350-380 °C or lower, HBr elimination reaction is more rapid than HCl elimination reaction.

IRMPD

Wavelength Selection. The IR spectrum of BCB taken with 10 cm cell shows a rather broad absorption near 1000 cm^{-1} where the CO_2 laser output wavelengths are located. Therefore it was not possible to select exact irradiation wavelength from the absorption spectrum alone. The dissociation yields at various laser output wavelengths were compared. Since 10R(20) and 10P(20) lines show the maximum dissociation yields among various laser lines, we chose the 10R(20) line, 10.234 um (977.14 cm^{-1}) and 10P(20) line, 10.59 um (944.20 cm^{-1}) for the irradiation wavelength.

Dependence on the number of laser pulses. Figure 3 shows the dependence of product yields on the number of laser pulses. The product yields increase linearly with the number of laser pulses indicating the homogeneity of the reaction and the absence of side reactions. 4-Chloro-1-butene,
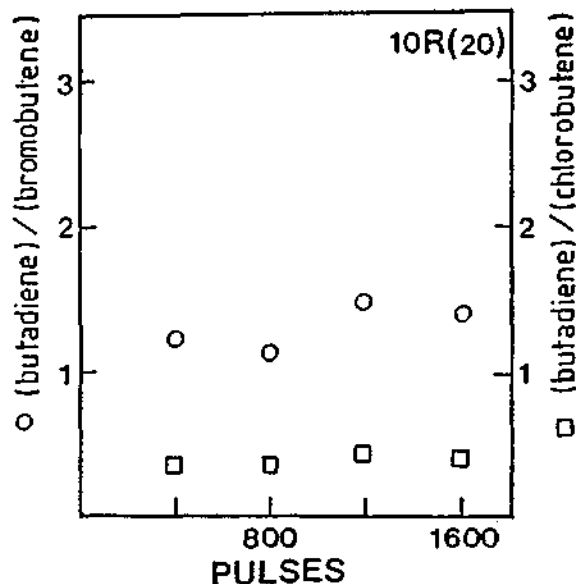
Figure 4. Product ratios vs. number of laser pulses. Same experimental conditions as in Figure 3.

Figure 5. RRKM Calculation of k_a (E) at various energies. k_a (E), L: k_a (E) for HBr elimination channel. k_a (E), H: k_a (E) for HCl elimination channel.

the HBr elimination product from BCB, is the major product while the 4-bromo-1-butene and butadiene are almost same amount. It would be interesting to know from where butadiene came; directly from BCB dissociation in the laser pulse or from the secondary reaction of the initial products. Figure 4 shows how the product ratios depend on the number of laser pulses.

From figure 4 we can conclude that butadiene was formed directly from the laser irradiation. If butadiene were formed by the secondary dissociation from the laser irradiation of primary products, the [butadiene]/[4-Bromo-1-butene] and [butadiene]/[4-chloro-1-butene] ratios would depend on the number of laser pulses. Since the laser pulse width is at least 40 nsec the dissociation of initially formed product can be occured during the molecules stay in the laser pulse width. This phenomena was also observed in the IRMPD of trichloroethylene.[7]

The [4-Bromo-1-butene]/[4-chloro-1-butene] = 1/5 ratio is a direct indication of reaction channel rate constant ratio in the IRMPD of BCB. From the experimentally observed ratio we can estimate the average excitation energy from the RRKM calculation of k_a(E). Figure 5 shows the RRKM cal-

Table 1. Molecular Parameters used in RRKM Calculation for the Reactant and the Activated Complexes

Reactant BrCH₂CH₂CH₂CH₂Cl	Complex(-HBr) H₂C=CHCH₂CH₂Cl Br···H	Complex(-HCl) BrCH₂CH₂CH=CH₂ H···Cl
2900(8)	2900(7)	2900(7)
1300(4)	1300(4)	1300(4)
1240(4)	1240(4)	1240(4)
1040(3)	1040(3)	1040(3)
680(4)	680(4)	680(4)
640(1)	640(1)	550(1)
550(1)	410(4)	410(4)
410(4)	300(2)	300(2)
300(2)	280(2)	215(2)
180(2)	200(1)	140(1)
90(1)	90(1)	90(1)
80(1)	80(1)	80(1)
60(1)	60(1)	60(1)

Units are in cm⁻¹

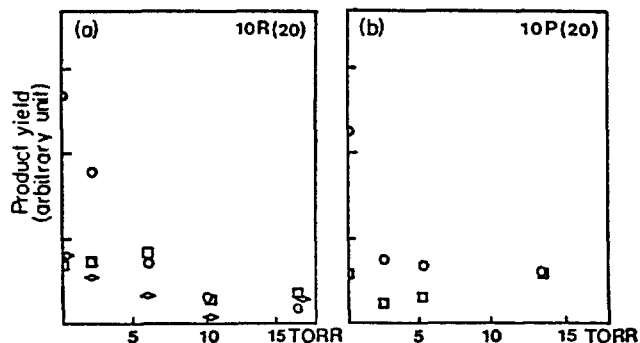| E_c		50.9 kcal/mole	55.2 kcal/mole
I_{ext}	4.69×10^{-112} g^3cm^6	5.53×10^{-112} g^3cm^6	4.92×10^{-112} g^3cm^6
S_o	97.31 e.u.	97.55 e.u.	99.12 e.u.

Figure 6. Pressure dependence on the product yields. (a) with 10R (20) laser irradiation. (b) with 10P(20) laser irradiation. ○: 4-Chloro-1-butene. □: 4-Bromo-1-butene. ◇: Butadiene.

culation of k_a(E)s for two dissociation channels, molecular parameters for the RRKM calculations are given in Table 1. From the figure, we can resonably say that the IRMPD with laser fluence (0.3J) with a focusing condition excites the molecule to $E_a = 80$ kcal/mole, which corresponds to 29 IR photons.

Pressure Dependence. Figure 6 (a) (b) shows the dependence of % product yield on the pressure in the reaction cell. In these experiments, total pressures were altered by changing the buffer gas pressure(He) while the BCB partial pressures were kept almost constant (≤0.5 torr). Both 10R(20) and 10P(20) irradiations gave similar results. First, the products, 4-chloro-1-butene and 4-bromo-1-butene, both decrease as the pressure increases. The decrease of 4-chloro-1-butene is more significant. As shown in the figure the amount of 4-Bromo-1-butene is almost constant while 4-chlo-

ro-1-butene concentration decreases more rapidly as the pressure in the system increases.

This result indicates that any collisional processes does not enhance the dissociation but mainly deactivate the excited molecules. Collision may occur during and after the pulse. During the pulse, the excited molecules above activation energy may proceed to three paths; further absorption of photons (pumping process), unimolecular decomposition and collisional deactivation. As the pressure increases, collisional deactivation can compete with the pumping process and unimolecular decomposition. Collisional effect will lead to decrease the average energy of molecules and so reduce the dissociation yield in general. After the pulse the excited molecules undergo either unimolecular decomposition or collisional deactivation. The collisional deactivation effectively occures in molecules with the long lifetime, and so the decrease of the dissociation yield of low energy dissociation channel will be more significant. The experimental result show that collisional deactivation by bath gas is more significant for low energy channel (HBr elimination) as expected.

Conclusion

(1) 1-Bromo-4-chlorobutane has two closely located dissociation channels: HCl and HBr elimination. The former has 55.2 kcal/mol activation energy and the latter has 50.9 kcal/mol activation energy.

(2) With focused geometry and 0.3J laser energy the experi-

mentally observed product ratios and the RRKM calculation lead us to conclude that the BCB molecule has been excited to ca. 80 kcal/mol, well above the dissociation limit.

(3) The pressure dependence of product yields lead us to conclude that the collisional deactivation by the inert gas decreases the yield of low energy dissociation channel more significantly.

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Reactivity of the Biheterocyclic Betaine with the *para*-Substituted Phenacyl Bromides for the Ring Transformation Reaction

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7-Dithiocarboxy-3-phenyl-5,6-dihydro imidazo[2,1-b]thiazolium-betaine (2) was prepared by treatment of 3-phenyl-5,6-dihydro imidazo[2,1-b] thiazole (1) with carbon disulfide in acetone at room temperature. On the reaction of 2 with *para*-substituted phenacyl bromides (4) having the electron withdrawing property by virtue of (+) resonance (R)<(−) inductive (I) or (−) resonance (R), (−) inductive (I) effect, ring transformation product *p*-substituted-2-[2-[7-(*p*-substituted benzoyl)-5-thioxo-2,3-dihydro-1H-imidazo[1,2-c] thiazol-1-yl]-2-phenylvinylthio] acetophenone (6) was obtained; however, when R is electron donating grops with (+) resonance (R)>(−) inductive (I) effect the quarternary ammonium salt 7-(*p*-substituted phenyl) carbonyl methyl-3-phenyl-5,6-dihydro imidazo [2,1-b] thiazolium bromide (8) is formed. The reaction of 2 with unsubstituted-phenacyl bromide (R = H), on the other hand, gives 6a and 8a to the similar ratio, respectively.

Introduction

N-bridged thiazolo compounds, 3-substituted-5,6-dihydro imidazo [2,1-b] thiazoles[1-3] and 3-substituted-6,7-dihydro-5H-thiazolo[3,2-a] pyrimidines[2,3,8] have been synthesized by condensing cyclic thioureas with α-halo ketones. Their thiazolium salts were well known for pharmacological property such as hypoglycaemic, growth promotant and acaricidal activity.[4-7]

3-substituted-5,6-dihydro imidazo[2,1-b]thiazoles react with electrophiles such as aryl isothiocyanate, aryl iso-

cyanate, alkyl isothiocyanate, alkyl isocyanate and carbon disulfide in acetone at room temperature to yield the corresponding betaines.[9,10] The ring transformation reaction by treatment of 8-phenyl(thiocarbamoyl)-3-phenyl-6,7-dihydro-5H-thiazolo[3,2-a] pyrimidinium-betaine with alkylating agents was reported in the earlier publications.[11,12]

We report here on the reactivity of 7-dithiocarboxy-3-phenyl-5,6-dihydro imidazo[2,1-b] thiazolium-betaine(2) with a series of *para*-substituted phenacyl bromides (4) and the preparation of new biheterocyclic compounds via ring transformation. The betaine (2) is easily obtained from the reac-