Dehydrochlorination of 1,2-Dichloropropane by CO_2 Laser-Induced Breakdown; Comparison with Thermal Elimination

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Keywords: Alkenes / Eliminations / Halogens / Laser chemistry / Photolysis

Dehydrochlorination of 1,2-dichloropropane (**DCP**) was conducted by thermal elimination and CO_2 laser-induced dielectric breakdown, which was induced by focusing the 10.6 µm lines of a CO_2 TEA laser. Thermal dehydrochlorination proceeded by a four-centered mechanism at > 425 °C and by a surface-catalyzed radical process at < 400 °C. The product distribution of the breakdown-induced reaction at < 400 °C resembled that of high temperature thermal elimination and the corresponding temperature was estimated to be > 2000 °C.

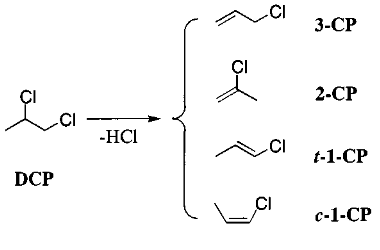
Introduction

Carbon dioxide lasers have been used extensively in the study of various chemical reactions.[1] Vibrational excitations by direct and sensitized photolyses are the main driving force in such IR laser-induced reactions, and multiphoton absorption is necessary to cause chemical reactions of organic compounds because the energy of a single photon is not sufficient for the cleavage of any kind of chemical bond in the molecules. Therefore, a good matching of the absorption of substrates or sensitizers with CO_2 laser emissions is indispensable for efficient multiphoton absorption in reactions that proceed by vibrational excitation. These reactions are usually carried out under low pressures to avoid relaxation of internal energy by collisions.

Laser-induced breakdown[2] is another class of reaction that can induce various organic reactions. The phenomenon of breakdown has been extensively studied from the physical standpoint by using very simple compounds, mainly noble gases and small inorganic molecules. Laser-induced breakdown has been classified into two categories: thermal breakdown and optical breakdown. Thermal breakdown occurs when compounds have high absorption coefficients and are irradiated by continuous or repetitive-pulsed lasers. Optical breakdown, on the other hand, occurs with short-pulse laser irradiation and proceeds by electron cascade and by direct ionization of the medium through multiphoton absorption. Optical breakdown is induced even in the absence of intense absorptions by substrates, a situation that can eliminate the requirement of the matching of laser emissions and the absorptions of substrates and sensitizers. These reactions can also be conducted with comparatively high substrate concentrations.

Several applications of laser-induced breakdown have been reported, such as spectroscopy[3] and inorganic materials processing.[4][5] However, only a limited number of studies have been carried out with organic molecules;[6][7] most of them are conducted from physical standpoints but only a few from the standpoint of organic chemistry, such as an application to the polymerization of methyl methacrylate[8] and reactions of simple molecules.[9]

In order to extend the applicability of laser-induced optical breakdown in organic reactions and to investigate the nature of the reactions, we have studied the dehydrochlorination of 1,2-dichloropropane (**DCP**) by using focused 10.6 µm emissions of a CO_2 TEA laser.[10] **DCP** was chosen as the substrate because it has practically no absorption at 10.6 µm and is therefore suitable for studying practically *pure* breakdown-induced reactions without considerable mixing of conventional photochemical processes. The dehydrochlorination of chlorinated alkanes is a common reaction and such a reaction of **DCP** has been reported by thermal processes[11] that include the use of various catalysts.[12] Four chloropropenes (**CP**s) are formed by the dehydrochlorination of **DCP**, i.e. 3-chloropropene (**3-CP**), 2-chloropropene (**2-CP**), *trans*-1-chloropropene (***t*-1-CP**), and *cis*-1-chloropropene (***c*-1-CP**) (Scheme 1). Photochemical eliminations of **DCP**[13] have also been reported, including direct and sensitized reactions by a CO_2 laser.[14]



Scheme 1. Dehydrochlorination of **DCP**

In this work, we report the CO_2 laser-induced breakdown of **DCP** in comparison with conventional thermal and photochemical eliminations. The product distribution of the breakdown-induced reaction resembled that of high-temperature thermal eliminations and the corresponding temperature was estimated to be at least 2000°C.

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Results

Dehydrochlorination of 1,2-Dichloropropane by Thermal Elimination

In the study of the reactions induced by dielectric breakdown, the standard data on the thermal eliminations were obtained by using the same reaction vessel and procedure as used in the breakdown-induced reactions because it is reported that the *wall effect* of the reaction vessel has a significant influence on the thermal dehydrochlorinations.[11]

Effect of Reaction Temperature on the Yields and Selectivities of Chloropropenes

Figures 1a, b show the reaction temperature dependence on the yields of **CP**s and benzene and on the consumption of **DCP** by thermal dehydrochlorination after reaction times of 20 and 60 min. As seen in the figures, the feature of the reactions started to change at ca. 400°C. In the case of a 20 min reaction time, the total yield was almost constant, which indicates that most of the consumed **DCP** was converted into the four **CP**s and benzene. In the case of the 60 min reaction time a significant decrease of **CP**s at 500°C was observed. The decrease in the total yield and the formation of an increasing amount of carbonaceous compounds on the surface of the reaction vessel were also observed at > 475°C.

Figures 1c, d show the reaction temperature dependence on the selectivities of **CP**s and benzene after reaction times of 20 and 60 min. The selectivities of **CP**s also changed at 350−400°C, which implies an alteration in the dehydrochlorination mechanism during the course of the reaction. A decrease in the selectivity of **3-CP** above 475°C can be explained by a secondary reaction of **3-CP** to form benzene.[15]

Effect of Reaction Time on the Yields and Selectivities of Chloropropenes

Figures 2a−c show the reaction time dependence on the yields of **CP**s and benzene and on the consumption of **DCP** at the reaction temperatures of 450, 475, and 500°C. As shown in the figures, the reaction proceeded with increasing reaction time and temperature. Glc detection of volatile compounds[16] and the formation of carbonaceous compounds were observed at the reaction conditions where the decrease in the total yield was observed.

Figures 2d−f show the reaction time dependence on the selectivities of **CP**s and benzene at the reaction temperatures of 450, 475, and 500°C. The figures also show that benzene was formed at the expense of **3-CP**.

Dehydrochlorination of 1,2-Dichloropropane by CO_2 Laser-Induced Breakdown

The breakdown was induced by using 10.6 μm lines of a CO_2 TEA laser, which was focused with a convex lens. The reported spectrum of **DCP**[17] has almost no absorption at 10.6 μm and the broadening of the spectrum at high temperature was almost negligible.[17] The absence of the absorption can eliminate the conventional photochemical processes that proceed by direct absorption of photons. The absorptions of **CP**s at this wavelength[17] are also small, except for that of **3-CP**.

Effect of Reaction Temperature on the Yields and Selectivities of Chloropropenes

Figures 3a, b show the reaction temperature dependence on the yields of **CP**s and benzene and on the consumption of **DCP** at reaction times of 20 and 60 min. Evidence for the occurrence of breakdown was provided by the obser-

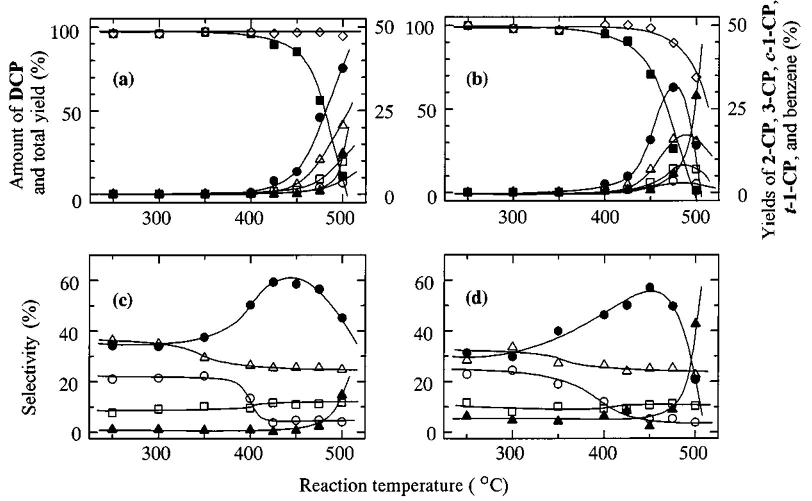


Figure 1. Thermal dehydrochlorination of **DCP**; effect of reaction temperature on the yields of **CP**s and benzene and on the consumption of **DCP** (a, b), and on the selectivities of **CP**s and benzene (c, d); reaction time: 20 min (a, c), 60 min (b, d); compounds; △: ***c*-1-CP**, □: ***t*-1-CP**, ○: **2-CP**, ●: **3-CP**, ▲: benzene, ■: **DCP**, ◇: total yield (***c*-1-CP** + ***t*-1-CP** + **2-CP** + **3-CP** + benzene + **DCP**)

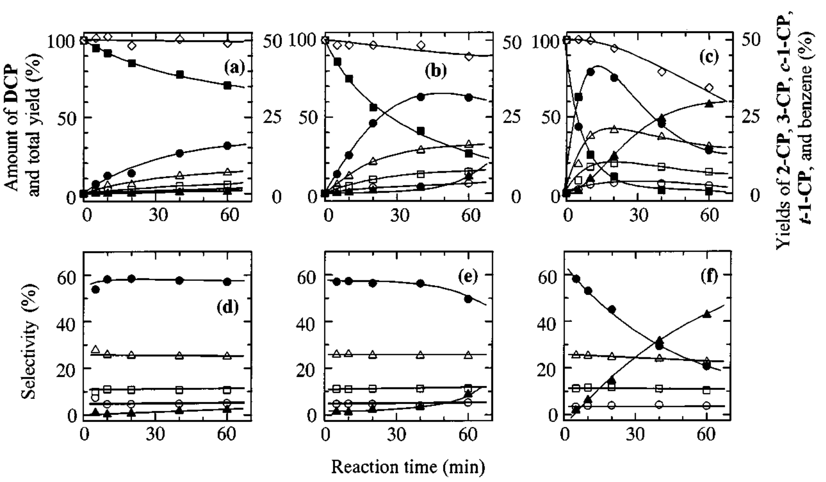


Figure 2. Thermal dehydrochlorination of **DCP**; effect of reaction time on the yields of **CP**s and benzene and on the consumption of **DCP** (a, b, c), and on the selectivities of **CP**s and benzene (d, e, f); reaction temperature: 450°C (a, d), 475°C (b, d), and 500°C (c, f); compounds; △: ***c*-1-CP**, □: ***t*-1-CP**, ○: **2-CP**, ●: **3-CP**, ▲: benzene, ■: **DCP**, ◇: total yield (***c*-1-CP** + ***t*-1-CP** + **2-CP** + **3-CP** + benzene + **DCP**)

vations of a bright blue-white spark at the focus and a loud audible sound for each laser pulse. The reactions at 250−400°C showed only a small consumption of **DCP** because the breakdown only occurred at the focus of the laser and the laser was irradiated with the frequency of 0.25 Hz. However, the consumption was increased by four- to five-fold compared with that in the thermal eliminations, which implies that the dehydrochlorination of **DCP** mainly proceeded by dielectric breakdown.

In contrast to the cases of thermal eliminations (cf. Figures 1a, b), a considerable decrease in the total yield was observed even in this temperature range. This result is due to the formation of carbonaceous substances and volatile compounds by breakdown. The carbonaceous substances were observed on the surface of the reaction vessel and the volatile compounds were detected by glc analysis. It was found that the formation of the carbonaceous substances predominated at lower reaction temperatures while the gen-

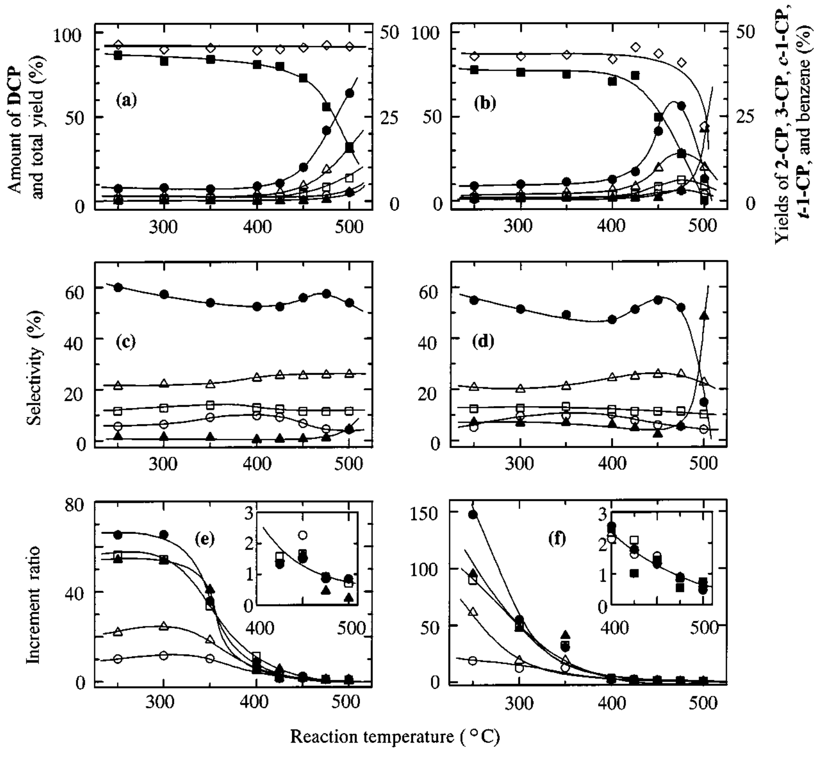


Figure 3. CO_2 laser breakdown-induced dehydrochlorination of **DCP**; effect of reaction temperature on the yields of **CP**s and benzene and on the consumption of **DCP** (a, b), on the selectivities of **CP**s and benzene (c, d), and on the increment ratios (e, f); reaction time: 20 min (a, c, e), 60 min (b, d, f); compounds; △: ***c*-1-CP**, □: ***t*-1-CP**, ○: **2-CP**, ●: **3-CP**, ▲: benzene, ■: **DCP**, ◇: total yield (***c*-1-CP** + ***t*-1-CP** + **2-CP** + **3-CP** + benzene + **DCP**)

eration of the volatile compounds predominated at higher temperatures.

At 400°C, an alteration of the reaction mechanism was observed that was similar to that in the thermal elimination (cf. Figures 1a, b). However, evidence for the breakdown phenomena was still observed at 400−475°C, so that the breakdown-induced process was superimposed on the predominant thermal process over this temperature range. The bright sparks and audible sounds began to cease at 475°C and completely disappeared at 500°C.

Figures 3c, d show the selectivities of **CP**s and benzene at reaction times of 20 and 60 min. Below 350°C, where breakdown-induced reaction predominated, the product distribution resembled that of the high temperature thermal elimination (cf. Figures 1c, d).

Figures 3e, f show increment ratios as a function of the reaction temperature. The ratio was defined by [yield of **CP** (or conversion of **DCP**) *with* laser irradiation]/[yield of **CP** (or conversion of **DCP**) *without* laser irradiation]. As shown in the figures, the reactions were largely accelerated by the breakdown at 250−400°C. However, the ratios became almost unity at 450−500°C; this result indicates that the products were mainly formed by the thermal process in this temperature range.

Effect of Reaction Time on the Yields and Selectivities of Chloropropenes

Figures 4a−c show the reaction time dependence on the yields of **CP**s and benzene and on the consumption of **DCP** at reaction temperatures of 450, 475, and 500°C. The feature of the reactions was similar to that of the thermal eliminations (cf. Figures 2a−c), except for the fact that the total yield was slightly reduced. The increment factors for **CP**s, benzene, and **DCP**, which correspond to Figures 4a−c at the initial stage of the reactions, were ca. 1.6 at 450°C and ca. 1.0 at 475 and 500°C.

Figures 4d−f show the selectivities of **CP**s and benzene at 450, 475, and 500°C. The selectivities of **2-CP**, ***t*-1-CP**, and ***c*-1-CP** at each reaction temperature were practically the same as those in the thermal reactions (cf. Figures 2d−f). This is also due to the predominance of the thermal processes over the breakdown-induced processes.

Stability of Chloropropenes under Different Reaction Conditions

The stability of ***t*-1-CP**, ***c*-1-CP**, **2-CP**, and **3-CP** were tested under the reaction conditions that were used in the dehydrochlorination of **DCP**. Table 1 shows the recovered yields of each **CP**. Each **CP** was separately subjected to the four reaction conditions shown in the table. It can be seen from these results that **3-CP** was very unstable to the high temperature thermal condition (thermal, 500°C) and a considerable amount of benzene was formed.[15] Compound **2-CP** was unstable to the breakdown-induced conditions. The combination of thermal and breakdown-induced conditions (CO_2 laser, 500°C) made ***t*-1-CP** and **2-CP** less stable than under the simple breakdown-induced (CO_2 laser, 250°C) or thermal (thermal, 500°C) conditions.

Table 1. Recovered yield of **CP**s under various reaction conditions

Reaction condition[a]	Recovered yield (mol-%)			
	3-CP[b]	***c*-1-CP**[c]	***t*-1-CP**[c]	**2-CP**
Thermal, 250°C	ca. 100 (5)	ca. 100	ca. 100	95
Thermal, 500°C	5 (40)	ca. 100	86	86
CO_2 laser, 250°C	89 (3)	99	86	66
CO_2 laser, 500°C	5 (30)	ca. 100	66	37

[a] Reaction time: 30 min. − [b] Formation of benzene was observed, with yields shown in brackets. − [c] The reactions were conducted with a mixture of ***c*-1-CP** and ***t*-1-CP**.

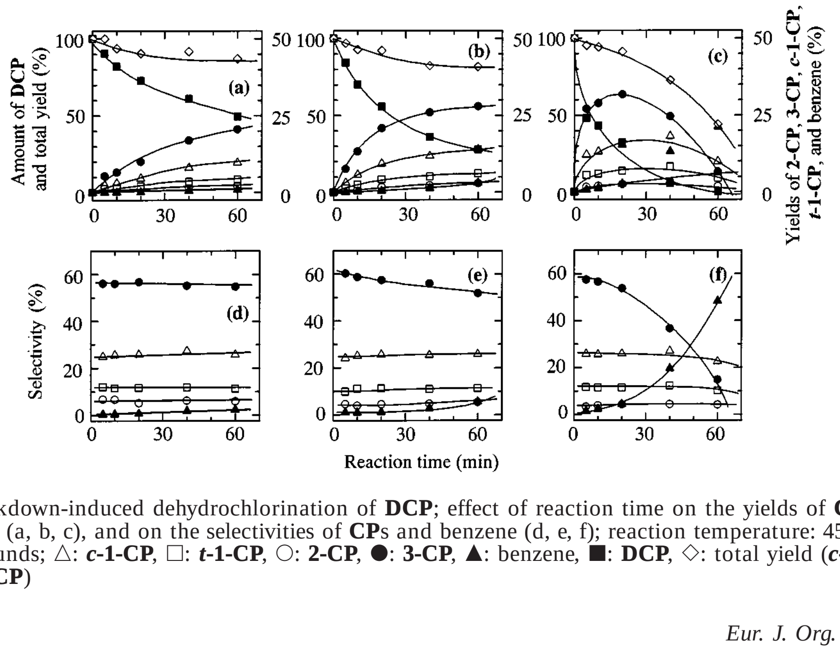
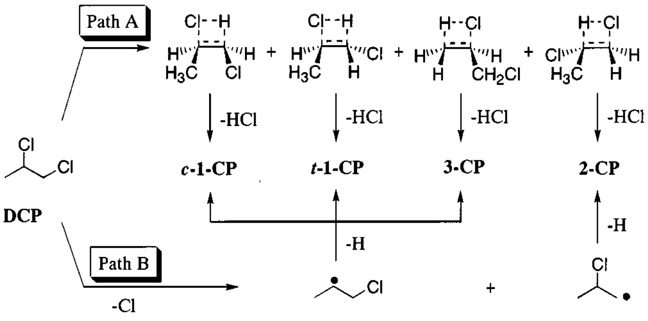


Figure 4. CO_2 laser breakdown-induced dehydrochlorination of **DCP**; effect of reaction time on the yields of **CP**s and benzene and on the consumption of **DCP** (a, b, c), and on the selectivities of **CP**s and benzene (d, e, f); reaction temperature: 450°C (a, d), 475°C (b, e), and 500°C (c, f); compounds; △: ***c*-1-CP**, □: ***t*-1-CP**, ○: **2-CP**, ●: **3-CP**, ▲: benzene, ■: **DCP**, ◇: total yield (***c*-1-CP** + ***t*-1-CP** + **2-CP** + **3-CP** + benzene + **DCP**)

Discussion

Thermal Elimination

In the thermal eliminations of **DCP**, considerable changes in the selectivities and the yields of the products were observed at 350−425°C (cf. Figure 1). These changes imply an alteration of the reaction mechanism at this temperature range. Indeed, such a change in the reaction mechanism has been also reported by Takashima[11d] and Martens et al.[11e] at 410°C and 400−450°C, respectively. The possibility of radical chain mechanism in the dehydrochlorination of **DCP** in the *high-temperature* range was excluded by several groups[11b,11e,11h] and the reaction mechanism operating at this temperature range was proved to be a unimolecular process;[11b,11e,11f] a four-centered mechanism was proposed for this unimolecular process (Scheme 2, Path A).[11b,11e]



Scheme 2. Two mechanisms for the dehydrochlorination of **DCP**

The regioselectivity of the reaction depends on the rate parameters [$k = A\exp(-E/RT)$] for the formation of each product. The order of the activation energies (E) and the frequency factors (A) obtained by the most reliable experiment were ***c*-1-CP** < **3-CP** < ***t*-1-CP** < **2-CP** and **3-CP** > ***t*-1-CP** > **2-CP** > ***c*-1-CP**, respectively.[14a] The order of the selectivities observed in our experiments in the *high-temperature* range, i.e. above 425°C, was **3-CP** > ***c*-1-CP** > ***t*-1-CP** > **2-CP** and this is in good agreement with the previous reports.[11c,11e,14a] The order reflects the effect of both activation energy (E) and frequency factor (A) of each reaction.

At higher temperatures and with longer reaction times a significant amount of benzene was formed. The formation of benzene was also observed in the previous studies and it was attributed to the secondary reaction of **3-CP** (cf. Table 1). The reaction is reported to be a radical condensation of two molecules of **3-CP**.[11d−f,15]

The *low-temperature* reaction, i.e. the reaction at < 350°C, seems to proceed by a different process because the consumption of **DCP** was small and, at the same time, the order of the selectivities of **CP**s (***c*-1-CP** > **3-CP** > **2-CP** > ***t*-1-CP**) was different to that of the *high-temperature* reaction. In this temperature range, the reaction is reported to proceed by a *surface-catalyzed* radical process (Scheme 2, Path B).[11b,11e,11f] In this temperature range, 250−400°C, different orders of the selectivities of **CP**s have been reported by separate groups[11d−h] and consistent experimental rate parameters are still not obtained. This is probably due to the difference in the surface properties of the reaction vessels used by each group.

CO_2 Laser-Induced Breakdown Reaction

Comparison of the results of the CO_2 laser-induced breakdown reactions with those of the thermal and photochemical[13] reactions leads to deductions with respect to the nature of the breakdown-induced process. In the reactions above 425°C, the consumption of **DCP** and the yields and selectivities of **CP**s were almost the same as those of the thermal eliminations. Although the occurrence of breakdown was observed in this temperature range, the result shows that the reaction mostly proceeded by the thermal four-centered process (Scheme 2, Path A).

The selectivities and the yields of the products below 400°C showed significant differences in comparison to those of the thermal eliminations. With an increase in the temperature from 250 to 400°C, the selectivities of **CP**s changed slightly towards those of the *low-temperature* thermal reactions. This slight change in the selectivities can be rationalized by the increasing ratio of thermal *surface-catalyzed* reaction (Scheme 2, Path B) to the breakdown-induced reaction.

The order of the selectivities of **CP**s at 250°C, where the participation of the *surface-catalyzed* reaction is very small, was **3-CP** > ***c*-1-CP** > ***t*-1-CP** > **2-CP**. This is entirely different from the order obtained in photochemical reactions at the same temperature. The photochemical reactions were conducted by KrF (248 nm)[13a] and ArF (193 nm)[13b] excimer lasers by using the same experimental set-up and procedure as the present thermal and CO_2 laser-induced experiments. The selectivities of **CP**s in the photochemical reactions were the same for the both excimer lasers and the order was **2-CP** > ***c*-1-CP** > **3-CP** > ***t*-1-CP**. Therefore, the order of selectivities obtained by the CO_2 laser-induced reaction at 250°C can be regarded as the result of breakdown-induced reaction.

The order of the selectivity of **CP**s in the breakdown-induced reactions was, in fact, similar to that of the *high-temperature* thermal elimination. This implies that the CO_2 laser breakdown has a similar effect as *high-temperature* thermolysis, which most likely proceeds by the four-centered process (Scheme 2, Path A). In order to estimate the corresponding temperature for the breakdown-induced reaction, we used the relationships for the calculated rate constant ratios **3-CP/2-CP** and **1-CP/2-CP** as a function of temperature, which were reported by Tsang et al.[14a] By applying the ratios obtained from our experiments, we can estimate the corresponding reaction temperature from the relationships. In the early stages of the breakdown-induced reactions, the ratios of the yields can be used as approximate values for the rate constant ratios. The ratios of the yields obtained in our CO_2 laser-induced breakdown reaction at 250°C and 20 min reaction time were **3-CP/2-CP** = 10.60 and **1-CP/2-CP** = 5.81. The corresponding reaction temperatures obtained from the relationships reported by

Tsang et al.[14a] were 1600°C for the former ratio and 2000°C for the latter. This difference in the temperature can be explained by the degree of the decomposition of each **CP** under the breakdown-induced reaction conditions, which causes a deviation in the ratios from the *real* values. When we take into account the decomposition of each **CP** during the reaction, we would expect an even higher temperature for the reaction because the degree of decomposition under CO_2 laser irradiation at 250°C was in the order **2-CP** > **3-CP** > **1-CP** (cf. Table 1). Therefore, it can be concluded that the reaction induced by CO_2 laser breakdown corresponds to thermal eliminations of at least 2000°C. The generation of considerable amounts of carbonaceous substances, even under the *low-temperature* breakdown-induced conditions, can be explained by this fact.

The advantage of CO_2 laser-induced breakdown reactions is that *high-temperature* thermal reactions can be performed without external heating and without consideration of the matching of the laser emissions with the absorptions of substrates or sensitizers. Therefore, breakdown-induced reactions may be used as a new tool for high temperature flash pyrolysis.

Conclusion

We have conducted an investigation into the dehydrochlorination of **DCP** by CO_2 laser-induced breakdown in comparison with the thermal reactions. Thermal dehydrochlorination was found to proceed by a four-centered mechanism at temperatures above 425°C and by a surface-catalyzed radical process at temperatures below 400°C. The CO_2 laser breakdown-induced reactions at temperatures above 425°C mainly proceeded by the thermal four-centered process. The product distribution of the breakdown-induced reaction below 400°C resembled to that of the high temperature thermal elimination. The corresponding temperature of the breakdown-induced reaction was estimated to be at least 2000°C.

Experimental Section

General Remarks: The reactions were carried out in a quartz cylindrical cell with a BaF_2 window (diameter: 25 mm, volume: 180 mL) having surface/volume ratio of 1.6 cm^{-1}. The data were obtained after conducting two runs of the dehydrochlorination of **DCP** in order to season the surface of the vessel. The cell was evacuated with a diffusion pump (ca. 10^{-5} Torr) and then 320 μL of degassed 1,2-dichloropropane (**DCP**; Tokyo Kasei Kogyo, Co., Ltd.; > 98.0%; no **CP**s were detected by glc analyses) was introduced through a small rubber septum inlet. Thermal reactions were conducted with external heating by a cylindrical electric furnace, with which the whole of the cell was heated. Breakdown-induced reactions were conducted by a focused CO_2 laser with external heating. The laser utilized was 10.6 μm lines of a CO_2 TEA laser [LUMONICS TEA-103−2; pulse width: 150 ms (fwhm), 4 J·$pulse^{-1}$; 0.25 Hz], which was focused at the center of the cell with a BaF_2 convex lens (f = 200 mm, fluence at the focus = 300 J·cm^{-2}). After the reaction, the cell was cooled to the room temperature and 25 mL toluene was introduced into the cell through the septum inlet and then the cell was further cooled to ca. 5°C.

The consumption of **DCP** and the yields of the four **CP**s and benzene were obtained by glc analyses of an aliquot of the toluene solutions (0.4 μL) in comparison with the authentic samples. The glc analyses were conducted by using a 3 m column of 5% TCP and 1% Tween 60 on 60/80 mesh C-22 support (GL Science) and a flame-ionization detector. The relative sensitivity factors for **DCP**, **CP**s, and benzene were obtained by analyses of known mixtures of authentic samples.

Decomposition of degassed **CP**s (65 μL) was examined under the four reaction conditions by using the same apparatus and procedure.

Acknowledgments

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