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KrF Excimer Laser-induced Dehydrochlorination of 1,2-Dichloropropane

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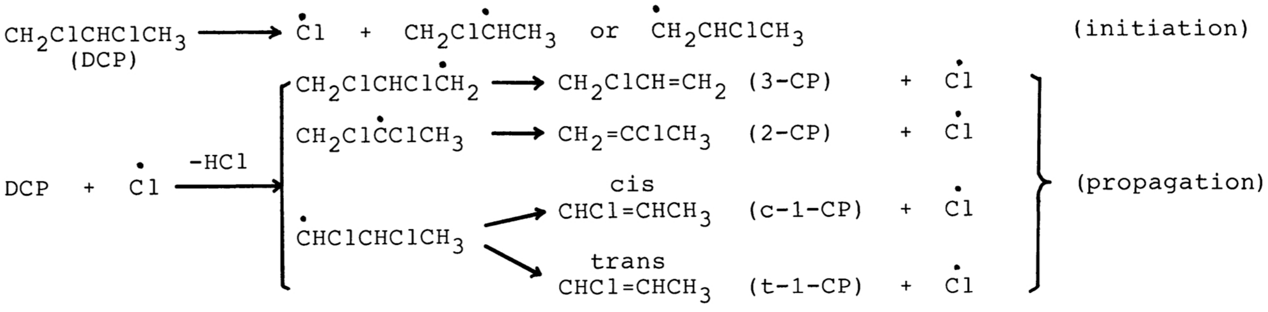
Dehydrochlorination of 1,2-dichloropropane was conducted with and without irradiation of KrF excimer laser (248 nm). It afforded four products, cis-1-, trans-1-, 2-, and 3-chloropropene. The reaction was remarkably accelerated with irradiation of laser especially at the low temperatures.

Chloroalkenes are widely used for organic syntheses not only in researches but also in chemical industries. Selective dehydrochlorination of polychloroalkanes, therefore, has significant importance in production of chloroalkenes. One of the ways to conduct dehydrochlorination of these compounds is thermally induced chain reaction. However, the reaction usually requires a high temperature and substantial amount of by-products are often formed. The temperature necessary for the initiation of such reaction is generally higher than that for the propagation. Hence, if the initiation is conducted by photochemical means and the temperature is maintained at minimum for continuing the propagation, the amount of thermally generated by-products will be reduced. Our works on the synthetic application of excimer lasers prompted us to focus our attention to laser-induced dehydrochlorination of polychloroalkanes.

A synthetic application of excimer laser has been reported for the dehydrochlorination of 1,2-dichloroethane.$^{1)}$ However, only a single product is expected from the reaction. To explore more general scope of the reaction, we chose 1,2-dichloropropane (DCP) for our study. DCP gives four products from its dehydrochlorination, cis-1-chloropropene (c-1-CP), trans-1-chloropropene (t-1-CP), 2-chloropropene (2-CP), and 3-chloropropene (3-CP, allyl chloride)$^{2)}$ (Scheme 1). In addition to the application of excimer lasers to organic syntheses, we thought it also important to discover the factors which control the selectivity of the reaction.



$$\underset{\text{(DCP)}}{CH_2ClCHClCH_3} \longrightarrow \dot{Cl} + CH_2Cl\dot{C}HCH_3 \text{ or } \dot{C}H_2CHClCH_3 \qquad \text{(initiation)}$$

$$DCP + \dot{Cl} \xrightarrow{-HCl} \left[\begin{array}{lll} CH_2ClCHCl\dot{C}H_2 \longrightarrow CH_2ClCH{=}CH_2 & \text{(3-CP)} & + \dot{Cl} \\ CH_2Cl\dot{C}ClCH_3 \longrightarrow CH_2{=}CClCH_3 & \text{(2-CP)} & + \dot{Cl} \\ \dot{C}HClCHClCH_3 \longrightarrow \overset{\text{cis}}{CHCl{=}CHCH_3} & \text{(c-1-CP)} & + \dot{Cl} \\ \dot{C}HClCHClCH_3 \longrightarrow \overset{\text{trans}}{CHCl{=}CHCH_3} & \text{(t-1-CP)} & + \dot{Cl} \end{array}\right\} \text{(propagation)}$$

Scheme 1.

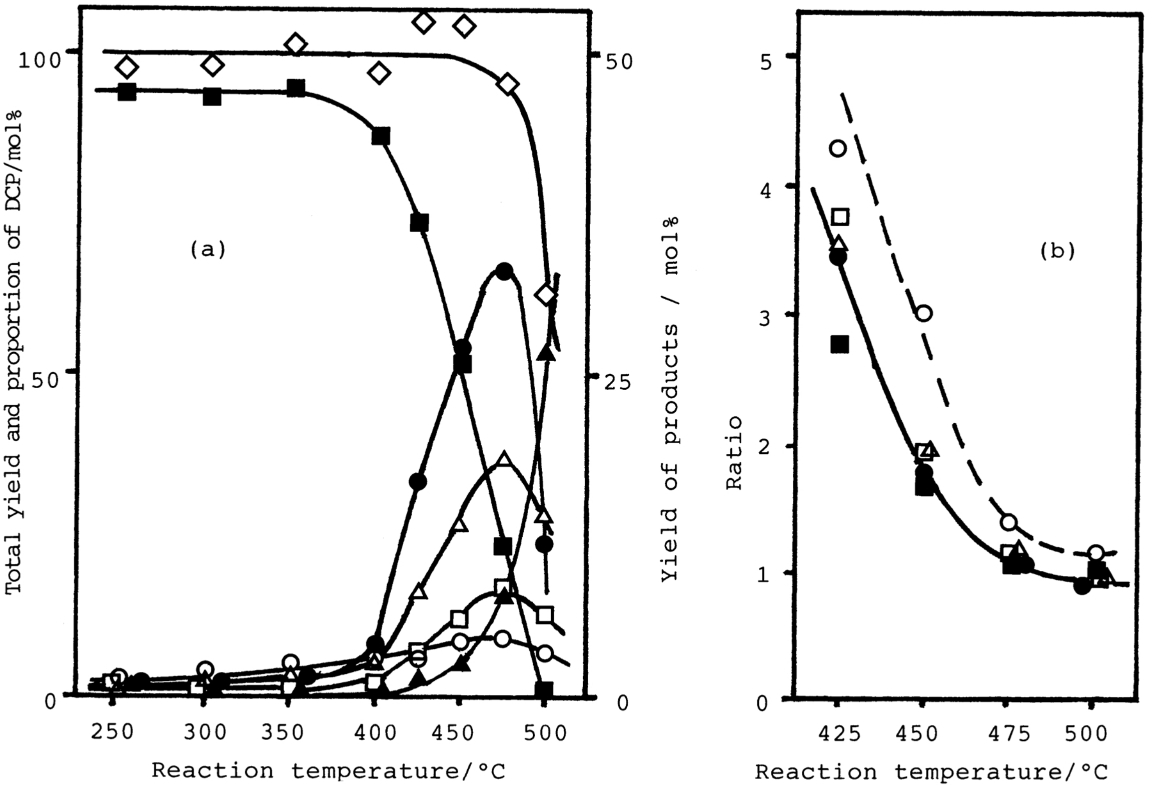


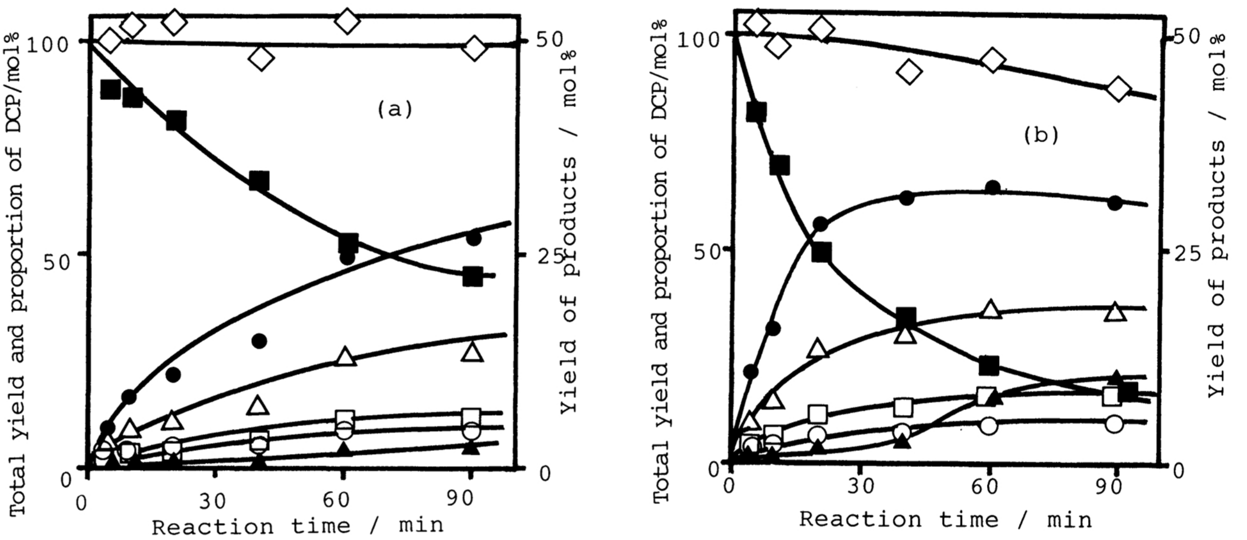
Fig.1. a) Total yield, proportion of DCP, and yields of products as a function of temperature for dehydrochlorination of DCP under 1 h KrF laser irradiation; b) Ratios for the yields of CPs and conversion of DCP; ■ :DCP; △:c-1-CP; □:t-1-CP; ○:2-CP; ●:3-CP; ▲:Benzene; ◇:total yield (DCP+c-1-CP+t-1-CP+2-CP+3-CP+Benzene).

The laser used was KrF excimer laser (Lambda Physics EMG-50) with 8 ns pulse duration, 60-80 mJ energy at 248 nm, ca. 1 Hz, and beam shape of 8 x 22 mm. Irradiation was carried out in a quartz cylindrical cell with Suprasil window (diameter: 25 mm, volume: 140 ml). The cell was evacuated with a diffusion pump through an outlet and then 250 μl of degassed DCP was introduced from septum inlet with a microsyringe. The reactions were conducted with heating by an electric furnace. After cooling the cell to room temperature, 20 ml of toluene was added through the inlet by a hypodermic syringe and further cooled to ca. 5 °C. The yields were obtained by the analyses of the toluene solution using gas chromatography in comparison with the authentic samples.

The results at various temperatures with 1 h reaction time are given in Fig. 1(a). The increase of product yields above ca. 400 °C indicates the beginning of propagation of the chain reaction. The major product was 3-CP. The figure also shows the production of significant amount of benzene at higher temperature, which was due to a secondary thermal reaction of 3-CP.[3)] Furthermore, the drop in total yield at 500 °C reflects the generation of substantial amount of volatile compounds and carbonized substances on the surface of the reaction vessel.[4)]

Figure 1(b) shows the effect of laser irradiation by increment ratio which was defined by the following equation:

$$\text{Ratio}=\frac{\text{Yield of product (or conversion of DCP) }\underline{\text{with}}\text{ laser irradiation}}{\text{Yield of product (or conversion of DCP) }\underline{\text{without}}\text{ laser irradiation}}$$



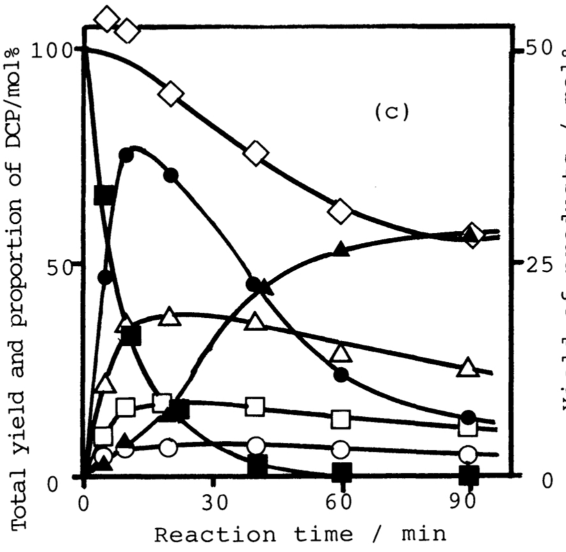


Fig.2. Product compositions in the course of the reaction a) at 450 °C; b) at 475 °C; c) at 500 °C; ■:DCP; △:c-1-CP; □:t-1-CP; ○:2-CP; ●:3-CP; ▲:Benzene; ◇:total yield (DCP+c-1-CP+t-1-CP+2-CP+3-CP +Benzene).

As shown in the figure, the reaction was considerably accelerated with irradiation of KrF excimer laser, especially at lower temperatures. In the case of 1-CPs, 3-CP, and DCP, 3.5-fold excess of products and conversion were obtained with the irradiation at 425 °C, whereas no acceleration was observed at 500 °C. It reflects the ratio of photochemically induced (PI) and thermally induced (TI) radicals for the initiation, i.e., PI<TI (at 500 °C) and (PI+TI)/TI≅3.5 (at 425 °C). In the case of 2-CP, the ratios were larger than the other products. It is suspected that these excesses are due to the photochemical process. It is supported by the fact that almost no 2-CP was detected in the reactions without laser irradiation at temperature between 250 and 350 °C, whereas some products were formed with irradiation in the same temperature region as shown in Fig.1(a).

As the reaction showed drastic changes between 425 and 500 °C, the product compositions were examined in the course of the reactions at several temperatures. Figures 2(a), 2(b), and 2(c) show product yields to the reaction times at 450, 475, and 500 °C respectively. At 450 °C, four products showed constant increase without generation of significant amount of benzene or other by-products. However, with the increase of the reaction temperature, especially at 500 °C as seen in Fig.2(c), drastic decomposition occurred with the generation of by-products as mentioned previously.

The present study has revealed that the utilization of KrF excimer laser has considerable effect on increase in products of the dehydrochlorination of DCP at low temperatures. It also showed an prominent advantage in increase of the yields by reduction of the reaction temperature, which suppressed the secondary thermal reactions, especially decomposition of 3-CP which is the major and most labile product. Further studies are now in progress.

References

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2) a) K.A.Holbrook and J.S.Palmer, Trans. Faraday Soc., 67, 80 1971;
b) G.J.Marfens, M.Godfroid, and L.Ramoisy, Int. J. Chem. Kinet., 11, 123 (1970); and see references cited therein.

3) Decomposition of CPs were examined under various conditions. Thus, 50 μl of each CP was subjected to the reaction conditions which are listed in Table 1 below. The apparatus and procedures were same as that in the text. It revealed that i) c-1-CP was stable to these conditions, ii) t-1-CP and 2-CP were fairly stable to these conditions, iii) t-1-CP was partly isomerized into c-1-CP by the irradiation of laser, iv) 3-CP was thermally unstable but photochemically stable, and v) benzene was generated from thermal decomposition of 3-CP.

Table 1. Decomposition of CPs under various reaction conditions

Reactants	Reaction conditions			Product yields / %				
	temp/°C	time/min	irradiation	c-1-CP	t-1-CP	2-CP	3-CP	Benzene
3-CP	250	30	-	0.2	0	0.02	106.6	4.6
	500	30	-	1.7	0	0.1	5.3	40.4
	250	30	KrF	0.2	0	0	106.4	4.9
	500	30	KrF	1.9	0	0.2	6.7	42.2
2-CP	250	30	-	0.2	0.3	94.8	0	-1.6
	500	30	-	0.2	0.2	86.4	0.2	-1.5
	250	30	KrF	0	0	88.6	0.02	-4.1
	500	30	KrF	0	0	88.8	0	1.0
1-CP a)	250	30	-	104.3	103.4	-	0	4.7
	500	30	-	105.1	85.6	-	0.2	2.8
	250	30	KrF	116.0	84.1	-	0	-1.1
	500	30	KrF	108.0	79.4	-	0.2	1.6

a) Reactions were conducted with mixture of *cis*-1-, *trans*-1-, and 2-CP (c-1-CP:t-1-CP:2-CP=3.26:3.87:1.00).

4) Analyses with GLC showed the production of a volatile compound which has smaller retention time compared with 2-CP. It is suspected to be propene.2b)

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