

A NOVEL LASER-INDUCED SYNTHESIS OF 1,1-DICHLOROETHYLENE FROM 1,1-DICHLOROETHANE

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As a new photochemical process for synthesizing 1,1-dichloroethylene (VC) from 1,1-dichloroethane (1,1-DCE), the laser-induced photochlorination of 1,1-DCE followed by its dehydrochlorination has been examined with excimer laser irradiation in a flow reactor under normal pressure and 298-623K.

In the laser-induced photochlorination of 1,1-DCE, a high selectivity for 1,1,1-trichloroethane (1,1,1-TCE), which was expected to yield VC uniquely in the following dehydrochlorination stage, was obtained in the lower temperature range. In the laser-induced photodehydrochlorination of 1,1,1-TCE, a small amount of Cl₂ addition promoted the formation of VC, and the yield of VC was strongly dependent on the Cl₂/1,1,1-TCE ration and the reaction temperature. By experimental work and kinetics study, both of these reactions are thought to proceed by a chain mechanism.

By connecting two reaction cells in series, in which the above two reactions are individually carried out, a new photochemical process for synthesizing VC from 1,1-DCE was designed. In this system, experimental results suggested that two factors, the complete consumption of substrate in the first cell and the addition of Cl₂ before the second cell, are important for attaining a higher selectivity for the desired product.

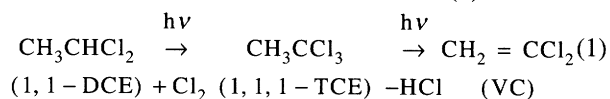
Introduction

The conventional process for synthesizing 1,1-dichloroethylene (VC) consists of two thermal reactions. The first is chlorination of vinyl chloride to 1,1,2-trichloroethane (1,1,2-TCE) catalyzed by FeCl₃, and the second is dehydrochlorination of 1,1,2-TCE by base catalysts, such as aq. Ca(OH)₂. There remain, however, some problems unsolved in this process. In particular, the selectivity for VC is limited because of random dehydrochlorination of 1,1,2-TCE. Recently, thermal chlorinolysis of 1,1-dichloroethane (1,1-DCE) was reported by Shinoda *et al.*¹⁶⁾, where 1,1,1-trichloroethane (1,1,1-TCE) and VC could be co-produced in fairly broad formation ratios by controlling the reaction conditions in laboratory- and pilot plant-scale experiments. They concluded that in the laboratory experiments the ratio of VC/(VC+1,1,1-TCE) could be changed in a broad range by controlling the reaction temperature. The reaction temperature was uncontrollable but maintained within the range of 733-753 K in pilot plant experiments, because the reaction proceeded adiabatically on the balance of exothermic chlorination with endothermic dehydrochlorination.

Compared to thermal reaction, photolytic initiation has a great advantage in lowering the activation energy for the overall reaction. Therefore, lower reaction temperatures can be adopted, which is desirable to minimize side reactions in such cases as oxidation of hydrocar-

bons^{12, 13)}. As a light source for photochemical reactions, lasers have such unique properties as high intensity, high monochromaticity and low divergence of the light beam, which can not only induce the excitation of a specific molecule to initiate chemical reactions or to change their course, but also can simplify the design of reactor vessels suitable for the intended chemical process. In recent years, several attempts in the use of lasers have been reported in the field of synthetic chemistry. In the synthesis of vinyl chloride²⁰⁾ and high-pressure polymerization of ethylene³⁾, for example, chain reactions have been successfully induced by excimer laser irradiation. As for photochlorination, the reaction of 1,1-DCE to 1,1,1-TCE using krypton or argon ion laser irradiation was reported by Clark *et al.*⁵⁾, in which the maximum value of the 1,1,1-TCE/1,1,2-TCE ratio was as high as 9 at 393 K. The authors have shown the possibility of laser-induced synthesis of VC from 1,1-DCE in brief¹¹⁾, where the kinetic analysis for the reaction was not sufficiently performed.

The objective of this work is to propose a new photochemical process for synthesizing VC from 1,1-DCE with excimer lasers, as shown in reaction (1).



The optimum reaction condition was investigated for each reaction: the laser-induced photochlorination of

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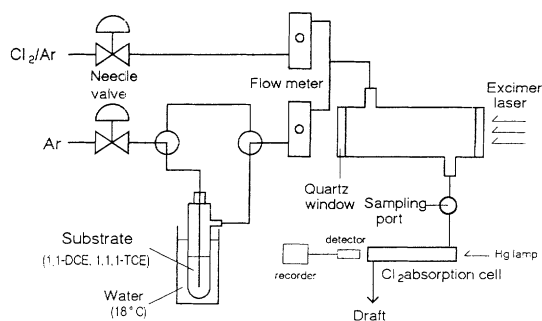


Fig. 1 Experimental apparatus

Table 1. Dependence of product distribution on reaction temperature in the photochlorination of 1, 1-dichloroethane

Reaction temperature [K]	298	373	473
Conversion of 1, 1-DCE [%]	40.5	35.8	44.2
Product selectivity [%]			
1, 1, 1-TCE	92.6	87.7	85.3
1, 1, 2-TCE	4.4	7.8	10.2
1, 1, 1, 2-tetrachloroethane	0.5	2.0	2.5
1, 1, 2, 2-tetrachloroethane	0.0	0.0	0.5
2, 2, 3, 3-tetrachlorobutane	2.5	2.8	1.6
1, 1, 1-/1, 1, 2-TCE ratio	20.8	11.2	8.4

Laser irradiation: 70 mJ/pulse, 5 Hz

Flow rate: 1,1-DCE 2,1, Cl₂ 0.7, Ar 67 cm³ min⁻¹

1,1-DCE for attaining a higher 1,1,1-TCE/1,1,2-TCE ratio, and the consecutive photodehydrochlorination of 1,1,1-TCE. By making a combination of these two reactions, the possibility of direct synthesis of VC from 1,1-DCE was investigated by light irradiation of flowing 1,1-DCE/Cl₂ mixed gases.

1. Experimental

As shown in **Fig. 1**, the experimental apparatus is the same as in the previous study¹¹⁾. The reactant gas, consisting of the substrate, Cl₂, and Ar as a buffer gas flowed through a Pyrex cylindrical reactor (length 16 cm, inner diameter 2.7 cm) equipped with Suprasil quartz windows at both ends. The substrate vapor was introduced to the reactor at its vapor pressure and 18°C, accompanied by Ar buffer gas. A XeF (351 nm) excimer laser irradiated the flowing gas at 50 Hz, 70 mJ/pulse. The residence time of the reactant gas was about three minutes, being calculated from the reactor volume and gas flow rate. The concentration of Cl₂ was monitored by its UV absorption. Products were all analyzed by gas chromatography.

2. Results and Discussion

2.1 Photochlorination of 1,1-dichloroethane

Temperature effect on product distribution in the chlorination of 1,1-DCE with XeF excimer laser irradiation is shown in **Table 1**. A very high selectivity for 1,1,1-TCE and a high 1,1,1-TCE/1,1,2-TCE ratio were achieved at 298 K. The ratio of 20.8 obtained under this reaction condition is much larger than the value of 9 reported by J. B. Clark⁵⁾. At higher temperatures, the selectivity for 1,1,1-TCE decreased, whereas that for tetrachloroethane became higher.

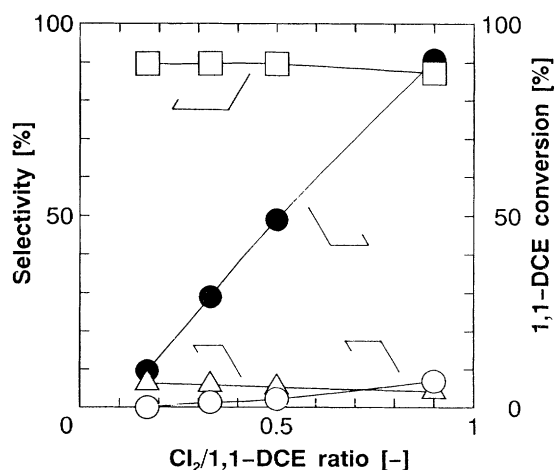


Fig. 2 Dependence of product distribution and 1,1-DCE conversion on Cl₂/1,1-DCE ratio at 298 K (filled circles for 1,1-DCE conversion, open squares, triangles and circles for the selectivities for 1,1,1-TCE, 1,1,2-TCE and tetrachloroethane respectively)

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Dependence of product distribution and conversion of 1,1-DCE on the Cl₂/1,1-DCE ratio are shown in **Fig. 2**. Under such condition that the ratio was smaller than unity, Cl₂ was not detected after passing the reactor, which suggests that Cl₂ introduced was entirely consumed within the reactor. The product distribution in **Fig. 2** indicates that the selectivity for 1,1,1-TCE was independent of the Cl₂/1,1-DCE ratio, whereas tetrachloroethane slightly increased with increase of the ratio. **Figure 2** also shows that the conversion of 1,1-DCE increased proportionally to the Cl₂/1,1-DCE ratio, which suggests that Cl₂ was the limiting reagent under the condition of Cl₂/1,1-DCE < 1, and that the overall stoichiometry of the reaction of 1,1-DCE and Cl₂ is 1:1.

Figure 3 shows the dependence of chain length on laser power. This value is defined by Eq. (2), in which the number of absorbed photons can be calculated by estimating both the total number of photons irradiated and the absorbance of Cl₂ at 351 nm by Lambert-Beer's law, using the absorption coefficient of Cl₂ at 351 nm, 42 l·mol⁻¹·cm³¹⁷⁾.

$$\text{chain length} = \frac{\text{the number of 1, 1 - DCE consumed}}{\text{the number of photons absorbed}} \quad (2)$$

The value of chain length is larger than unity, about 330 at a pulse energy of 0.2 mJ, indicating that this chlorination proceeds through a chain reaction. **Figure 3** also shows that the chain length decreased with increase of laser pulse energy. Irradiation with higher pulse energy generates a larger concentration of radicals, which leads to the condition favorable for radical-radical recombina-

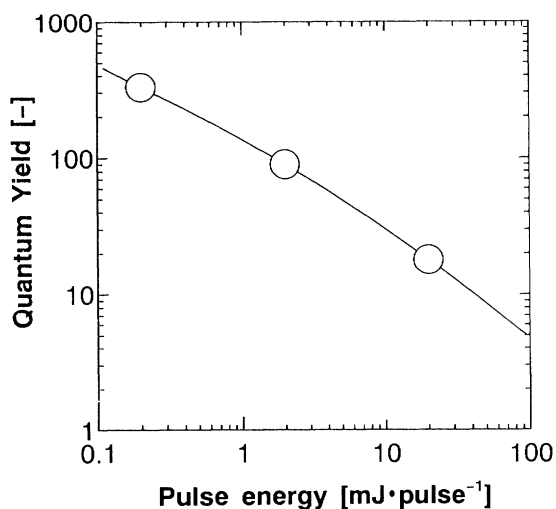


Fig. 3 Dependence of quantum yield on pulse energy of laser irradiation in the photochlorination of 1,1-DCE

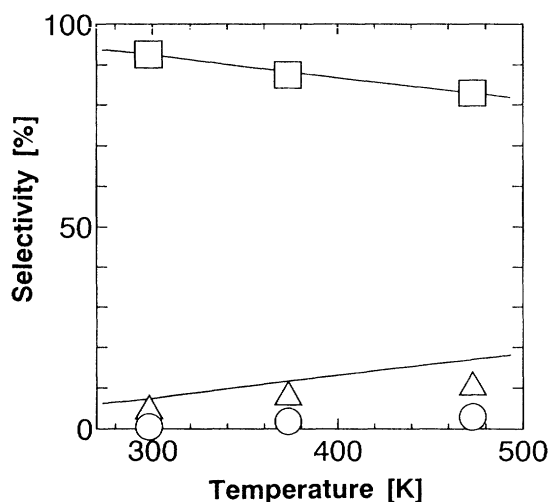
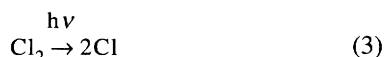


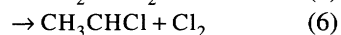
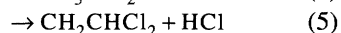
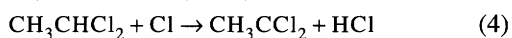
Fig. 4 Comparison of product distributions obtained from simulation works corresponding to 1,1,1-TCE (upper line) and 1,1,2-TCE (lower line) and experimental results (plotted with open squares, triangles and circles, corresponding to the selectivities for 1,1,1-TCE, 1,1,2-TCE and tetrachloroethane respectively)

tion (the termination step of chain reactions), and, therefore causes the chain length to be shortened.

Based on these experimental results, the reaction scheme is proposed as follows. The initiation step is photolysis of Cl_2 to yield two Cl atoms,



In the reaction of Cl with the substrate, three channels ((4)-(6)) are possible; two types of hydrogen atom abstraction and one of chlorine atom abstraction.



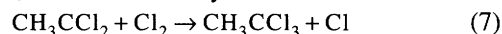
Among them, reaction (4) is considered to be the fastest one at lower temperatures ($k_4 = 7.8 \times 10^{11} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 300 K)¹⁸. The radicals produced by reactions (4)-(6)

Table 2. Kinetic parameters used for the simulation work^a

Reactions	log A	Ea	Ref.
$\text{CHCl}_2\text{CH}_3 + \text{Cl} \rightarrow \text{CCl}_2\text{CH}_3 + \text{HCl}$	12.8	5.4	4
$\text{CHCl}_2\text{CH}_3 + \text{Cl} \rightarrow \text{CHCl}_2\text{CH}_2 + \text{HCl}$	12.8	11.7	4
$\text{CCl}_2\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CCl}_3\text{CH}_3 + \text{Cl}$	11.8	3.8	7 ^b
$\text{CHCl}_2\text{CH}_2 + \text{Cl}_2 \rightarrow \text{CHCl}_2\text{CH}_2\text{Cl} + \text{Cl}$	11.8	3.8	7 ^b
$\text{CCl}_3\text{CH}_3 + \text{Cl} \rightarrow \text{CCl}_3\text{CH}_2 + \text{HCl}$	12.4	15.0	4
$\text{CCl}_3\text{CH}_2 + \text{Cl}_2 \rightarrow \text{CCl}_3\text{CH}_2\text{Cl} + \text{Cl}$	11.8	17.1	1 ^c
$\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$	15.7	0.0	19 ^d
$\text{CCl}_2\text{CH}_3 + \text{Cl} \rightarrow \text{CCl}_3\text{CH}_3$	13.8	0.0	10 ^e
$\text{CHCl}_2\text{CH}_2 + \text{Cl} \rightarrow \text{CHCl}_2\text{CH}_2\text{Cl}$	13.8	0.0	10 ^e

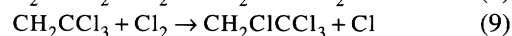
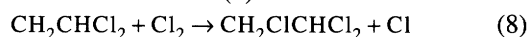
^aUnits for A and Ea are $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $\text{kJ} \cdot \text{mol}^{-1}$, respectively. ^bThe kinetic parameters for the $\text{C}_2\text{H}_3\text{Cl}_2 + \text{Cl}_2$ reaction are used. ^cThe kinetic parameters for the $\text{C}_2\text{H}_2\text{Cl}_3 + \text{Cl}_2$ reaction are used. ^dFrom the reported value of rate constant, A factor, whose unit is $\text{cm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$, is calculated on the assumption that Ea = 0. ^eThe kinetic parameters for the $\text{CCl}_3\text{CHCl} + \text{Cl}$ reaction are used, because of lack of experimental data for this reaction.

react with Cl_2 . Reaction (7), whose kinetic parameters have not been reported, is presumed not to be slow, so that chain reaction may proceed via reactions (4) and (7) to form 1,1,1-TCE dominantly.



According to the literature¹⁸, the activation energy of reaction (5) ($E_5 = 11.7 \text{ kJ} \cdot \text{mol}^{-1}$) is larger than that of reaction (4) ($E_4 = 5.4 \text{ kJ} \cdot \text{mol}^{-1}$), which gives a good explanation for the experimental result that lower temperatures are favorable to the formation of 1,1,1-TCE as shown in Fig. 4.

For checking the validity of this reaction mechanism in more detail, a simulation was carried out to predict the product distribution from the mixture of 1,1-DCE, Cl_2 , and Ar in the temperature range of 300-500 K. The simulation program for solving the differential equations was based on the Gear method. The rate constants of the elementary reactions were computed using the kinetic parameters found in the literature, which are listed in Table 2. Because the kinetic parameters of reaction (7) have not been reported, the authors adopted the same kinetic parameters as those of reaction (8), chlorination of 1,1-dichloro-2-ethyl radical⁷. For the same reason, the kinetic parameters of the reaction of Cl_2 with $\text{C}_2\text{H}_2\text{Cl}_3$ ¹, whose isomeric structure has not been identified, were used for reaction (9).



The result of this simulation work suggests that the chain reaction would terminate within 0.01 second for each laser pulse irradiation, and that the radical concentration would be negligibly small at the next pulse irradiation. As for product selectivity, the calculated distribution agrees fairly well with the observed one within experimental error, as shown in Fig. 4, suggesting the correctness of the proposed mechanism except for the selectivity for tetrachloroethane, which was calculated to be <0.1% at any temperature in the simulation

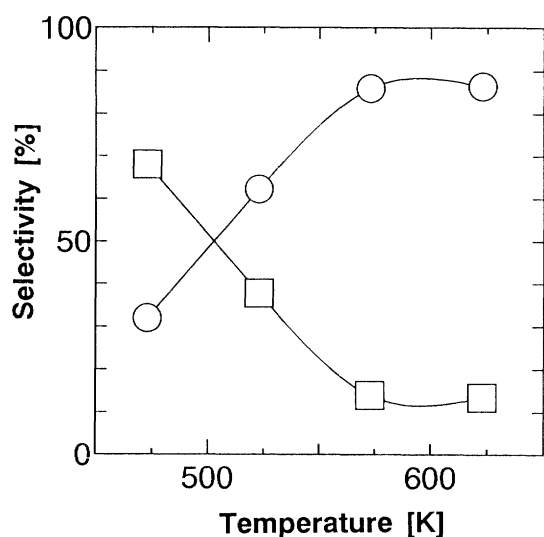


Fig. 5 Temperature dependence of product selectivities in the photodehydrochlorination of 1,1,1-TCE (open circles for VC and open squares for 1,1,1,2-tetrachloroethane)

Table 3. Dependence of product distribution on Cl_2 flow rate in the photodehydrochlorination of 1, 1, 1-trichloroethane at 623K

Cl_2 flow rate [$\text{cm}^3\text{min}^{-1}$]	0.07	0.12	0.35	0.69
Conversion of 1, 1, 1-TCE [%]	9.4	11.0	14.5	30.6
Product selectivity [%]				
1, 1-dichloroethylene (VC)	81.7	73.1	43.4	14.2
1, 1, 1, 2-tetrachloroethane	11.0	18.5	39.2	41.4
trichloroethylene	7.3	8.4	17.4	40.1
tetrachloroethylene	0.0	0.0	0.0	4.3
Yield for VC ^a	7.7	8.0	6.3	4.3

Laser irradiation: 70 mJ/Pulse, 5 Hz

Flow rate: 1, 1, 1-TCE 1.4, Ar 56 $\text{cm}^3\text{min}^{-1}$

^aDefined as 1, 1, 1-TCE conversion multiplied by the selectivity for VC

work. This minor discrepancy is considered to be owing to the adopted kinetic parameters of reaction (9).

2.2 Photodehydrochlorination of 1,1,1-trichloroethane

In the dehydrochlorination of 1,1,1-TCE with XeF excimer laser irradiation, no reaction took place in the absence of Cl_2 below 573 K, which means that the reaction is initiated by photolysis of Cl_2 .

Temperature dependence of product distribution is shown in **Fig. 5**. Two products, VC and 1,1,1,2-tetrachloroethane, were dominantly formed below 623 K at lower Cl_2 flow rate, though the reactant conversion was very small ($< 3\%$), and it seems that higher temperature is favorable to the yield of VC.

Dependence of product distribution on Cl_2 flow rate at 623 K is shown in **Table 3**, which indicates that higher selectivity for VC was obtained at lower Cl_2 flow rate, though 1,1,1-TCE conversion monotonously increased with increase of Cl_2 flow rate. At higher Cl_2 flow rate, the selectivities for 1,1,1,2-tetrachloroethane and trichloroethylene (supposed to be formed by dehydrochlorination of tetrachloroethane) were higher, indi-

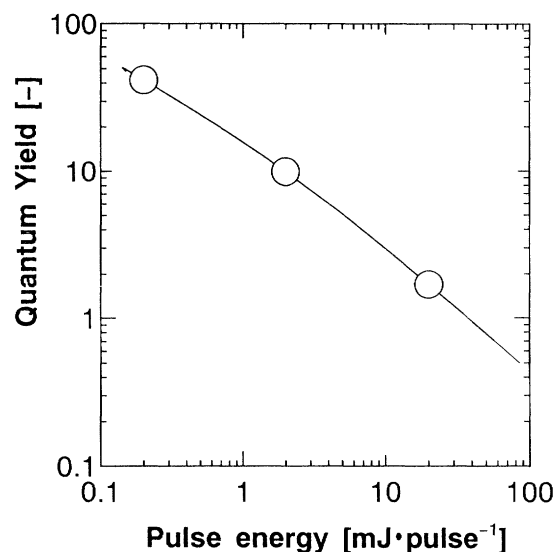


Fig. 6 Dependence of quantum yield on pulse energy of laser irradiation in the photodehydrochlorination of 1,1,1-TCE

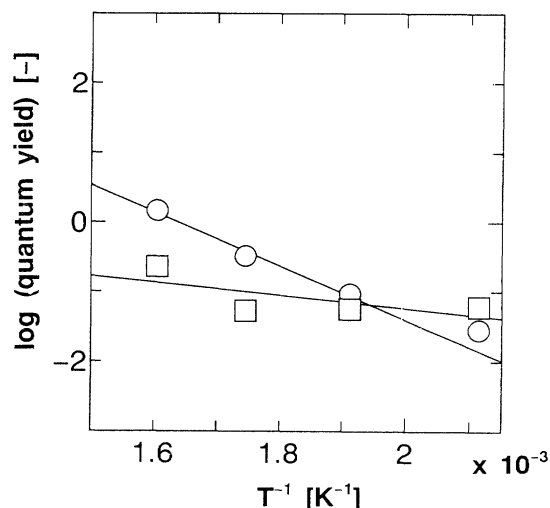


Fig. 7 Arrhenius plots for VC and 1,1,1,2-tetrachloroethane in the dehydrochlorination of 1,1,1-TCE (open circles for VC and open squares for 1,1,1,2-tetrachloroethane)

cating that the chlorination reaction of 1,1,1-TCE became dominant. Thus, it is suggested that there exists an optimum Cl_2 flow rate for attaining a high yield for VC, defined as 1,1,1-TCE conversion multiplied by the selectivity for VC.

Figure 6 shows the dependence of chain length on laser power in the dehydrochlorination of 1,1,1-TCE at 623 K. Eq. (2) is used to define the chain length of this dehydrochlorination reaction by substituting the consumption of 1,1,1-TCE in place of that of 1,1-DCE. That the chain length was larger than unity at any laser pulse energy suggests that the dehydrochlorination as well proceeds through chain reaction as the chlorination of 1,1-DCE.

Dependence of chain length on reaction temperature was also investigated. From the experimental data of chain length and product distribution at each reaction temperature, Arrhenius plots were made for VC and

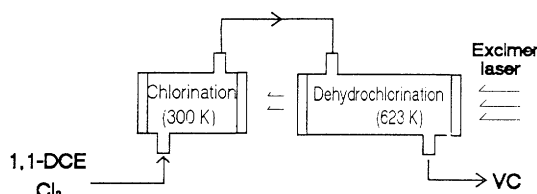


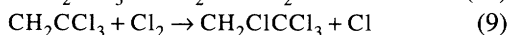
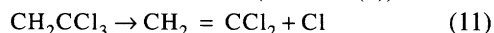
Fig. 8 Model of the direct synthesis of VC from 1,1-DCE

1,1,1,2-tetrachloroethane, as shown in **Fig. 7**, in which activation energies of the formation of VC and 1,1,1,2-tetrachloroethane are calculated to be 63.1 and 17.6 kJ·mol⁻¹ respectively.

The reaction mechanism is thought to be as follows. Atomic chlorine, formed by photolysis of Cl₂, abstracts a hydrogen atom from 1,1,1-TCE to produce CH₂CCl₃ radical (reaction (10)).

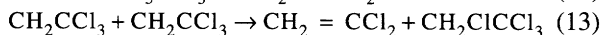


Two competitive reaction paths may be possible for the CH₂CCl₃ radical; one is unimolecular decomposition forming VC (reaction (11)), and the other is chlorination forming 1,1,1,2-tetrachloroethane (reaction (9)).



In the literature, reaction (11) has been reported to possess a larger activation energy (74.4 kJ·mol⁻¹)⁹ than reaction (9) (17.1 kJ·mol⁻¹ for C₂H₂Cl₃ + Cl₂)¹. The fact that the experimental value of the overall activation energy for formation of VC and 1,1,1,2-tetrachloroethane seems to be in good agreement with the reported values of reaction (11) and (9), respectively, supports the proposed chain mechanism, and also suggests that these reactions are rate-determining steps for the formation of the products.

There are two other plausible mechanisms for the formation of VC. One is direct dehydrochlorination from 1,1,1-TCE by molecular elimination of HCl (reaction (12)), as suggested by the work of Reilly *et al.*¹⁵, and the other is the disproportionation reaction of 1,1,1-trichloro-2-ethyl radicals to form equimolar VC and 1,1,1,2-tetrachloroethane (reaction (13)).



These reactions, however, are concluded to make little contribution to the formation of VC for the following reasons. The former has been reported to possess a very large activation energy, 206.9–237.0 kJ·mol⁻¹^{2, 6, 9, 14}, and thus a negligibly small reaction rate in the lower temperature range. A similar conclusion has been reported by Holbrook *et al.*⁸ in the continuous-wave CO₂ laser-induced SF₆-sensitized decomposition of 1,1,1-TCE. As to the latter, it is necessary to take radical-radical reaction into account in this system because of the very large concentration of radicals compared to thermal reaction systems. If, however, reaction (13)

Table 4. Product distribution in direct synthesis of 1, 1-dichloroethylene from 1, 1-dichloroethane

	Run-1	Run-2	Run-3
Conversion of 1, 1-DCE [%]	74.8	80.6	99.2
Product selectivity [%]			
1, 1-dichloroethylene (VC)	1.2	3.6	14.7
vinyl chloride	0.3	3.6	1.3
1, 2-dichloroethylene	0.0	0.6	1.5
trichloroethylene	0.0	0.2	4.4
1, 1, 1-trichloroethane	92.1	87.4	70.4
1, 1, 2-trichloroethane	4.3	2.9	0.8
tetrachloroethanes	1.9	1.4	6.1
others	0.2	0.3	0.8

Run-1: Two stages were simply connected in series.

Laser irradiation: 70 mJ/pulse, 50 Hz. Flow rate: 1, 1-DCE 0.9, Cl₂ 0.7, Ar 59 cm³min⁻¹

Run-2: Four sheets of steel mesh were inserted between two cells, by which the intensity of irradiation to the first cell was reduced to about 1%. Other conditions were the same as in Run-1.

Run-3: Cl₂ was added to the gas flowing before the entrance of the second stage.

Laser irradiation: 20 mJ/pulse, 50 Hz

Initial flow rate: 1,1-DCE 4.5, Cl₂ 5.0, Ar 106 cm³ min⁻¹

Added gas flow rate: Cl₂ 0.5, Ar 8.3 cm³ min⁻¹

would be dominant, both the ratio of VC yield to 1,1,1,2-tetrachloroethane yield and the chain length should be unity at any temperature, which should lead to a quite different result from the experimental result obtained. With kinetic parameters of reaction (13) (pre-exponential factor has been reported to be 10^{12.2} cm³·mol⁻¹·s⁻¹^{1, 18}) and initial concentration of radicals, the initial rate of this reaction can be estimated, which suggests that reaction (13) would make less contribution to VC formation than reaction (11).

2.3 Direct synthesis of VC from 1,1,1-TCE by connecting two stages

Taking the experimental results in sections 2.1 and 2.2 into consideration, the possibility of a novel direct synthesis of VC is investigated with irradiation by a XeF excimer laser to 1,1-DCE/Cl₂ mixed gases.

Two cylindrical reactors, 2.7 cm in inner diameter and 9 cm and 16 cm in length respectively, were connected in series, as shown in **Fig. 8**, and their temperatures were controlled independently. The first cell for the chlorination of 1,1-DCE was kept at room temperature to obtain a higher 1,1,1-TCE selectivity, and the second cell for the consecutive dehydrochlorination was heated to 623 K for higher 1,1,1-TCE conversion and VC yield. These cells were set co-axially to the laser light beam, and the light was irradiated in the opposite direction of gas flow.

The initial Cl₂/1,1-DCE ratio must be chosen carefully because the product distribution is sensitively affected by this ratio, as mentioned in sections 2.1 and 2.2. In the chlorination of 1,1-DCE, the conversion of substrate strongly depends on this ratio when the ratio of Cl₂/1,1-DCE is smaller than unity, whereas the selectivity for 1,1,1-TCE decreases owing to further chlorination of trichloroethanes when the ratio is larger than

unity. In the dehydrochlorination of 1,1,1-TCE, Cl_2 is an indispensable reagent for the initiation process of the chain reaction system, but has an optimum in its concentration, perhaps the smaller the amount the better, for attaining a high yield of VC.

Table 4 shows the experimental results. The product distribution in Run-1 seems to be almost the same as that in the photochlorination of 1,1-DCE in Table 1, suggesting that Cl_2 was entirely consumed in the course of chlorination in the first cell, and that no dehydrochlorination took place in the second cell.

Then an attempt to depress the conversion of Cl_2 in the first stage was made in Run-2 by setting several sheets of steel mesh between the first and the second cell (the intensity of irradiation to the first cell was reduced to about 1%), which caused an increase in the selectivity for VC as well as vinyl chloride. According to the literature, the rate constant of H-atom abstraction by Cl atom from 1,1-DCE is about 18 times that from 1,1,1-TCE at 623 K, which means that, if a small amount of 1,1-DCE exists in the second stage, Cl may react with 1,1-DCE in preference to 1,1,1-TCE. The experimental result suggests that there remained not only Cl_2 but also 1,1-DCE at the end of the first cell, followed by dehydrochlorination of 1,1-DCE forming vinyl chloride in the second cell.

As it turns out to be very difficult to obtain high yield for VC at any initial Cl_2 /1,1-DCE ratio, a small amount of Cl_2 , about 1/10 of the initial 1,1-DCE concentration, was added to the flowing gas upstream of the entrance of the second cell (Run-3). The initial Cl_2 /1,1-DCE ratio was chosen to be 1.1, which proved to be the minimum value for complete conversion of 1,1-DCE to 1,1,1-TCE in the first stage, and steel mesh was not used in this run. In this system, the selectivity for VC is very high compared to others, as shown in Table 4, suggesting that two factors seem necessary for attaining higher selectivity for VC in this process: complete consumption of 1,1-DCE in the first cell, and addition of Cl_2 before the second cell.

By making a combination of these two stages, the possibility of direct synthesis of VC from 1,1-DCE by irradiation of the flowing 1,1-DCE/ Cl_2 mixed gases was experimentally suggested, though further investigation to determine the optimum conditions seems to be necessary.

Conclusion

A new photochemical process for synthesizing VC from 1,1-DCE with excimer laser irradiation was proposed.

(1) In the laser-induced photochlorination, the 1,1,1-TCE/1,1,2-TCE ratio depends on reaction temperature, and a very high value of 20.8 was obtained at room

temperature. The dependence of 1,1-DCE conversion on Cl_2 /1,1-DCE ratio suggests that the overall stoichiometry of the reaction of 1,1-DCE and Cl_2 would be 1:1. Based on these experimental facts, a plausible reaction scheme was proposed and was supported by simulation works.

(2) In the laser-induced photodehydrochlorination, a small amount of Cl_2 addition promoted the formation of VC, and the yield of VC was strongly dependent on Cl_2 /1,1,1-TCE ratio and reaction temperature. From the experimental work and kinetic study, this reaction is thought to proceed through a chain mechanism.

(3) By connecting two stages in series, a new photochemical process for synthesizing VC from 1,1-DCE was proposed. In this system, two factors, the complete consumption of 1,1-DCE in the first stage and the addition of Cl_2 before the second stage, are important in attaining higher selectivity for VC.

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