

A Novel Laser-induced Synthesis of 1,1-Dichloroethylene from 1,1-Dichloroethane

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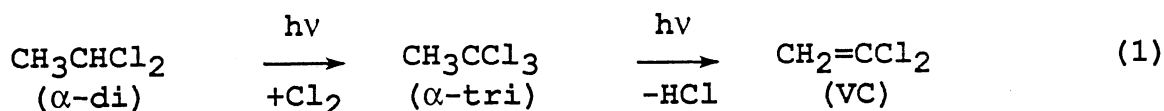
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The laser-induced photochlorination of 1,1-dichloroethane followed by its dehydrochlorination has been examined in a flow reactor under normal pressure at 25 - 200 °C, which has been proved to be a novel direct synthesis of vinylidene chloride.

The conventional process for synthesizing vinylidene chloride (VC) uses a two stage thermal reaction; the first stage is chlorination of vinyl chloride to 1,1,2-trichloroethane (β -tri) catalyzed by FeCl_3 , and the second stage is dehydrochlorination of β -tri by use of base catalysts, usually aq. $\text{Ca}(\text{OH})_2$. In this process, however, there remains some problems unsolved, particularly limited selectivity for VC due to random dehydrochlorination of β -tri.

Compared to the thermal reaction, the photolytic initiation has a great advantage in order to lower the activation energy for the overall reaction. Therefore, lower reaction temperatures can be adopted which are desirable to minimize side reactions. In fact, the photochlorination of 1,1-dichloroethane (α -di) to 1,1,1-trichloroethane (α -tri) using a krypton or argon ion laser was previously reported by Clark et al.¹⁾ in which the maximum value of the α : β ratio was as high as 9:1 at 120 °C.

The objective of this work is to investigate a new photochemical process for synthesizing VC from α -di with excimer laser, as shown in Eq. 1. In this paper, we investigated the optimum reaction conditions for attaining higher α -tri/ β -tri ratio in the laser-induced photochlorination of α -di which seems to be necessary for obtaining higher VC selectivity in the consecutive dehydrochlorination, and also the possibility of the photo-dehydrochlorination of α -tri with laser irradiation. If the irradiation with the same laser gives the reasonable yield and high selectivity for both reaction stages, a direct synthesis of VC from α -di might be realized for the flowing α -di/ Cl_2 mixed gases.

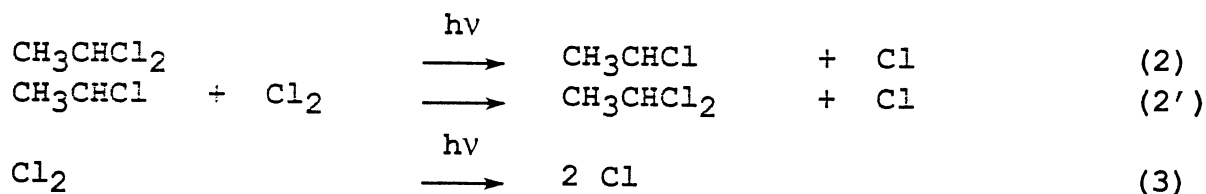


The experimental apparatus is shown in Fig.1. The reactant gas, consisted of the substrate, Cl_2 , and Ar

as a buffer gas, flows through the pyrex tube reactor (length 16 cm, inner diameter 2.7 cm) equipped with Suprasil quartz windows at both ends. The substrate vapor is introduced at its vapor pressure accompanied by the Ar buffer gas. Such excimer laser as KrF (248 nm) or XeF (351 nm) irradiates the flowing gas at 50 Hz, 70 mJ/pulse. The residence time of the gas is about 3 minutes, being calculated from the reactor volume and gas flow rate. All products are all analyzed by gas chromatography.

The temperature effect on the product distribution in the chlorination of 1,1-dichloroethane with KrF excimer laser irradiation is shown in Table 1. A very high selectivity for α -tri and high α/β ratio are achieved at 25 °C. The value of α/β ratio, 19.3, obtained under this reaction condition is much larger than the value of 9 reported by Clark.¹⁾ At the higher temperature, the selectivity for α -tri becomes lower, whereas that for tetrachloroethane is rather higher.

The mechanism of this reaction is considered as follows. The initiation step is photolysis of either α -di or Cl_2 to yield Cl, as shown below.



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

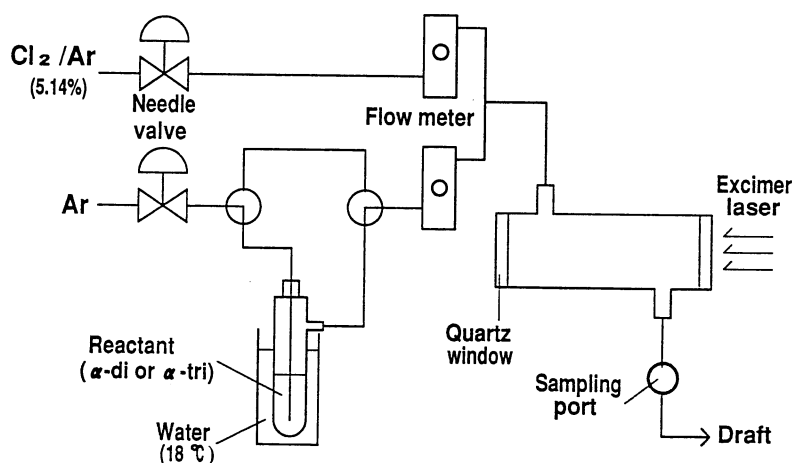
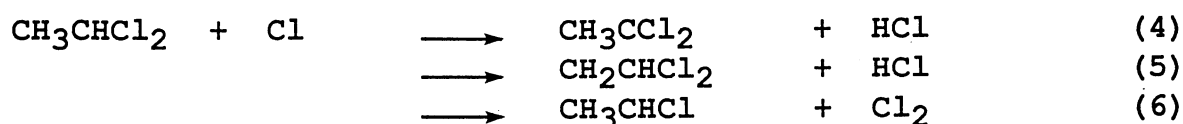


Fig. 1. Experimental apparatus.

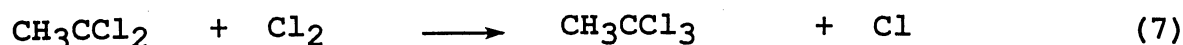
Table 1. Dependence of product distribution on reaction temperature in the photochlorination of 1,1-dichloroethane with KrF (248 nm) excimer laser irradiation a)

Reaction temperature / °C	25	200
Selectivity / %		
1,1,1-Trichloroethane (α -tri)	92.6	83.1
1,1,2-Trichloroethane (β -tri)	4.8	6.3
Tetrachloroethanes	1.2	7.8
Pentachloroethane	0.0	0.5
α -tri/ β -tri	19.3	13.2

a) Flow rate : 1,1-dichloroethane $1.3 \text{ cm}^3 \cdot \text{min}^{-1}$,
 Cl_2 $0.7 \text{ cm}^3 \cdot \text{min}^{-1}$, Ar $20 \text{ cm}^3 \cdot \text{min}^{-1}$.



Among them, Eq. 4 is considered to be the fastest at lower temperatures ($k_4 = 3.53 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K).²⁾ The radicals produced by Eqs. 4 - 6 are expected to react with Cl_2 . Equation 7, whose kinetic parameters have not been reported, is presumed not to be slow, so that chain reaction may proceed by way of Eqs. 4 and 7 to form α -tri dominantly. According to the literature,²⁾ the activation energy of Eq. 5 ($E_5=14.2$ kJ/mol) is larger than that of Eq. 4 ($E_4=8.0$ kJ/mol), which gives a good explanation to the experimental result that lower temperatures are favorable for the formation of α -tri.



In the photoreaction of α -tri in the presence of Cl_2 by KrF or XeF excimer laser irradiation, the product distribution, especially the selectivity for VC, was found to be dependent on the laser, reaction temperature, Cl_2 flow rate, and α -tri/ Cl_2 ratio, as will be followingly described in detail.

In the case of XeF excimer laser irradiation, higher selectivity for VC is obtained at higher temperature and lower Cl_2 flow rate. Otherwise chlorination reaction becomes a dominant one to produce chlorinated products, as shown in Table 2. The reaction mechanism is supposed as follows. In the XeF excimer laser irradiation, no reaction takes place in the absence of Cl_2 , which means that the reaction is initiated by photolysis of Cl_2 . Atomic chlorine, formed by photolysis of Cl_2 , abstracts hydrogen atom of α -tri to produce CH_2CCl_3 radical. Two competitive reaction paths may be possible for CH_2CCl_3 radicals formed by Eq. 8; one is the unimolecular decomposition forming VC (Eq. 9), and the other is the chlorination forming 1,1,1,2-tetrachloroethane (Eq. 10). Equation 9 may be concluded to possess larger activation energy than Eq. 10 according to the experimental result that higher temperature and lower Cl_2 flow rate are favorable for the higher selectivity for VC.

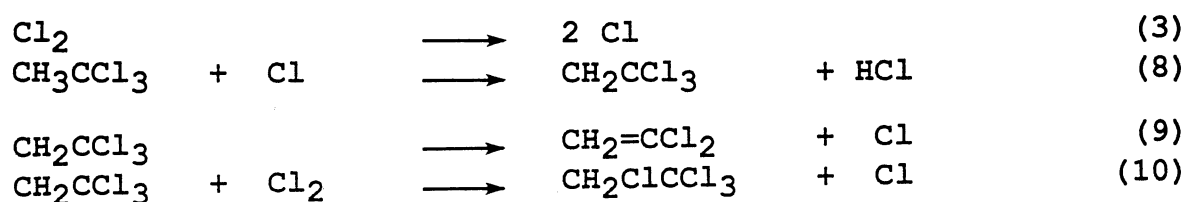


Figure 2 shows the effect of Cl_2 flow rate on product distribution in the case of KrF excimer laser irradiation. Even in the absence of Cl_2 , absorption of laser light by α -tri gave rise to produce VC directly, the selectivity for which is about 50%, together with other C_2 chlorinated olefins such as chloroethyne, 1,2-dichloroethylene and trichloroethylene, as well as C_1 chlorides such as methyl chloride and chloroform. A possible mechanism of producing VC is the direct formation of VC from α -tri with molecular elimination of HCl as suggested by the work of Reilly et al.,³⁾ who observed four-centered $\beta\beta$ photoelimination of HCl from vinyl chloride. Because of such a dissociative absorption of the substrates, KrF excimer laser seems to have a disadvantage as a light source for this dehydrochlorination reaction. In the presence of Cl_2 , the conversion of α -tri and the selec-

tivities for C_2 chlorinated paraffins increase, whereas the selectivity for VC monotonously decreases with increase of Cl_2 flow rate, which suggests that Cl_2 not only behaves as a photoabsorber to generate chlorine atoms but also enhances the chlorination reaction of the substrate to give ethane derivatives containing four or more Cl atoms.

In summary, the possibility of a novel direct synthesis of VC is revealed by irradiation of KrF or XeF excimer laser to α -di/ Cl_2 mixed gases considering that a very high α -tri/ β -tri ratio is achieved in the photochlorination of α -di and consecutive dehydrochlorination also occurs under the laser irradiation. Further discussion about the reaction mechanism is now under investigation in order to find out the optimum condition for the process.

The present work is partially supported by Kanegafuchi Chemical Industry Co. Ltd.

Table 2. Effect of reaction temperature and Cl_2 flow rate on product selectivity in the dehydrochlorination of 1,1,1-trichloroethane with XeF (351 nm) excimer laser irradiation a)

Reaction temperature / °C	25		200	
Cl_2 flow rate / $cm^3 \text{ min}^{-1}$	0.06	0.22	0.06	0.22
Conversion of 1,1,1-trichloroethane / %	0.9	1.6	1.0	3.2
Selectivity / %				
Vinylidene chloride	4.7	2.4	25.9	4.8
1,1,1,2-Tetrachloroethane	89.9	92.5	61.3	88.5
Pentachloroethane	5.3	5.1	0.0	2.7
Others	0.1	0.0	12.8	4.0

a) Flow rate of 1,1,1-trichloroethane: $1.0 \text{ cm}^3 \cdot \text{min}^{-1}$

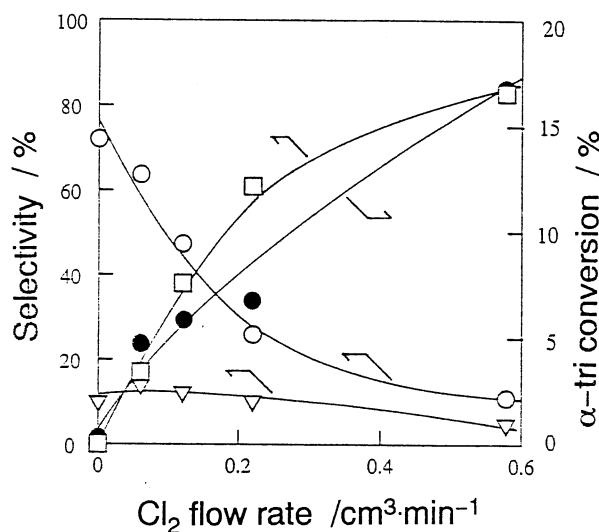


Fig. 2. Dependence of conversion and product distribution on Cl_2 flow rate in the photoreaction of 1,1,1-trichloroethane (●) with KrF excimer laser irradiation (total selectivities for C_2 chlorinated olefins(○), C_1 chlorides(▽) and C_2 chlorinated paraffins(□), respectively).

References

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(Received August 21, 1991)