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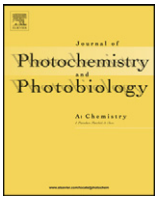

Laser photolysis of trans-dichloroethylene at 193 nm: Quantum yields of photoproducts

Kanekazu Seki*, Takanori Kobayashi, Kazukiyo Ebata

Division of Materials Science and Chemical Engineering, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

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ABSTRACT

The photodissociation of trans-dichloroethylene (trans-DCE) was studied using an ArF excimer laser at 193 nm. Acetylene, chloroacetylene and hydrogen chloride are observed as products, but the chlorine molecule is not observed. The yields are determined to be 0.47 ± 0.10 and 0.35 ± 0.05 for acetylene and chloroacetylene, respectively. On the basis of the reaction mechanism, the sum of the quantum yields of hydrogen chloride molecules ($\Phi = 0.35$) and chlorine atoms ($\Phi = 0.94$) dissociated from trans-DCE is estimated to be greater than unity. These results indicate that two chlorine atoms are successively dissociated from the parent molecule by the photolysis at 193 nm.

1. Introduction

Wijnen [1] reported that the products produced in the photolysis of cis-1,2-dichloroethylene (cis-DCE) are acetylene and chloroacetylene and suggested that chloroacetylene is formed via a molecular elimination of HCl. Since then molecular elimination of HCl and dissociation to form Cl atoms have been studied in the UV photolysis of chlorinated ethylene compounds [2–17]. Many chemical dynamic methods were applied to reveal the dissociation mechanism, especially to measure the translational, rotational, vibrational and electronic energy distribution of the dissociated fragments [6–16]. IR emission studies revealed the vibrational distribution of HCl [6,7]. Highly vibrationally excited vinyl radical and C_2H_2 were also detected. A study of time of flight (TOF) mass spectroscopy showed the translational energy distribution of HCl and Cl fragments at 193 nm photolysis [8]. Also Doppler spectroscopy [9–11] and two-dimensional ion imaging methods [12,16] were applied not only to the translational energy distribution but also to the electronic energy distribution at various excitation wavelengths. The HCl rotational distribution was measured by the resonance-enhanced multiphoton ionization (REMPI) method [11,13–15]. A theoretical treatment approach was also made [17].

In this paper we propose two kinds of Cl dissociation processes in the photolysis of trans-1,2-dichloroethylene (trans-DCE). Umemoto et al. [8] first reported that there are two kinds of Cl atoms with different translational energies based on TOF mass spectroscopy. They suggested that the direct crossing of the (π,π^*) state to the (n,σ^*) state produce the higher energy Cl atom, while the crossing from the lowest excited singlet, $S_1(\pi,\sigma^*)$, state to another lower (n,σ^*) state produces the lower energy Cl atom. Other studies [9–16] also propose this mechanism. However there is another possible process which produces two kinds of Cl atoms,

$$C_2H_2Cl_2 + h\nu \rightarrow C_2H_2Cl + Cl \rightarrow C_2H_2 + Cl + Cl,$$

where two Cl atoms dissociate successively. This process was not clearly mentioned in the previous studies [8–16]. We try to reinvestigate the reaction mechanism of trans-DCE photochemistry based on measuring of the absolute quantum yields of photoproducts. Using an excimer laser as a light source the products were analyzed. We have revealed the reaction mechanism of acetylene derivatives by this method [18–20]. This publication is the first in a series in which we hope to shed further light on the primary process occurring in the photolysis of cis-DCE, trans-DCE and 1,1-dichloroethylene (1,1-DCE).

2. Experimental

A 193 nm ArF excimer laser (MPB, PSX-100) was used as a light source. The quantum yield of products is based on the yield of CO (=0.95) from the 193 nm photolysis of acetone [21]. The photolysis procedure was described before [18]. In brief, the 193 nm laser beam was simultaneously directed to an acetone cell (10 cm path length) as a chemical actinometry and a sample cell (12 cm) using a beam splitter to determine the total quanta of incident light absorbed. Acetone pressures of 7 Torr or more absorbed 99.9% of the 193 nm light in the 12 cm path [18]. The amount of CO produced was obtained from the pressure in Torr (MKS Baratron 122A) and

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* Corresponding author. Tel.: +81 45 339 3947; fax: +81 45 339 3947.
E-mail address: kseki@ynu.ac.jp (K. Seki).

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the volume of the system including the cell and gauge. The CO gas was separated from other gases by a liquid nitrogen trap.

A few hundred laser shots were used to excite 3.5% or less of trans-DCE. The quantum yields of acetylene and chloroacetylene were found to decrease with an increase of exposure. Hence, trans-DCE excitation was limited to 3.5% or less. The laser fluence was always maintained at 0.5 mJ cm^{-2} or less to avoid multiple photon processes.

The quantum yield of products has been determined using a mass spectrometer (MKS, PPT-200EM). Mass spectrometric intensities of acetylene and chloroacetylene are calibrated using pure samples. The amount of photolysis products, acetylene and chloroacetylene, was measured from the relative intensity of the mass peak to that of an internal standard gas, krypton. A known amount of krypton was introduced into the reaction cell after the photolysis to avoid the quenching by krypton. A calibration chart for each compound was needed because the relative intensities of mass peaks were not proportional to the pressures of each compound. The amount of photoproduct was determined from the calibration chart. The detection limit of acetylene and chloroacetylene by mass analysis was about 0.2 mTorr. To separate the large amount of trans-DCE from the photoproducts, the sample cell was immersed into a cold trap (about −100 °C).

Commercial research-grade trans-DCE, acetylene and acetone were purified by bulb-to-bulb distillation at low temperatures. The amount of acetone in purified acetylene was less than 0.01%, since no peak at $m/e = 58$ was found. High-purity argon and krypton (99.9999%) were used without further purification. Chloroacetylene was prepared by Bashhold's method [22]. The purity was checked by IR and mass spectroscopy. Acetylene and chloroacetylene samples were used for intensity calibration. The UV absorption cross section of trans-DCE was measured in the 191–240 nm range by a Hitachi U-3210 spectrophotometer with a bandwidth of 0.5 or 1 nm using a quartz cell of 12.0 cm in length.

3. Results and discussion

We have detected acetylene, chloroacetylene and hydrogen chloride produced from the photolysis of trans-DCE excited by the ArF excimer laser at 193 nm. Acetylene and chloroacetylene could be quantitatively analyzed using the mass spectrometer. However hydrogen chloride rapidly adsorbed on the walls of the reaction cell, and it was difficult to determine the amounts in the cell. In our experiment chlorine molecule (Cl_2) was not detected. Umemoto et al. [8] and Sato et al. [23] also reported no Cl_2 signal in the photolysis of trans-DCE at 193 nm using TOF mass spectroscopy under molecular beam conditions. Ausubel and Wijnen [3] suggested that molecular chlorine is produced from the photolysis of trans-DCE in the range 200–240 nm. However they did not directly detect Cl_2, but they inferred Cl_2 as a counter part of acetylene. Moss et al. [6] reported an infrared emission peak at 1330 cm^{-1} attributed to acetylene, then suggested Cl_2 or two Cl atoms detached from trans-DCE photolysis at 193 nm. In these previous studies the process of two Cl atom detachment was not clearly mentioned, although Cl_2 was not directly detected. Absence of the Cl_2 molecule and the detection of acetylene strongly indicate that two Cl atoms are produced from trans-DCE photolysis at 193 nm, as described in the later section in detail.

Fig. 1 shows the dependence of the relative quantum yield of chloroacetylene formation on the % excitation of trans-DCE. The relative quantum yield is constant within the error limits when the excitation is 4% or less. It decreases as the excitation of trans-DCE increases. Since the decrease is due to the secondary reactions, all experiments to determine the quantum yield were performed at 3.5% excitation or less.

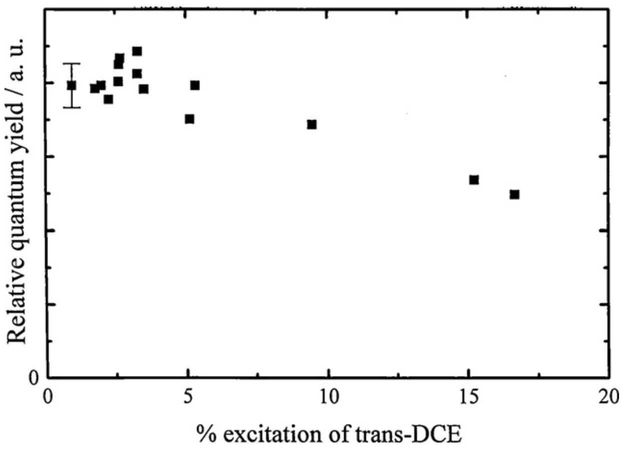

Fig. 1. Relative quantum yield of chloroacetylene from 1 Torr of trans-DCE at 193 nm as a function of % excitation of trans-DCE.

In order to determine quantum yield of products the absorption cross section of trans-DCE in the 190–230 nm region was measured as shown in Fig. 2. The cross section at 193 nm is $3.5 \pm 0.2 \times 10^{-17}$ cm^2 molec^{-1} (base e), which is in good agreement with former results [14]. No fine structure of trans-DCE is apparent as shown in Fig. 2. This broad band assigned to a (π,π^*) state indicates that the (π,π^*) state strongly couples with the dissociation channels. The cross section at 193 nm may not be exactly the same as that at the ArF laser line, because (1) the absorption cross section of trans-DCE near 193 nm changes drastically near this wavelength and (2) the ArF line has a half width (FWHM) of 0.8 nm and is modified by an absorption of oxygen in air. However the absorption cross section measured by the monochromator was used to determine the quantum yield, because the absorption of trans-DCE in the ArF laser line area is diffuse and the mismatch can be neglected. On the other hand we used acetone as the actinometer at the saturation condition for absorption.

The photolysis of trans-DCE was performed at various trans-DCE pressures. The quantum yields of acetylene, $\Phi(C_2H_2)$, and chloroacetylene formation from trans-DCE at 193 nm are shown in Fig. 3. The error is mainly due to the amounts of products estimated by the mass spectrometer. Acetylene and chloroacetylene are the main products of trans-DCE photolysis. $\Phi(C_2H_2)$ remains constant at 0.47 ± 0.10 in this pressure range. On the other hand the quantum yield of chloroacetylene, $\Phi(C_2HCl)$, decreases from 0.35 to 0.29, and 0.35 ± 0.05 is estimated at a low pressure limit. The decrease may be due to the quenching of the hot

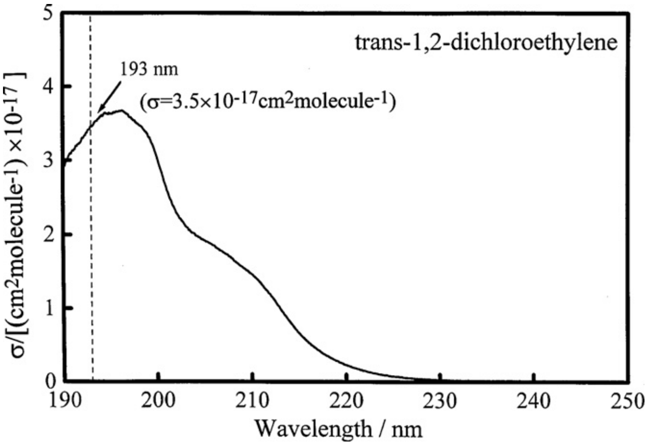

Fig. 2. Absorption cross section of trans-DCE in the 190–250 nm region.

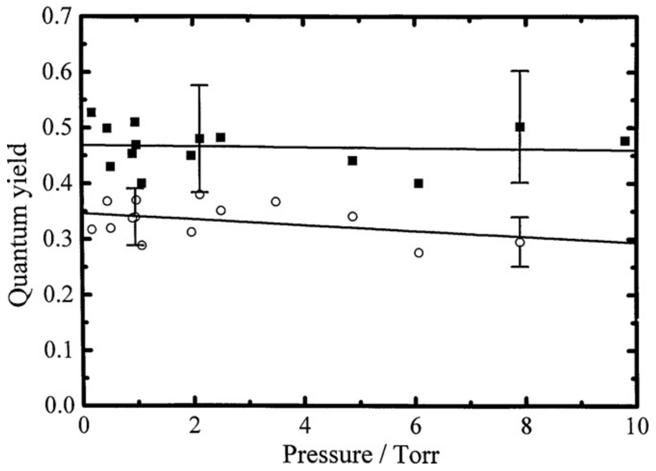

Fig. 3. Quantum yield of acetylene (■) and chloroacetylene (○) formation from the 193 nm laser photolysis of trans-DCE in the pressure range form 0.1 to 10 Torr. The lines are least squares fits. Error bar is mainly based on the measurements of amounts of products by the mass spectrometer.

ground state of trans-DCE which dissociate to HCl molecule and chloroacetylene.

We consider the primary process of the photolysis of trans-DCE, especially to produce Cl and HCl on the basis of the quantum yields of acetylene and chloroacetylene. The following processes are thermodynamically possible to produce acetylene from the primary photo-reaction process of trans-DCE.[1]

$$\text{trans-}C_2H_2Cl_2 + h\nu(193\,\text{nm}) \rightarrow C_2H_2 + 2Cl: \quad E_{\text{avl}} = 36.5\,\text{kcal mol}^{-1}, \tag{1}$$

$$\text{trans-}C_2H_2Cl_2 + h\nu(193\,\text{nm}) \rightarrow C_2H_2 + Cl_2: \quad E_{\text{avl}} = 94.7\,\text{kcal mol}^{-1}, \tag{2}$$

where E_{avl} is the total available energy. The Cl_2 molecule was not detected in our experiment. Process (2) suggested by Ausubel and Wijnen [3] is based on the results of the detection of acetylene but not on the direct detection of Cl_2. Umemoto et al. [8] reported no Cl_2 from trans-DCE photolysis using a TOF mass spectrometer, but their instrument had poor sensitivity for a heavy fragment because of the orthogonal detection angle of the molecular beam. More recently Sato et al. [23] and Hua et al. [16] also did not detect Cl_2 using other techniques with more sensitivity for the heavy fragment by the near collinear detection angle. Therefore we consider that process (2) can be neglected in the acetylene formation process. This conclusion also is supported by the following discussion about the quantum yield.

Furthermore, we consider that the primary photo-reaction processes for chloroacetylene (C_2HCl) are

$$\text{trans-}C_2H_2Cl_2 + h\nu(193\,\text{nm}) \rightarrow C_2HCl + HCl: \quad E_{\text{avl}} = 119\,\text{kcal mol}^{-1}, \tag{3}$$

$$\text{trans-}C_2H_2Cl_2 + h\nu(193\,\text{nm}) \rightarrow C_2HCl + H + Cl: \quad E_{\text{avl}} = 16\,\text{kcal mol}^{-1}. \tag{4}$$

The H atom dissociation yield for the photolysis of trans-DCE at 193 nm was reported, which was at least ten times less than that of Cl atom [10]. Therefore we can neglect process (4).

Table 1
Quantum yields of products from the photolysis of trans-DCE at 193 nm.

Product	Quantum yield
C_2H_2	0.47 ± 0.10[a]
C_2HCl	0.35 ± 0.05[a]
HCl	0.35 (=$\Phi(C_2HCl)$)[b]
Cl	0.94 (=$2\Phi(C_2H_2)$)[b]

[a] Obtained from direct measurements.
[b] Estimated from reaction mechanism.

The effects of the secondary reactions following the photo-reactions (1)–(4) on $\Phi(C_2H_2)$ and $\Phi(C_2HCl)$ will be discussed. Since reactive species are only Cl and H atoms after the photo-reactions, we have to consider the role of Cl and H in the secondary reactions. The major secondary reactions of Cl are following, and the reaction rates were reported at room temperature [27,28],

$$Cl + \text{trans-}C_2H_2Cl_2 \rightarrow C_2H_2Cl_3: \quad k_2 = 9.58 \times 10^{-11}\,\text{cm}^3\,\text{molec}^{-1}\,\text{s}^{-1}, \tag{5}$$

$$Cl + Cl + M(1\,\text{Torr}) \rightarrow Cl_2: \quad k_2 = 1.7 \times 10^{-15}\,\text{cm}^3\,\text{molec}^{-1}\,\text{s}^{-1}, \tag{6}$$

where k_2 means a second order reaction rate, M is a third body. These reaction rates indicate that the Cl atoms produced from the primary photo-reactions mainly react with trans-DCE, it is an insert reaction, and become more complex species like $C_2H_2Cl_3$. On the other hand the secondary reaction with H atoms is not affected to the quantum yields of acetylene and chloroacetylene because H atoms are minor products. Therefore we conclude that acetylene and chloroacetylene do not form from the secondary reactions.

Table 1 summarizes the quantum yields of the products from the photolysis of trans-DCE at 193 nm. The quantum yield of Cl atoms produced from the primary photo-reaction is estimated from the equation of $2\Phi(C_2H_2) = \Phi(Cl)$, because acetylene is mainly produced through reaction process (1). On the other hand the quantum yield of HCl is based on $\Phi(C_2HCl) = \Phi(HCl)$ from reaction (3). The previous study using a molecular beam technique [8] revealed that the nascent branching ratio, $\Phi(Cl)/\Phi(HCl)$, is 2.2 ± 0.4. This is in agreement with our estimated value of 2.7 ± 0.2. It is indicated that acetylene and chloroacetylene are produced from photolysis processes (1) and (3), respectively, but not from the secondary reactions. This result supports that no Cl_2 are observed from the photolysis because if Cl_2 is produced from process (2), the ratio ($\Phi(Cl)/\Phi(HCl)$) estimated from our results should be much larger.

These results require a reinterpretation of mechanism for trans-DCE photolysis. Beginning with the work of Umemoto et al. [8] many researchers have reported that the two kinds of Cl atoms with different translational energies are produced from the photolysis of trans-DCE at 193 nm and made exertions to explain the observation for two kinds of Cl atoms. Umemoto et al. [8] suggested that the direct crossing of the (π,π^*) state to the (n,σ^*) state produces the higher energy Cl atom, while the crossing of the S_1(π,σ^*) state to another lower (n,σ^*) state produces the lower energy Cl atom. Basically other studies also propose the same kind mechanism. Mo et al. [10] pointed out that another possible mechanism for producing lower energy Cl is a radiationless transition to the ground state followed by dissociation on this surface. However these reaction schemes cannot reveal the presence of acetylene as a primary photoproduct and they did not refer the acetylene formation except Sato's group.

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[1] Total available energies for all reactions were taken from Refs. [24–26].

We consider the mechanism for Cl detachment process using our experimental results, that is, acetylene formation is one of the main photochemical process ($\Phi(C_2H_2) = 0.47$) and no Cl_2 is observed. It is impossible to explain these results, if only one Cl atom is produced from one trans-DCE after photolysis and the counterpart:C_2H_2Cl does not dissociate into another Cl atom. Then we suggest the following scheme,

$$\text{trans-}C_2H_2Cl_2 + h\nu(193\,\text{nm}) \rightarrow C_2H_2Cl^{\#} + Cl : \quad E_{avl} = 59\,\text{kcal mol}^{-1}, \tag{7a}$$

$$C_2H_2Cl^{\#} \rightarrow C_2H_2 + Cl, \tag{7b}$$

$$\text{trans-}C_2H_2Cl_2 + h\nu(193\,\text{nm}) \rightarrow C_2H_2 + Cl + Cl : \quad E_{avl} = 36.5\,\text{kcal mol}^{-1}. \tag{8}$$

(7a) and (7b) are sequential dissociation processes and (8) is simultaneous. Sato et al. suggested that chlorinated vinyl radical ($C_2H_2Cl^{\#}$) produced by reaction (7a) is energetically possible to dissociate to $C_2H_2 + Cl$ at 193 nm photolysis [23]. Since total translational energy after (7a) reaction is 26 kcal mol^{-1} for high energy Cl atom [8], internal energy of $C_2H_2Cl^{\#}$ is 23.4 kcal mol^{-1} (calculation from 59.4 to 26) and larger than the ΔH (22.9 kcal mol^{-1}) of (7b) reaction [24,25]. Sato also evaluated the reaction rate constant: $1 \times 10^{13}\,s^{-1}$ using RRK calculation and suggested (7b) reaction has no barrier. The scheme for (7a) and (7b) sequential reactions can produce the acetylene and two kinds Cl atoms. On the other hand it is difficult to explain the presence of two kinds of Cl atoms produced from reaction (8).

Next we try to explain other studies using the sequential scheme. Suzuki et al. [12] reported the translational energy distributions of Cl atom produced from the photolysis of trans-DCE at 193, 210 and 235 nm using a two-dimensional ion imaging technique. The yields of the two different Cl energy channels in trans-DCE vary with the wavelength of the exciting light. At 193 nm the yield of the lower energy component (P_{low}) is comparable to that of higher energy (P_{high}). On the other hand at 235 nm P_{low} is about 4 times smaller than P_{high}. They explained these results by an avoided crossing between the (π,π^*) and repulsive states in the C=C twist coordinate. Now we can show a simple explanation for the Cl yields based on the sequential scheme. The wavelength dependence indicates that the second Cl detachment depends on the excess energy. That is, at 235 nm excitation the excess energy of C_2H_2Cl as a counterpart of the first Cl detachment is not enough to dissociate the second Cl atom completely.

In conclusion we have measured the absolute quantum yields of acetylene and chloroacetylene, which is 0.47 and 0.35, respectively, at 193 nm. Consideration of the reaction mechanism gives the quantum yields of Cl ($\Phi = 0.94$) and HCl ($\Phi = 0.35$). These results imply that two Cl atoms with different kinetic energies are successively dissociated from the photolysis of one trans-DCE molecule at 193 nm. We plan to measure the quantum yields for cis-DCE and 1,1-DCE at 193 nm photolysis.

Acknowledgement

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