

Continuous-wave CO₂ Laser-induced Chain Reaction of 1,2-Dichloroethane

Peihua Ma,* Julin Liu, Guancheng Chen, Minxiong Chu, Yan Jing and Bin Wu
Qinghai Institute of Saline Lakes, Chinese Academy of Sciences, Xining, Qinghai 810008,
People's Republic of China

The chain reaction of 1,2-dichloroethane induced by a CW CO₂ laser has been studied in the presence of SF₆ as a sensitizer. Vinyl chloride and hydrogen chloride are the main products. The photosensitized decomposition of 1,2-dichloroethane mainly depends on the irradiated laser frequency and is governed by the excitation of the vibrational mode and collisional energy transfer. Arrhenius plots show two distinct regimes, corresponding to the respective activation energies: 96.3 kJ mol⁻¹ for the low-temperature regime and 50.2 kJ mol⁻¹ for the high-temperature regime. The inhibiting and promoting effects of propene and chlorine, respectively, on the chain reaction are examined. The kinetics proposed for the chain reaction are in agreement with the observed data, and mechanisms for molecular excitation and intramolecular energy transfer have been discussed. By using an IR laser, active centres can be generated, and initiation and propagation of a chain reaction at lower temperatures than is possible thermally can be achieved. This may be a way to decrease the energy expenditure and reduce the number of by-products in the chain reaction.

The deposition of vibrational energy in a molecule *via* the absorption of infrared photons can drastically affect chemical reactions involving the molecule. The gas-phase reactions induced by a CW CO₂ laser exhibit thermal reaction characteristics and proceed in quasi-steady state. When a CW CO₂ laser is used to induce reaction, a wide range of effective temperatures is easily created by controlling the absorption of infrared photons. Meanwhile, the laser heating of gaseous reactants can be confined within a certain zone of reactor and the wall effect of the reaction can be significantly reduced. These features are very favourable for the study of gas-phase reactions and several studies on the kinetics of gas-phase pyrolysis powered by a CW CO₂ laser have been reported.^{1–6}

Pyrolysis and isomerization driven by a CW CO₂ laser generally show low quantum yields of products owing to strong collisional deactivation between molecules. However, some features of lasers, such as the controllability of irradiated space and duration probably play important roles in chain reactions. Generating active centres by laser-induced reaction can initiate the propagation of a chain, and as a result the quantum yield of products can be enhanced. Moreover, the chain propagation and termination reactions generally require low activation energy and therefore can be made to proceed at a lower temperature. In this way the energy expenditure and the formation of by-products in the chain reaction can be reduced.

The pyrolysis of 1,2-dichloroethane produces vinyl chloride, which is of vital importance in the chemical industry. The pyrolysis proceeds in a chain mechanism, where the rupture of the highly endothermic C–Cl bond produces Cl active centres, followed by chain propagation involving hydrogen abstraction from the substance by Cl atoms and by the subsequent unimolecular decomposition of 1,2-dichloroethyl radicals.^{7,8} The chain initiation and propagation can be affected by inhibitor, promoter and surface effects.^{9,10} The UV photolysis of 1,2-dichloroethane using a xenon lamp also proceeds through the chain reaction mechanism.¹¹ In recent years, Wolfrum and Schneider^{12,13} and Holbrook and co-workers¹⁴ have observed a high quantum yield of 10⁴ in the UV photolysis of 1,2-dichloroethane by a rare-gas halide laser.

At present, the CW CO₂ laser has a high reliability in

operation and its operating cost is much cheaper than that of a rare-gas halide laser. The CH₂ rocking vibration band of the *gauche* 1,2-dichloroethane molecule matches with the P branch of the 00⁰1–10⁰ transition of the CO₂ laser.¹⁵ Unfortunately, the band shows only a weak absorption coefficient of 2 × 10⁻⁴ Torr⁻¹ cm⁻¹.¹⁶ 1,2-Dichloroethane in the absence of sensitizer cannot be decomposed by CO₂ laser radiation at an intensity of 200 W cm⁻². Pola and Kubat^{17,18} and Holbrook and Oldershaw¹⁹ observed the CW CO₂ laser-induced decomposition of 1,2-dichloroethane in the presence of SF₆. We have studied the CW CO₂ laser-induced chain reaction of 1,2-dichloroethane in the CH₂ClCH₂Cl–SF₆ mixture and the results are reported here. The difference in absorption coefficients between SF₆ and 1,2-dichloroethane at the 10.6 μm band of the CO₂ laser has been determined to be 10²–10³. Both photosensitizer and reactant molecules are excited by the resonant absorption of laser radiation. The near-resonant V–V energy transfer in the collisions between SF₆ and CH₂ClCH₂Cl molecules causes a climbing of the low vibrational levels occupied by 1,2-dichloroethane molecules. The 1,2-dichloroethane molecules excited into the quasi-continuum regime of their vibrational levels may absorb more infrared photons, thus leading to the rupture of the C–Cl bond. In the present work, the effect of laser frequency, laser power and added chain inhibitor and promoter on the chain reaction is investigated and a mechanism consistent with observed results is proposed.

Experimental

1,2-Dichloroethane (>99.0%) was purchased from Shanghai Chemical Co., SF₆ (99.99%) and Cl₂ (99.9%) were from Wuxi Specific Gas Co. and propene was from Wako Chemical Co. The chemicals were used directly without further purification. A line-tunable CW CO₂ laser was employed as irradiation source in these studies. The laser operated with a single-line output of 2–7 W and the spot size of the laser was 1.7 mm. For all experiments the laser beam was used unfocused.

The chain reaction of 1,2-dichloroethane in the presence of SF₆ was studied by irradiating a cylindrical glass reactor of length 12 cm and diameter 17 mm. The cell was equipped with two pairs of criss-cross NaCl windows. Among them a

pair was used for monitoring infrared absorption. The variations in the concentrations of reactants and products were instantaneously monitored, using an IR spectrometer (Specord 75, Carl Zeiss), at 1238 cm^{-1} for 1,2-dichloroethane and 1620 cm^{-1} for vinyl chloride, respectively. The initial partial pressures of 1,2-dichloroethane and SF_6 were 40 and 8 mbar, respectively, in all experiments including the chlorine-promoted and propene-inhibited runs. After the reactions, analyses of the products and reactants were carried out using a GC-MS system which combined a gas chromatograph (GC) (Shimadzu GC-9AM) with a mass spectrometer (MS) (Riber SQ-156).

The rates of product formation are obtained by observing the variations of the characteristic absorption bands of the products. The maximum rate constants are derived from the examined rates according to the procedure reported elsewhere.⁵ Only initial rates are used for data. The maximum temperatures are calculated from the heat-conduction equation, which uses the laser energies absorbed by photosensitizers and reactants together with their thermal conductivities.⁵ The thermal conductivities of SF_6 and 1,2-dichloroethane at 300 K are 1.3 and $0.85\text{ mW cm}^{-1}\text{ K}^{-1}$, respectively.^{20,21} The thermal conductivities of the binary mixtures are calculated in terms of the Ribblett approximate formula.²²

Results and Discussion

Rate Constants at Different Laser Frequencies

When neat 1,2-dichloroethane was exposed to the unfocused CW CO_2 laser radiation at an intensity of about 250 W cm^{-2} , we did not observe the decomposition of 1,2-dichloroethane at any of the frequencies of the CO_2 laser. The chain reaction could be generated by adding SF_6 to the cell as a photosensitizer, while SF_6 remained unreacted in all experiments. The products detected were vinyl chloride, hydrogen chloride and a trace of acetylene. The ratio of vinyl chloride to acetylene remains at 99.4 : 1, until the conversion fraction of 1,2-dichloroethane reaches 92%. Fig. 1 shows Arrhenius plots of the rate constant, k , for the formation of vinyl chloride vs. the reciprocal maximum translational temperature, T^{-1} . The data indicate two linearly dependent temperature regimes. In both temperature regimes the same products were detected but the average activation energies determined are different. At the low-temperature regime, the production of vinyl chloride is characterized by an average activation energy, E_a , of 96.3 kJ mol^{-1} , with an estimated net error of $\pm 4.0\text{ kJ mol}^{-1}$. The data at higher temperatures show an E_a of $50.2 \pm 1.0\text{ kJ mol}^{-1}$.

The data in Fig. 1 also demonstrate the effect of laser frequency on the rate constant for the production of vinyl chloride. At fixed translational temperature, the irradiation at relatively low laser frequency increases the magnitude of the rate constant, k , except that the reactivity at 934.9 cm^{-1} is slightly higher than that at 933.0 cm^{-1} , while the activation energies are essentially unaffected by changes in the frequencies of the irradiating laser.

Table 1 presents the absorption coefficients of SF_6 and 1,2-dichloroethane at the P branch of the $10.6\text{ }\mu\text{m}$ band of the CO_2 laser, together with the reaction rates for the production of vinyl chloride at these frequencies. The rates listed in Table 1 were obtained at an incident laser power of 5.5 W. The data in Table 1 indicate that the reaction rate depends on the laser frequency differently in two distinct regions: the red frequency region, $944.21\text{--}932.96\text{ cm}^{-1}$, and the blue frequency region, $952.89\text{--}944.21\text{ cm}^{-1}$. An abrupt turn in the reaction

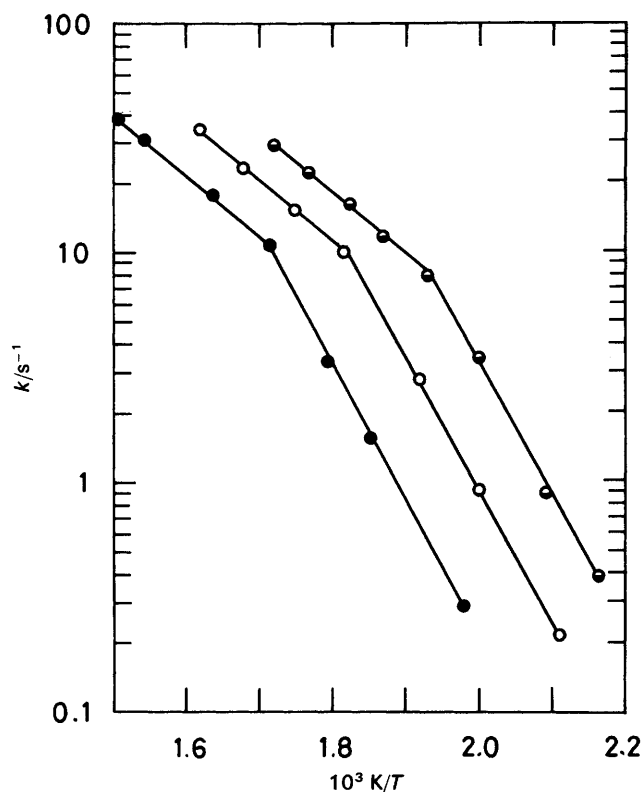


Fig. 1 Rate constant, k , for $\text{C}_2\text{H}_3\text{Cl}$ production vs. reciprocal translational temperature, $1/T$, at laser frequencies (○) 932.96 , (○) 934.90 and (●) 936.80 cm^{-1}

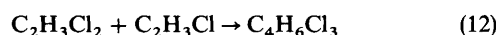
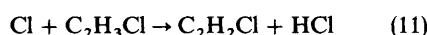
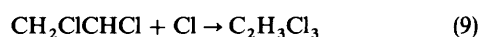
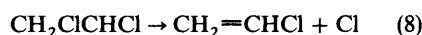
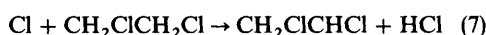
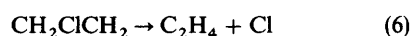
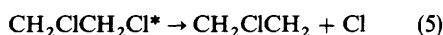
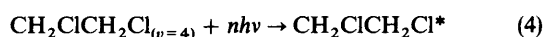
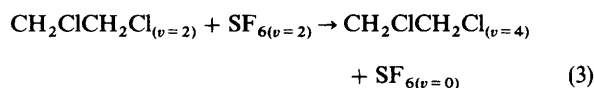
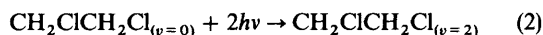
rates occurs at 944.2 cm^{-1} . In the red region, the chain reactions of 1,2-dichloroethane proceeded at rapid rates, but, in contrast, irradiating in the blue region produced only vinyl chloride at a very low rate; no products could be detected even at laser frequencies of 951.20 and 952.89 cm^{-1} . To the blue of the 10P branch, however, SF_6 shows the strongest absorption, and as a result, the translational temperatures at the entrance window should be higher than those under irradiation to the red. The strong absorptivity must correspond to a short absorption path and can affect the total rate of chain reaction. However, when a laser frequency corresponding to a weaker absorptivity, for example 951.20 cm^{-1} where the absorption coefficient is the same as at 940.56 cm^{-1} , was used for the irradiation, the rate of the chain reaction was very slow.

Table 1 Rates and absorption coefficients at different laser frequencies

CO ₂ laser frequency /cm ⁻¹	absorption coefficient /cm ⁻¹ Torr ⁻¹		rate /mol dm ⁻³ s ⁻¹
	SF ₆	1,2-dichloroethane	
933.00	0.028	1.6×10^{-4}	2.34×10^{-5}
934.92	0.027	2.0×10^{-4}	2.72×10^{-5}
936.83	0.049	2.4×10^{-4}	1.26×10^{-5}
940.56	0.24	2.7×10^{-4}	1.09×10^{-5}
944.21	0.53	2.5×10^{-4}	3.14×10^{-6}
945.99	0.60	2.1×10^{-4}	8.78×10^{-7}
947.75	0.85	2.2×10^{-4}	1.37×10^{-7}
949.49	0.43	2.1×10^{-4}	1.23×10^{-7}
951.20	0.25	2.7×10^{-4}	1.14×10^{-7}
952.89	0.014	2.9×10^{-4}	3.60×10^{-8}

Reaction Scheme

In these experiments the ratio of 1,2-dichloroethane to SF₆ was generally taken as 5 : 1, but the absorption coefficients of SF₆ are much higher than those of 1,2-dichloroethane by a factor of 10²–10³. The incident laser power is absorbed mainly by SF₆ molecules if the average photon absorption rate per molecule is calculated in terms of the expression $\alpha I/n\varepsilon$, where α is the optical absorption coefficient, I is the beam intensity, n is the molecular density and ε is the photon energy. The effective translational temperature in the irradiated zone depends mainly on the density of the SF₆ molecules. Considering the translational energy exchange occurring in molecular collisions, the translational temperatures at the irradiated zone near the entrance window at a constant SF₆ partial pressure of 8 mbar are estimated to be 450–650 K. These temperatures are 200 °C lower than that in the thermal pyrolysis of 1,2-dichloroethane, but the rates of the chain reactions at such low translational temperatures are determined to be much higher than in the thermal pyrolysis. So, it is conceivable that there is a reaction mechanism different from that observed in the homogeneous pyrolysis of 1,2-dichloroethane. In the present infrared laser-initiated reaction the collisional V–V energy transfer and the following internal excitation must dominate the initial dissociation of 1,2-dichloroethane, producing Cl atoms. The chain propagation and termination are believed to be similar to those in the homogeneous pyrolysis. The reaction mechanism for the CO₂ laser photosensitized chain reaction of 1,2-dichloroethane can be considered as



Excitation Process

In the proposed scheme for the excitation of 1,2-dichloroethane, the ν_3 vibrational mode of SF₆ molecule and the ν_7 band of *gauche* 1,2-dichloroethane are excited by the resonant absorption of CO₂ laser photons. The collisional V–V energy transfer between SF₆ and 1,2-dichloroethane molecules excited into the lower vibrational states may make 1,2-dichloroethane molecules occupy higher vibrationally excited states, and the consequent radiative pumping results in the high excitation and dissociation of the molecules. We have calculated the vibrational-state densities of 1,2-dichloro-

ethane, according to the Whitten–Rabinovich approximation.²³ The state densities of *gauche* 1,2-dichloroethane at $\nu_7 = 3, 4$ and 5 reach 10, 40 and 150 cm⁻¹, respectively. This means that the target molecule excited at $\nu_7 = 4$ or 5 has entered its ‘quasi-continuum’ regime, where the spectral dependence for excitation is narrow and the further radiative pumping depends mainly on the fluence, the energy per unit cross-sectional area of the beam, rather than the radiation intensity.^{24,25} The intensity effect, however, must clearly be important in both driving the molecule through the rate-determining discrete-level regime and affecting the lifetime of the dissociating species in the quasi-continuum regime. We consider that at higher laser fluence, both 1,2-dichloroethane and SF₆ absorb infrared photons at a high transition rate and the 1,2-dichloroethane molecule excited to $\nu_7 = 4$ by intramolecular quantum exchange may be pumped further into its dissociation regime by multiple-photon absorption. In this case, the initial decomposition rate of the highly excited 1,2-dichloroethane molecule should depend on the absorption rate of photons and the rate of vibrational quantum exchange.

It is plausible that the climbing of vibrational levels to $\nu_7 = 4$ for the 1,2-dichloroethane molecule is mainly governed by the $\nu_3 = 1$ to $\nu_3 = 2$ transition probability of the SF₆ molecule and, in turn, the probability of intermolecular vibrational energy transfer. The energy difference E_{21} ($=E_2 - E_1$) of the ν_3 mode of the SF₆ molecule is 5 cm⁻¹ smaller than E_{10} ($=E_1 - E_0$) owing to the anharmonicity. In the present experiments, an obvious chain reaction did not occur under irradiation both at the centre of the ν_3 band of SF₆ and at the ν_7 band of 1,2-dichloroethane, and a >5 cm⁻¹ ‘red shift’ of the irradiated laser frequency against the ν_3 centre of the SF₆ molecule could significantly enhance the rate of the chain reaction. Kitazima and Iwasawa have investigated the transition from $\nu_3 = 1$ to $\nu_3 = 2$ and relaxation process in SF₆ by using two tunable pulse CO₂ lasers.²⁶ The probe spectra demonstrate that at an excited intensity of 100 W cm⁻² and laser frequencies of 940.6–933.0 cm⁻¹, the absorption coefficients of SF₆ are higher than its linear absorption coefficients and at these irradiated laser frequencies the SF₆ molecule is easily pumped from $\nu_3 = 0$ to $\nu_3 = 2$ by an ‘induced absorption’. The induced absorption reaches a maximum at 934.9 cm⁻¹, which is well in accord with the rate constants we examined at different laser frequencies, as shown in Fig. 1.

Kinetics

The kinetics data shown in Fig. 1 indicate two temperature regimes corresponding to the following activation energies: 96.3 kJ mol⁻¹ for lower temperatures and 50.2 kJ mol⁻¹ for high temperatures. The difference in activation energies should be attributed to different reaction mechanisms. The rate equations for the formation of vinyl chloride can be deduced from the mechanism proposed above. We characterize the elementary reactions in the above-mentioned reaction scheme with the rate constants k_i and activation energies $E_{a,i}$ except for reaction (5). The rate constants for these elementary reactions obtained from the literature are listed in Table 2. The initial photodecomposed probability of 1,2-dichloroethane for reaction (5) is defined by $P_{(I)}$, which depends on the irradiated frequency, fluence and the pressure of sensitizer. For brevity we represent the concentrations of some species as follows: $A = [\text{C}_2\text{H}_4\text{Cl}_2]$, $B = [\text{C}_2\text{H}_3\text{Cl}]$, $X = [\text{C}_2\text{H}_3\text{Cl}_2]$, $Y = [\text{Cl}]$ and $Z = [\text{C}_2\text{H}_4\text{Cl}]$. By using the steady-state approximation, the radical concentrations X , Y and Z are constant in time and the rate equations for the

Table 2 Rate coefficients for the chain reaction of 1,2-dichloroethane

reaction	$\log(A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ or $\log(A/\text{s}^{-1})$	$E_a/\text{kJ mol}^{-1}$	ref.
7	10.8	13.0	27
8	13.9	96.3 ± 4	8, 9, 13
9	11.3	0	28
10	9.9	1.0	29
11	10.4	5.8	30
12	8.2	32.0	31

radical concentrations X , Y and Z are, respectively,

$$k_7 AY - k_8 X - k_9 XY - 2k_{10} X^2 - k_{12} BX = 0 \quad (\text{I})$$

$$P_{(I)}A + k_6 Z - k_7 AY + k_8 X - k_9 XY - k_{11} BY = 0 \quad (\text{II})$$

$$P_{(I)}A - k_6 Z = 0 \quad (\text{III})$$

Algebraic elimination of Z and combination of equations results in two equations involving X and Y :

$$2P_{(I)}A + 2k_8 X + 2k_{10} X^2 + k_{12} BX = 2k_7 AY + k_{11} BY \quad (\text{IV})$$

$$2P_{(I)}A - 2k_{10} X^2 - k_{12} BX = 2k_9 XY + k_{11} BY \quad (\text{V})$$

Considering that B is much smaller than A at the initial stage of reaction, $k_7 A \gg k_{11} B$, $k_{10} X \gg k_{12} B$, $k_9 X \gg k_{11} B$ and $k_8 \gg k_{10} X$, the above equations can be significantly simplified to

$$P_{(I)}A + k_8 X = k_7 AY \quad (\text{VI})$$

$$P_{(I)}A - k_{10} X^2 = k_9 XY \quad (\text{VII})$$

From eqn. (VI) and (VII) we obtain an expression for the concentration of CH_2ClCHCl radical

$$X = [P_{(I)}/k_{10}(k_8 k_9/k_7 k_{10} + A)]^{1/2} A \quad (\text{VIII})$$

The formation rate of vinyl chloride is given by

$$d[\text{C}_2\text{H}_3\text{Cl}]/dt = k_8 X - k_{11} BY - k_{12} BX \quad (\text{IX})$$

Since only traces of by-products were detected in the present experiments, the formation rate of vinyl chloride can be expressed by

$$d[\text{C}_2\text{H}_3\text{Cl}]/dt = k_8 X \quad (\text{X})$$

The initial concentration of 1,2-dichloroethane used in the present experiments was generally $1.8 \times 10^{-3} \text{ mol dm}^{-3}$. For the high-temperature regime, the aforementioned ratio $k_8 k_9/k_7 k_{10}$, for example at 650 K, is 0.3 mol dm^{-3} , so the formation rate of vinyl chloride is simplified to

$$d[\text{C}_2\text{H}_3\text{Cl}]/dt = (P_{(I)} k_7 k_8/k_9)^{1/2} [\text{C}_2\text{H}_4\text{Cl}_2] \quad (\text{XI})$$

The rate expression for the formation of vinyl chloride at the high-temperature regime is similar to the form obtained in homogeneous pyrolysis, except that the decomposition probability $P_{(I)}$ is defined for the initial photo-dissociation step, reaction (5). In the thermal decomposition, the activation energy for the formation of vinyl chloride has been determined to be $196.7 \text{ kJ mol}^{-1}$ and is greatly affected by reaction conditions such as the surface and the mobility of the gas.^{8,9} However, in the present infrared laser pyrolysis the activation energy determined at high laser intensities is only 50.2 kJ mol^{-1} , which is consistent with the activation energy

obtained from eqn. (XI), $1/2(E_7 + E_8 - E_9)$. This value is also the same as that obtained from UV photolysis.¹¹

On the other hand, at the low-temperature regime, the value of $k_8 k_9/k_7 k_{10}$ is of the order of $10^{-5} \text{ mol dm}^{-3}$ and can be neglected in comparison with the concentration of 1,2-dichloroethane; eqn. (VIII) then becomes

$$d[\text{C}_2\text{H}_3\text{Cl}]/dt = k_8 (P_{(I)}/k_{10})^{1/2} [\text{C}_2\text{H}_4\text{Cl}_2]^{1/2} \quad (\text{XII})$$

The activation energy for the production of vinyl chloride at the low-temperature regime is determined to be 96.3 kJ mol^{-1} from the data shown in Fig. 1. The activation energy determined is also in accord with the value calculated from eqn. (XII), if E_8 takes a corresponding activation energy of $92\text{--}100 \text{ kJ mol}^{-1}$.^{8,9,13}

Inhibition of Chain by Propene

The photosensitized chain reaction induced by the CW CO_2 laser can be inhibited by propene and the inhibited process was examined by changing the concentration of added propene for the laser frequency 936.80 cm^{-1} at an intensity of 250 W cm^{-2} . The results are shown in Fig. 2 and 3. As can be seen from Fig. 2, the propene-inhibited runs showed slow initial rates and the rates gradually increased with reaction

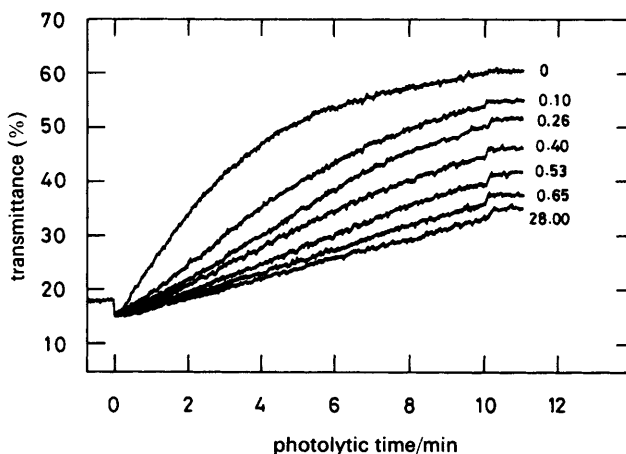


Fig. 2 Variation of reaction rate with added propene (pressures in mbar given on the curve) during laser irradiation at the laser frequency 936.8 cm^{-1} . The curves were obtained at an incident laser power of 5.6 W .

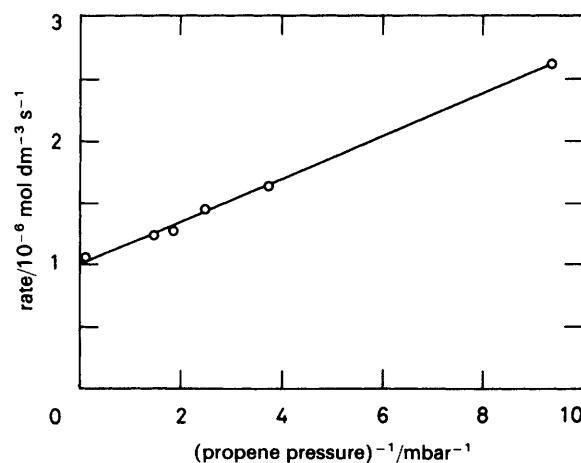


Fig. 3 Effect of added propene on reaction rate for the decomposition of 1,2-dichloroethane. The experimental conditions are the same as in Fig. 2.

time. This indicates that propene was gradually consumed in the reaction.

The photosensitized chain reaction in the presence of propene can be quantitatively understood, if the termination step, reaction (13), is included in the mechanism from reactions (1) to (12).



The steady-state equations based upon reactions (5)–(12) and (13) are obtained in the manner used above,

$$P_{(I)}A + k_8X + 1/2k_{13}[\text{C}_3\text{H}_6]X = k_7AY \quad (\text{XIII})$$

$$P_{(I)}A - k_{10}X^2 - 1/2k_{13}[\text{C}_3\text{H}_6]X = k_9XY \quad (\text{XIV})$$

Further, we assume that $k_8 \gg k_{13}[\text{C}_3\text{H}_6]$, $k_8k_9 \gg k_7k_{10}A$ and $k_7k_{13}[\text{C}_3\text{H}_6] \gg k_9P_{(I)}$. The assumptions are consistent with the kinetics data listed in Table 2 and the concentrations of the species used in the experiments. The equations can be amalgamated to

$$k_8k_9X^2 + 1/2k_7k_{13}[\text{C}_3\text{H}_6]AX - k_7P_{(I)}A^2 = 0 \quad (\text{XV})$$

By solving the equation, the concentration of dichloroethyl is given by

$$[\text{C}_2\text{H}_3\text{Cl}_2] = \{-k_7k_{13}[\text{C}_3\text{H}_6]A + (k_7^2k_{13}^2[\text{C}_3\text{H}_6]^2 + 16k_7k_8k_9P_{(I)}A^2)^{1/2}\}/4k_8k_9 \quad (\text{XVI})$$

This may be simplified to $[\text{C}_2\text{H}_3\text{Cl}_2] = 2P_{(I)}A/k_{13}[\text{C}_3\text{H}_6]$ from consideration of the overwhelming magnitude of $k_7^2k_{13}^2[\text{C}_3\text{H}_6]^2$ under the root sign. Hence,

$$d[\text{C}_2\text{H}_3\text{Cl}]/dt = P_{(I)}k_7[\text{C}_2\text{H}_4\text{Cl}_2]/k_{13}[\text{C}_3\text{H}_6] \quad (\text{XVII})$$

Expression (XVI) gives an inverse dependence of the rate of $\text{C}_2\text{H}_3\text{Cl}$ production on the pressure of added propene, which is confirmed by the experimental data shown in Fig. 3.

Chlorine-promoted Reaction

It was established by previous studies that the chain reaction of 1,2-dichloroethane in the presence of chlorine can be initiated at lower temperatures.^{30,32} In the present experiments the 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ - SF_6 mixtures containing chlorine were irradiated at 946.0 cm^{-1} , where SF_6 shows the strongest absorption but the reaction in the absence of chlorine showed very low quantum yield. The SF_6 -sensitized decomposition was significantly accelerated by adding chlorine. Fig. 4 presents the relationship between rate and the pressure of chlorine.

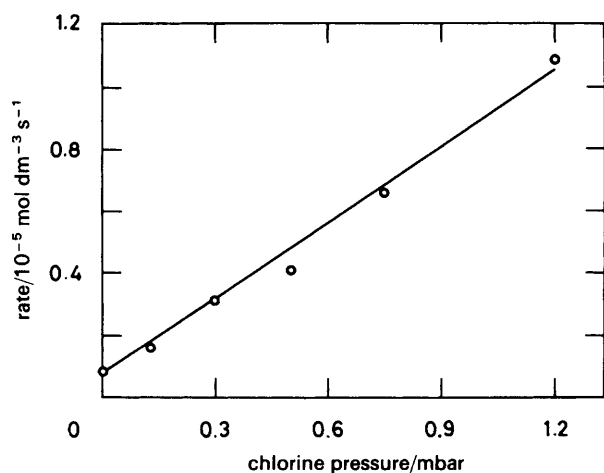


Fig. 4 Effect of added chlorine on reaction rate at the laser frequency 945.68 cm^{-1} and an incident power of 5.6 W

The chlorine-promoted runs are of first order in chlorine. A change in irradiation intensity did not obviously affect the rates, for instance, a change in the irradiated intensity from 250 to 170 W cm^{-2} just decreases the reaction rate from 3.28×10^{-6} to $2.9 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$.

For the photosensitized chain reaction in the presence of chlorine, we suggest that the chain generation should be attributed mainly to chlorine atoms produced from chemisorbed chlorine molecules.



If the reaction mechanism includes reactions (7)–(9) and (14), the rate obtained by the steady-state method is given by eqn. (XVIII)

$$d[\text{C}_2\text{H}_3\text{Cl}]/dt = k_7k_{14}k_9^{-1}[\text{Cl}_2][\text{C}_2\text{H}_4\text{Cl}_2] \quad (18)$$

Thus, in agreement with the results shown in Fig. 4, eqn. (XVIII) predicts that the chlorine-promoted reactions are first order in chlorine, and the fact that the change of laser intensity did not seriously affect the rates suggests that the activation energy for the chlorine-promoted reactions is small.

In summary, we have demonstrated that the chain reaction of 1,2-dichloroethane can be initiated by IR laser radiation in the presence of photosensitizer SF_6 . Vinyl chloride with high purity was produced from the chain reaction with high conversion yield. The generation of Cl active centres from the substance depends on the excitation of low vibrational levels and is followed by intramolecular energy transfer. The dependence of reaction rate on temperature reveals two linearly dependent temperature regimes. In each temperature regime, the corresponding activation energies have been determined. The kinetics and mechanism for the chain reaction have been studied by examination of the rates of production of vinyl chloride. The dependence of the chain reaction on added propene and chlorine has been investigated. These studies have revealed some typical behaviour of CW CO_2 laser-induced chain reactions in bimolecular systems.

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