

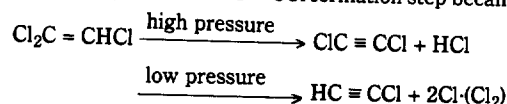
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Isotope Selectivity in the CO₂ Laser Induced Decomposition of Trichloroethylene-H and Trichloroethylene-D

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The infrared multiphoton decomposition of trichloroethylene-H (TCE-H) and trichloroethylene-D (TCE-D) was studied by using the high power CO₂ laser. The pressure dependence of TCE-H decomposition showed that the HCl elimination channel to form ClC ≡ CCl was the major step at high pressures, while the HC ≡ CCl formation step became important at low pressures.



The IRMPD of TCE-H and TCE-D mixtures with 10P(20) laser line showed that optimum conditions of large isotope selectivity were the low system pressures and high laser powers. The experimentally observed dependence of the branching ratios on the pressure and laser fluence, and the isotope selectivity coefficients were quantitatively explained by using the modified energy grained master equations (EGME) model.

Introduction

In recent years the process of unimolecular dissociation by intense infrared radiation has been the subject of extensive studies. The initial impetus came from the very obvious practicality of *selective* multiphoton decomposition¹. It is well understood that the IR selective nature can be effectively used in the isotope separation², and selective dissociation-elimination of unwanted impurities³. There have been many theoretical⁴ and experimental papers dealing with selective multiphoton decomposition of various isotopes.

There are several approaches to LIS (Laser Isotope Separation), all of which rely on one common phenomena, the so-called "isotope shift", which theoretically makes possible the selective excitation. In practice, the separation is seldom achieved because of thermal collisions between molecules, because of the Doppler effect on the laser wavelengths, and because of anharmonicity, etc. When the absorption wavelengths of two isotopes are far apart, it is relatively easy to find and tune a laser to resonate at the absorption wavelength of one isotope, thus pumping energy into the selected isotope leaving no effect on unwanted isotope. For laser excitation

to remain selective, there must be a minimization of collisional exchange of vibrational energy between the excited and unexcited isotope species.

During the last one and a half decade, many works on deuterium isotope separation have been reported. Typical molecules used for deuterium isotope separation were formaldehyde⁵, freon 123⁶, and fluoromethanes⁷. Other examples of laser isotope separation includes isotopes of boron (BCl₃), carbon (CF₃I, CF₃COCF₃), silicon(SiF₄), sulfur(SF₆), chlorine(CF₂Cl₂), selenium(SeF₆), molybdenum(MoF₆), Osmium(OsO₄ and Uranium(UF₆, U(OCH₃)₆) where the precursor molecules are indicated in the parentheses.

The IRMPD (Infrared Multiphoton Dissociation) of trichloroethylene-H (TCE-H) was previously investigated in molecular beam⁸ and in static cell⁹. Lee and coworkers⁸ observed that C-Cl bond fission, C₂HCl₃ → ·C₂HCl + Cl·, was a primary dissociation channel in their molecular beam-IRMPD system. In contrast to this Steinfeld and coworkers⁹ reported that trichloroethylene underwent HCl elimination, C₂HCl₃ → HCl + C₂Cl₂, as the major reaction path at 10 torr TCE pressure in a static cell. Choo and coworkers¹⁰ resolved the above apparent discrepancy by a detailed study on the

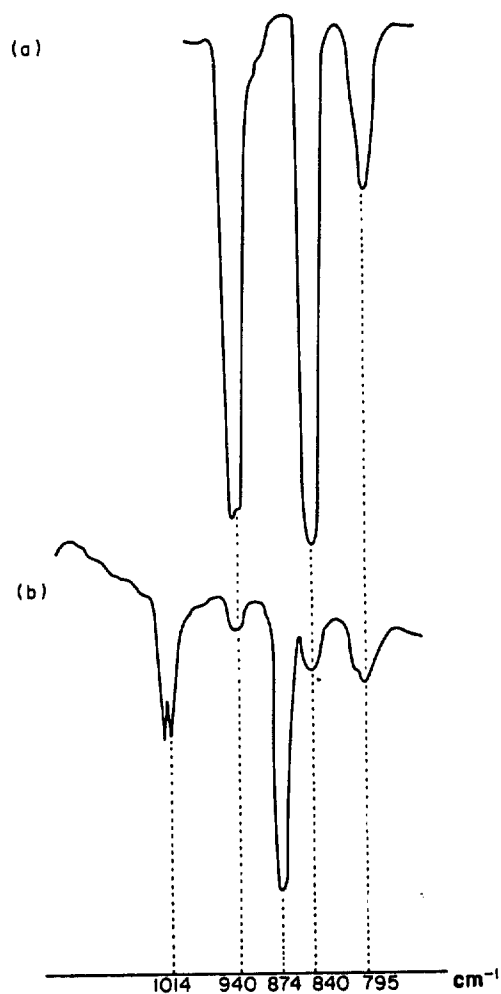


Figure 1. IR spectrum (around 1,000 cm⁻¹ of TCE-H(a) and (90% TCE-D + 10% TCE-H) mixture(b).

pressure dependences of the product yields. They observed unusually large dependence of the product ratios on the system pressure.

In this report we wish to present our results on the IRMPD of trichloroethylene-H (TCE-H) and trichloroethylene-D (TCE-D). The purposes of our research are; first, to get information on the isotope selectivity in the IRMPD of trichloroethylene, second, to elucidate a detailed mechanism for the pressure dependence of the branching ratios and thirdly, to apply the EGME (Energy Grained Master Equation) approach for quantitative explanation of the experimental results.

Experimental

Materials. Trichloroethylene-H (Merck and Aldrich) was purified by several freeze-pump-thaw cycles until no detectable impurities was found in G.C. and M.S. Helium (Matheson) was used without further purification.

Trichloroethylene-D was synthesized by base-catalyzed deuterium exchange reaction between D₂O and TCE-H¹¹. The following is the brief description of our TCE-D synthesis. TCE-H was refluxed with NaOD (Aldrich, Gold Label) at 81-84°C overnight. The two phases were separated, and TCE was dried by molecular sieves and distilled.

Table 1. Absorption Cross Sections of Trichloroethylene

CO ₂ Laser line	Wavelength(μm)	Cross section(cm ²)
10P(20)	10.591	2.88 × 10 ⁻¹⁹
10P(18)	10.571	1.13 × 10 ⁻¹⁹
10P(22)	10.611	2.31 × 10 ⁻¹⁹
10P(16)	10.551	8.65 × 10 ⁻¹⁹
9P(14)	9.504	
9R(all)	—	too small to be measured
10R(all)	—	<10 ⁻²⁰

Table 2. Dependence of Relative Yields on the System Pressures. Laser Energy = 0.28 J

Pressure (torr)	1	2	4	8	14
$\frac{[C_2Cl_2]}{[C_2HCl]}$	2.5	3.1	5.5	11	22

The exchange was repeated with a new charge of NaOD using the same procedure. Five exchanges resulted in the preparation of 86% TCE-D. Synthesized TCE-D was degassed and transferred to the reaction cell after several freeze-pump-thaw cycles in the vacuum line. Figure 1 shows the IR spectrum (700 cm⁻¹-1100 cm⁻¹ range) of TCE-H and (TCE-D + TCE H) mixture.

The Laser and the Irradiation Cell. The detailed schematic diagram and a general description of the instrumentation were shown in the previous publication¹² in our laboratory.

Product Analysis. The reaction products were identified with Gas Chromatography (Fid, Cenco), IR spectroscopy (Perkin Elmer), and mass spectrometry (UTI) with 21 eV ionization voltage to detect molecular ion peaks more efficiently. For the analysis of (TCE-D and TCE-H mixture) and (Cl-C=C-H and Cl-C=C-D mixture) by mass spectrometry, we assumed the same ionization efficiencies for both H and D compounds.

Results and Discussions

1) IRMPD of TCE-H

a) Absorption cross-sections of TCE-H

Walzer and Tacke¹³ reported the high resolution optoacoustic spectrum of TCE-H in the 9-11 μm range. We have measured the absorption cross sections of TCE-H with a 50 cm length cell at various CO₂ laser wavelengths. The measured cross sections, shown in Table 1, are in fair agreement with the optoacoustic spectrum. Since our CO₂ laser output is high at 10P(20) line and TCE-H also has a high absorption cross section at 10P(20) (see Table 1) we used 10P(20) line in most experiments.

b) Pressure dependence of product ratios in the IRMPD of TCE-H

C₂Cl₂, C₂HCl, and HCl were found to be the major products under all IRMPD conditions. Some Cl₂ was also found (by mass spec.) in some runs. In general the dissociation yield increased with increasing the laser powder and system pressures. Table 2 and Figure 2 show the dependence of the

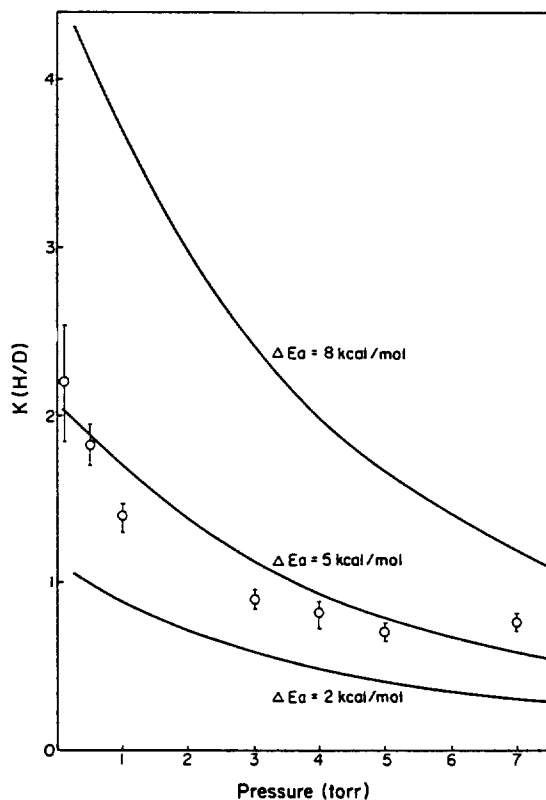


Figure 5. Dependence of the selectivity (K) on system pressures at 10P(20) line and 0.3 J laser energy. \circ : experimental data. —: Theoretical calculation, data taken from Figure 1.

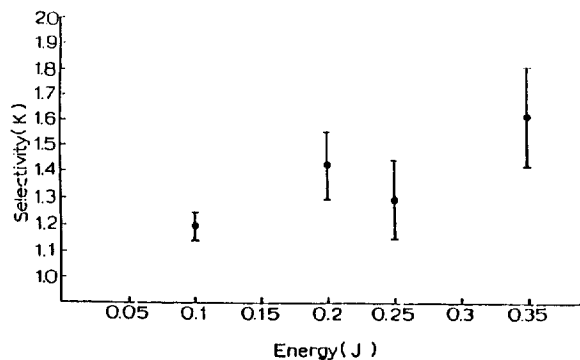


Figure 6. Dependence of K on the laser energy. 10P(20) line and 1.5 torr pressure.

not give any noticeable dissociation.

2) IRMPD of TCE-H and TCE-D Mixtures

a) Laser frequency dependence of TCE-D dissociation

As shown in Figure 1 the low resolution IR spectrum of TCE-D did not show any apparent absorption peak around $(940 \text{ cm}^{-1} \pm 50 \text{ cm}^{-1})$ our CO₂ laser output wavelengths. However, 10R(18) line (974.7 cm^{-1}) gave some dissociation of TCE-D.

b) Isotope selectivity vs. system pressures at 10P(20) line

For the IRMPD of (TCE-H + TCE-D) mixture the isotope selectivity coefficient K is defined by the following equation.

$$K(\text{H/D}) = \frac{(\text{H/D}) \text{ ratio in the product } (\text{C}_2\text{H}(\text{D})\text{Cl})}{(\text{H/D}) \text{ ratio in the initial reactant } (\text{C}_2\text{H}(\text{D})\text{Cl}_3)}$$

Therefore, from the known ratio of (TCE-H + TCE-D) mix-

ture the selectivity coefficient K can be obtained by monitoring C₂HCl and C₂DCl in the products. Figure 6 shows the dependence of K on the system pressures at 0.3 J laser energy and with 10P(20) line (944.2 cm^{-1}) laser irradiation. As shown in the figure K was ca. 2.2 (meaning more H containing product) at 0.25 torr of the system pressure. As the pressure increases (by adding inert gas, helium) K value decreases to 1 (meaning no separation of isotopes) and at higher pressures the value becomes 0.7 (meaning more D containing products). The dependence of K on the system pressures could be originated from several routes. They are; the dependence of branching ratios (cf. Figure 2) on the system pressures, the pressure dependence of the inter- and intramolecular energy transfer processes, and the possibility of the dependence of the microscopic rate constants on the system pressures, etc.. The detailed theoretical treatment of these possibilities will be discussed in section 3).

c) Isotope selectivity vs. laser energy at 10P(20) laser line

Figure 6 shows the variation of K with the change of the laser energy at a constant pressure (0.5 torr). The isotope selectivity (K) increases as the laser energy increases. This trend is also observed at different system pressures. The result is in accord with a common sense that the selectivity should increase when the molecule is pumped to high energy state more rapidly (with higher energy) to reduce the effect of the subsequent collisional events.

From the results in b) and c) we can conclude that the efficiency of the isotope separation increases as one lowers the system pressure and increases the laser energy.

3) Theoretical Model of TCE-H and TCE-D IRMPD

The general differential equation to model the IRMPD of TCE is the following¹⁵⁾ energy grained master equation (EGME) approach;

$$\frac{dN_i}{dt} = R_{i-1}^a N_{i-1} + R_i^e N_{i+1} - (R_i^a + R_{i-1}^e) N_i + \beta \sum_j Z P_{ji} N_j - \beta \sum_j Z P_{ij} N_i - \{k_i(\text{HCl}) - k_i(\text{Cl}_2)\} N_i \quad (1)$$

where N_i ; the population in energy level i

R_i^a ; the absorption rate constant from level i to level $i+1$

R_i^e ; the stimulated emission rate constant from level $i+1$ to i

β ; collision efficiency

Z ; the hard sphere collision frequency

P_{ij} ; the probability of a molecule making a transition from level j to level i upon collision

k_i ; the dissociation rate constant from i th level

$k_i(\text{HCl})$; the dissociation rate constant for HCl elimination channel to give ClC \equiv CCl product

$k_i(\text{Cl}_2)$; the dissociation rate constant for Cl₂ (or 2Cl) elimination to give HC \equiv CCl product

k_i is set equal to zero when i th energy level is below the activation energy. The vibrational energies were assumed to be divided into equally spaced levels corresponding to the laser frequency.

The absorption rate constants, R_i^a , can be described as,

$$R_i^a = \sigma_i I(t) / h\nu \quad (2)$$

where σ_i is the absorption cross section for a transition from level i to $i+1$, $I(t)$ is the laser intensity, and $h\nu$ is the photon energy. The stimulated emission rate constant may be given

by the detailed balance as follows,

$$R_i^e = R_i^a (g_i / g_{i+1}) \quad (3)$$

where g_i is the number of vibrational states within the laser bandwidth center at the energy, $E_i = ih\nu$. For narrow laser lines, g_i is proportional to the density (ρ) of vibrational states at energy E_i ,

$$g_i / g_{i+1} = \rho_i / \rho_{i+1} \quad (4)$$

The density of vibrational states can be calculated by using the direct count method with the vibrational frequencies.

Rate constants, $k_1(\text{HCl})$ and $k_2(\text{Cl}_2)$ can be calculated from RRKM theory. The input parameters for the RRKM calculations were published in our laboratory¹⁴. For $k_2(\text{Cl}_2)$ calculations only E_a was changed with the same A factor as that of $k_1(\text{HCl})$. The collisional transition probabilities, P_{ij} , were determined by using the stepladder model¹⁵. The down (P_{ji}) and up (P_{ij}) transitions are assumed to have the following properties;

$$\begin{aligned} P_{ij} &= 1.0 - P_{ji} \text{ for } E_i - E_j = \langle \Delta E_a \rangle \\ P_{ij} &= 0 \text{ for } E_i - E_j \neq \langle \Delta E_a \rangle \end{aligned} \quad (5)$$

The up-transition probabilities are found from the detailed balance;

$$\frac{P_{ij}}{P_{ji}} = \frac{g_i}{g_j} \exp(- (E_i - E_j) / kT) \quad (6)$$

Since the absorption cross section at level $i(\sigma_i)$ is impossible to be determined, it is assumed that σ_i is equal to σ_0 which is the absorption cross section for 0-1 vibrational transition.

The EGME model was fit to the experimental data by using an iterative fitting procedure in which the following parameters were adjusted;

1. the collision frequency
2. pulse duration and shape

The original differential equations were solved by a direct numerical integration according to the Bulirsch-Stoer procedure¹⁶. The equations were integrated to the time with the laser "on" (ie, pulse duration), and then integrated with the laser "off" (ie, R_i^a and R_i^e were set equal to zero) until the molecular populations in levels above the critical energy became negligible.

a) Pressure dependence of the branching ratio for TCE-H IRMPD

The original EGME model assumes that the laser energy, once absorbed by a molecule, may rapidly and statistically be distributed to all the effective vibrational modes in the molecule. Therefore the R_i (dissociation rate constant for molecules with energy E_i) can be calculated from the statistical method such as RRKM theory. A change of system pressures will affect the $\beta \sum_j Z P_{ij} N_j$ and $\beta \sum_j Z P_{ji} N_j$ terms in EGME model, as well as the RRKM calculation for k_i . We have tried numerous unsuccessful attempts to simulate our experimental pressure dependence (Figure 2) of the TCE-H IRMPD with reasonable changes of various parameters within the framework of original EGME model. Figure 2 shows the calculated pressure dependence of the branching ratios with assumed differences in activation energies. As shown in the figure it was totally impossible to reproduce the sensitive pressure dependences with reasonable parameters. In the EGME model the system pressures only affect the collisional activation-deactivation step so that the variation of the k_1/k_2

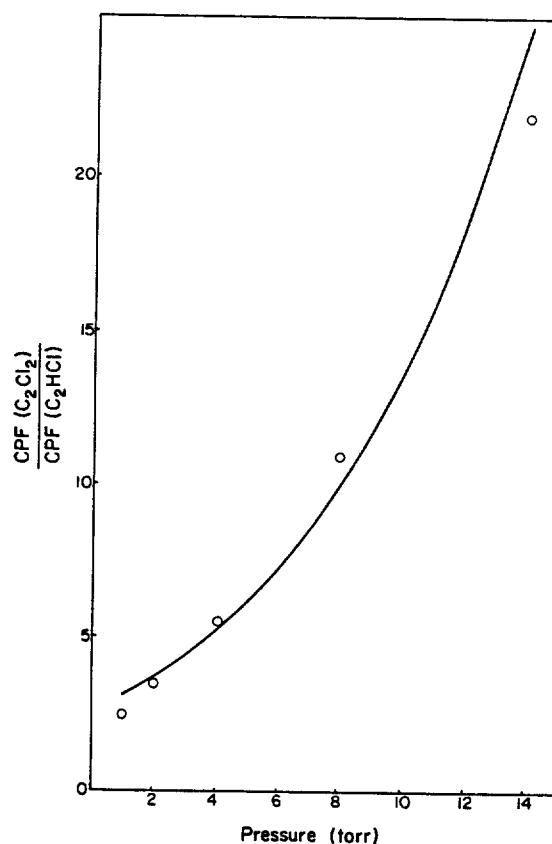


Figure 7. Calculated relative yields vs. pressures for TCE-H IRMPD with a modified EGME model (see text). —: calculation, $f = \exp\{-290/(P + 50)\}$. ○: experimental data.

ratio with the change of the pressure is very small.

To simulate the experimental result it is apparent that one of the rate constants (k_1 or k_2) must be much more sensitively dependent on the system pressures. Since the TCE-H molecules initially absorb 10P(20) CO₂ laser line which matches with C=C-Cl stretching (ν_4) mode, C-Cl bond fission (rather than HCl elimination) may be more preferable if there is not intramolecular energy randomization. If the initial energy is fully randomized, then the low energy, HCl elimination, channel will also be possible. Let us assume that only some fraction of initially absorbed energies may be redistributed into other modes, and further assume that the fraction (f) is also a function of the system pressure. Under above assumptions f can have any value smaller than 1 (approach 1 at high pressure limit and 0 at lower pressure limit). The new rate constant for HCl elimination channel becomes

$$\begin{aligned} k_f(\text{HCl}) &\rightarrow f k_f(\text{HCl}) \\ 0 &< f < 1 \\ f &= f(P) \end{aligned}$$

The assumption that f is a function of pressure implies that the intramolecular energy redistribution can be affected by the presence of other molecules. To affect the energy redistribution step by intermolecular collisions under our experimental conditions (1-10 torr system pressures) the intramolecular energy redistribution may not be completed in ca. 10^{-7} sec. Recent years there are indications that in some chemical reactions the couplings between different oscillators in a molecule are not always very efficient¹⁷. In some molecules

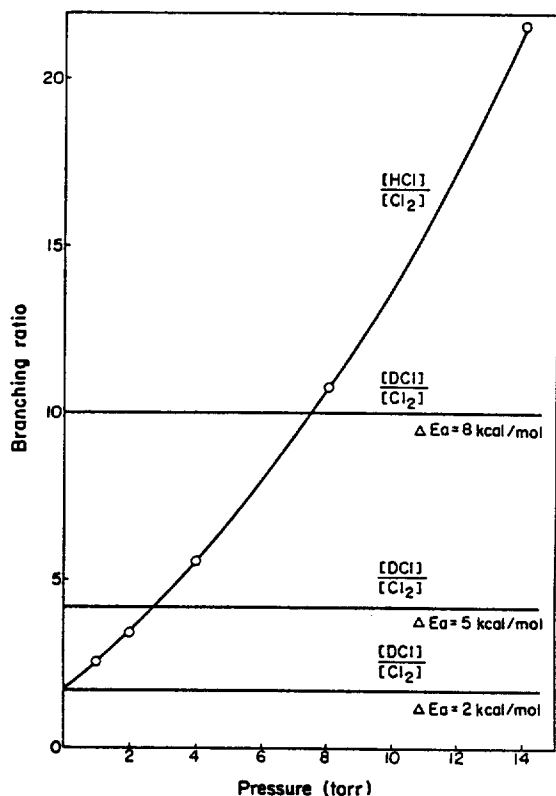


Figure 8. Calculated branching ratios vs. pressures with assumed E_a for HCl-Cl_2 and DCI-Cl_2 channels. Best fit: $\Delta E_a = 5$ Kcal/mole.

the intramolecular energy redistribution may be quite slow (10^{-7} sec) due to the inefficient coupling between the oscillators. At present we do not have quantitative theory on the calculation of the degree of coupling between oscillators at a given energy content.

Figure 7 shows the calculated branching ratios with a modified EGME model. The best fit value for the f was found to be $f = \exp\{-290/(P + 50)\}$ where P was expressed in torr unit. The calculated result is in excellent agreement with the experimental values, indicating that the inclusion of f (energy redistribution probability) in the original EGME model is justified.

b) The dependence of isotope selectivity on the system pressures

As mentioned above, the 10P(20) line excites TCE-H molecules mode-selectively. Therefore the branching ratios sensitively depend on the system pressures. In contrast, TCE-D molecules gain energies by a random excitation so that we can apply the original EGME model for the IRMPD

of TCE-D. Figure 8 shows the calculated pressure dependence of TCE-D decomposition with 10P(20) line irradiation. By combining Figure 7 and Figure 8 we can obtain the calculated selectivity vs. pressure curves, as shown in Figure 5. A very good agreement with experimental data indicates the validity of our modified EGME approach for the quantitative explanation of IRMPD of TCE-H and TCE-D.

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