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# Determination of Arrhenius parameters for unimolecular reactions of chloroalkanes by IR laser pyrolysis

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A simple and reliable method is elaborated for accurate measurements of thermal rate constants of homogeneous gas phase unimolecular reactions. A pulse of CO<sub>2</sub> laser radiation was used to multiphoton excite SiF<sub>4</sub> sensitizer molecules and consequently produce temperatures in the range 1100–1400 K. Expansion of the heated gas column quenches pyrolysis reactions on a 10  $\mu$ s time scale. There are no hot surfaces to induce chemistry. HCl elimination from C<sub>2</sub>H<sub>5</sub>Cl,  $E_a = 57.4$  kcal/mol and log  $A(s^{-1}) = 13.8$ , was used as an internal temperature standard. For the molecular elimination CCl<sub>3</sub>CH<sub>3</sub>  $\rightarrow$  HCl + CCl<sub>2</sub>CH<sub>2</sub>,  $E_a = 49.5 \pm 1.3$  kcal/mol and log  $A(s^{-1}) = 13.1 \pm 0.3$ , were determined. In these experiments the major decomposition products of CHCl<sub>2</sub>CH<sub>2</sub>Cl are HCl and *cis*- or *trans*-CHClCHCl with  $E_a = 58.5 \pm 2$ , log  $A = 13.9 \pm 0.4$ , respectively. HCl elimination to give CCl<sub>2</sub>CH<sub>2</sub> and C-Cl bond breaking to CHClCH<sub>2</sub>Cl radical have higher activation energies. The method is generally useful for kinetics at high temperature.

# I. INTRODUCTION

Multiphoton excitation by infrared laser light (MPE) has been widely used to study the dynamics and chemical kinetics of molecules with distinctly nonthermal distributions of vibrational excitation.<sup>1,2</sup> MPE followed by collisional energy transfer may be used to produce high temperature *thermal* excitation in gases. The consequently well-defined energy distribution, i.e., temperature, can allow quantitative studies of high temperature chemical kinetics.

In this work a purely thermal excitation of a reactive gas was produced by CO<sub>2</sub> laser MPE of a nonreactive sensitizer molecule,  $SiF_4$ .<sup>3</sup> Rapid energy transfer among vibrational, rotational and translational degrees of freedom thermalized the gas on a submicrosecond time scale and initiated thermal chemistry of the reactive components of the gas mixture. Reaction was quenched on a 10  $\mu$ s time scale as the high temperature gas along the laser beam path expanded against the surrounding cold gas. Shaub and Bauer<sup>4</sup> have shown that for cw lasers this geometry greatly discourages the inhomogeneous pyrolysis which often occurs on the walls of thermal reactors. The short time scale resulted in a higher temperature range for a given reaction than typical for thermal reactors or shock tubes. The usefulness of pulsed sensitized laser pyrolysis had previously

been demonstrated in qualitative studies of reaction pathways.  $^{5-7}$ 

For quantitative work the temperature must be known as a function of position and time throughout the reaction cell. This problem is greatly eased by introduction of an internal standard reactant with known kinetics similar to those of the compound under study.<sup>6</sup> In this way only an approximate quantitative knowledge of the temporal and spatial variation of the temperature, as may be calculated from a gas dynamic model, is required for accurate rate constant measurements. The molecular elimination of HCl from ethyl chloride (EtCl) served in this work as the standard for a study of 1, 1, 1-trichloroethane (111-TCE) and 1, 1, 2-trichloroethane (112-TCE) pyrolyses in the temperature range 1100-1400 K. McMillen et al.<sup>9</sup> have developed this method along similar lines with a simpler gas dynamic treatment and applied it successfully to several other molecules.

The experimental method and raw data are presented below in Secs. II and III. Section IV treats the laser heating and gas dynamics, and extracts rate constants from the raw data. Section V analyzes the limitations of the method in detail. The chemical kinetics of unimolecular decomposition of the trichloroethanes are discussed in Sec. VI. Arrhenius parameters for several HCl elimination reactions are determined and some of the problems posed by radical chain reactions are illustrated.

# **II. EXPERIMENTAL**

The beam of a pulsed  $CO_2$  laser was passed along the axis of a cylindrical cell. SiF<sub>4</sub> molecules within the laser beam absorbed many photons and heated the

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FIG. 1. (a)  $CO_2$  laser beam transverse profile. Shown here are the horizontal scans at the vertical maximum. The vertical profile is similar. (o)-incident laser energy corrected for the entrance window loss. (**•**)-transmitted laser energy corrected for exit window loss. (b) The profile of absorption by  $SiF_4$ . (**•**), from (a), and (×) are for 0.18 J/pulse incident energy; ( $\nabla$ ) for 0.12 J/pulse.

chloroalkane reagent gases. The heated volume was a small fraction of the total. After many pulses, the gases were removed from the cell and analyzed by gas chromatography (GC).

A grating-tuned Tachisto model 215 CO<sub>2</sub> TEA laser was used. With an internal iris set at 8.0 mm diameter the multimode beam had a near-Gaussian profile, Fig. 1 (a), with a FWHM of  $4.0 \pm 0.4$  mm. The transverse profile was measured by attaching a 0.2 mm pinhole 2 mm in front of the sensor of a Molectron model J-3 pyroelectric detector mounted on a 3-D translator. The laser pulse for pyrolysis at 1027.4 cm<sup>-1</sup> [P(40) line] was typically 0.2J/pulse. Pulse-to-pulse energy variation was  $\pm 10\%$  and long term energy stability about 10%. The total pulse duration was 1.3  $\mu$ s. The initial 70 ns spike peaked at 35 ns and contained 40% of the energy. The laser beam was used without focusing or collimation. A polished NaCl flat was placed in front of the laser at 45° to reflect about 5% of the beam to a Scientech power meter for monitoring the long term drift of the laser energy during the experiment.

The laser beam was sent through the pyrolysis cell and into a calibrated Scientech power meter. The pyrolysis laser energy was calculated as the average energy of the incident beam into the gas mixture after the first cell window. All of the experimental parameters linearly related to the laser energy have an uncertainty of  $\pm 5\%$ -10% because of the laser energy fluctuation. The percentage absorption of the beam by the gas mixture was determined by the ratio of the pulse energies after the cell with the gas mixture in the cell and with the mixture frozen in the sidearm at liquid  $N_2$ temperature. Polished flats of CaF<sub>2</sub>, NaCl or Ge were placed between the NaCl beam splitter and the cell in order to obtain the desired pulse energy. Between 20% and 30% of the 0.2-0.08 J/pulse laser energy entering the cell was absorbed by the mixture. The laser was operated at 0.87 Hz repetition rate for pyrolysis with energy  $\gtrsim 0.15$  J/pulse and at 0.33 Hz for lower energies. The slow repetition rate was meant to allow complete diffusion of the products and reactants throughout the cell between two consecutive laser pulses. It was estimated from a calculated diffusion constant that roughly 0.2 s are needed for the products to diffuse a distance of 2 mm in the 5.6 Torr mixture at room temperature. The higher temperature induced by the laser excitation in the reaction zone hastened mixing both by convection and diffusion. For lower fluences, a slower repetition rate was used to guarantee a complete mass diffusion. The power meter was calibrated for different repetition rates of laser pulses with a Scientech model 362 powerenergy meter.

Pyrolysis samples were handled in a vacuum line with greaseless stopcocks pumped down to  $10^{-6}$  Torr. Unless otherwise specified, a Pyrex cell 3.8 cm long and 3.8 cm diameter with two polished NaCl windows attached by Torrseal epoxy, and a gas mixture consisting of  $4.9 \pm 0.1$  Torr SiF<sub>4</sub>,  $0.37 \pm 0.02$  Torr EtCl, and  $0.37 \pm 0.02$  Torr reactant (either 112-TCE or 111-TCE) were used for each pyrolysis. Gas pressures were measured by a calibrated variable-reluctance manometer (Validyne) with a 50 Torr range. Each component of the pyrolysis mixture was admitted into the cell at a measured pressure and condensed through a stopcock into a sidearm at 77 K. The sample was then vaporized into the cell and allowed to mix for at least 20 min.

After the pyrolysis, the mixture was immediately condensed at 77 K into a 4 cm<sup>3</sup> volume GC sample loop which was attached to the cell and pumped clean on the vacuum line before the preparation of the mixture. A Varian 3700 GC with gas sample injection and a flame ionization detector was used with a column of 100/120 mesh Porapak Q in 12 ft of 1/8 in. diameter stainless steel tubing for separating the reactants and the products. The GC peak areas for all the reactants and products (except C<sub>2</sub>HCl and C<sub>2</sub>HCl<sub>3</sub>) were calibrated absolutely. The GC peak area measurement and the detector response calibration gave a combined uncertainty of  $\pm 8\%$  for the product yields. HCl, Cl<sub>2</sub>, and SiF<sub>4</sub> do not respond to flame ionization detection.

The IR fluorescence from the irradiation zone was monitored and temporally resolved for a single sample composition. The Pyrex fluorescence cell was 4 cm in length and 5.1 cm in diameter with ends sealed by NaCl windows. A pair of 1.7 cm diameter holes through the center section of the cylindrical walls was sealed with NaCl windows for transmitting the fluorescence. A liquid He cooled 3 mm $\times$ 10 mm Hg : Ge photoconductive IR detector was placed above a fluorescence window with the element aligned along the cell axis. The distance between the irradiation volume and the detector was about 20 cm. A 50 mm diameter CaF<sub>2</sub> lens of 50 mm focal length was placed midway between the detector and the laser path. The response time for the detector with its amplifiers was about 0.4  $\mu$ s. The signal was recorded and averaged for 32 pulses using a Biomation transient recorder and a Northern NS-575A digital signal analyzer. A liquid  $N_2$  cooled 3-6  $\mu$ m circular variable filter mounted inside the detector Dewar selected a 60 cm<sup>-1</sup> FWHM bandpass centered about 5.0  $\mu$ m.

All of the chemicals, originally reagent grade or technical grade, were purified by fractional distillation. The purity was found by GC to be >99.9% for EtCl, >99.6% for 112-TCE, >99.5% for 111-TCE, and >99.9% for SiF<sub>4</sub>. No impurities of pyrolysis product molecules were detected (>0.01%). Photolysis samples of HCl, *cis*-1, 2-dichloroethene, and 1, 1-dichloroethene each contained less than 0.5% impurity.

## III. RESULTS

## A. Energy deposition

The initial temperature distribution in the cell following thermalization of the energy absorbed from the laser pulse depends on the radial profile of the laser beam and the absorbance of the sample. The profile of the incident laser beam is substantially narrowed [Fig. 1(a)] and distorted upon passing through the cell. The decrease in absorption coefficient of SiF<sub>4</sub> with increase in laser intensity causes this narrowing and yields the relatively flat-topped, radial temperature profile (FWHM =6.4±1 mm) defined roughly in Fig. 1(b). The SiF<sub>4</sub> attenuates the laser pulse energy by 33% at 0.09 J/pulse and by 24% at 0.21 J/pulse. The decrease in beam fluence (J/cm<sup>2</sup>) due to absorption along the beam axis is



FIG. 2. Fluorescence trace at  $5.0 \ \mu m$  from 5 Torr SiF<sub>4</sub>, 0.38 Torr EtCl, and 0.38 Torr 111-TCE excited by 0.175 J/pulse. The first spike is shown enlarged in Fig. 8. The baseline droop below zero is caused by the ~10 Hz low frequency amplifier cutoff.

reduced by the decreasing beam diameter. The resulting decrease in the initial heating of the gas from the entrance to the exit window will be 1/4 to 1/2 of the fractional attenuation of the laser. The volume of the heated column estimated from Fig. 1(b) is approximately 1.3 cm<sup>3</sup>; it does not depend strongly on pulse energy. The total cell volume is 50 cm<sup>3</sup> and thus 2.6% of the gas is initially heated. SiF<sub>4</sub> molecules in the heated column absorbed an average of 7-13 photons.

# B. Infrared emission

A strong fluorescence was observed at 5.0  $\mu$ m. This can only be assigned to the  $\Delta v = 2$  transition of the 1022 cm<sup>-1</sup> mode of SiF<sub>4</sub>. The series of sharp peaks of decreasing amplitude (Fig. 2) are due to the radial (and to a small extent axial) shock waves propagating from the laser-heated column to the cell walls and reflecting back.<sup>9b</sup> The 3.5-fold decrease in intensity from first to second peaks indicates that thermal chemistry will

	Incident energy <sup>b</sup>	Absorbed energy	Number of	Pulse rate	C <sub>2</sub> H <sub>5</sub> Cl Dissociation	Product yield fro	om CCl <sub>3</sub> CH <sub>3</sub> (%) <sup>°</sup>
Sample <sup>a</sup>	(J/pulse)	(J/pulse)	pulses	(Hz)	yield (%) <sup>c,d</sup>	CCl <sub>2</sub> CH <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> Cl
L-I	0,188	0.046	50	0.87	9.20	29.1	0.41
L-I	0.133	0.034	100	0.34	3.53	16.2	0.090
L-I	0.121	0.028	100	0.34	1.82	10.2	0.042
L–I	0.086	0.029	200	0.34	0.15	1,18	0.007
S–II	0.150	0.045	150	0.87	5.2	22.0	0.45

TABLE I. Experimental results for sensitized laser pyrolysis of  $SiF_4/C_2H_5Cl/CCl_3CH_3$  mixtures.

<sup>a</sup>L-I, 4.9 Torr SiF<sub>4</sub>/0.37 Torr C<sub>2</sub>H<sub>5</sub>Cl/0.37 Torr CCl<sub>3</sub>CH<sub>3</sub> in the 3.8 cm long cell. S-II, 21.5 Torr SiF<sub>4</sub>/1.64 Torr C<sub>2</sub>H<sub>5</sub>Cl/1.64 Torr CCl<sub>3</sub>CH<sub>3</sub> in the 0.9 cm short cell.

<sup>b</sup>All the L-I samples were irradiated by P(40) line. S-II was irradiated by P(34) line. The uncertainty for the pulse energy is  $< \pm 10\%$ .

The per pulse yield in the irradiation volume is reported here. The uncertainty is  $\pm 8\%$  of the measured yield.

<sup>d</sup>From C<sub>2</sub>H<sub>4</sub> product.

TABLE II. Experimental results for sensitized laser pyrolysis of the  $SiF_4/C_2H_5Cl/CHcl_2CH_2Cl$  mixtures.

	Incident energy <sup>b</sup>	Absorbed	Number of pulses	Pulse rate (Hz)	C <sub>2</sub> H <sub>5</sub> Cl Dissociation yield (%) <sup>c</sup>	Product yield from CHCl <sub>2</sub> CH <sub>2</sub> Cl (%) <sup>c,d</sup>				
Sample <sup>a</sup>	(J/pulse)	(J/pulse)				cis-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	$trans-C_2H_2Cl_2$	CCl <sub>2</sub> CH <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> Cl	C2HCl <sup>e</sup>
	0.198	0.052	200	0.87	18.4	15.6	13.3	0.44	1.58	0.4
L-l	0.207	0.048	100	0.87	13.6	10.3	8.13	0.33	0.82	0.3
L-I	0.210	0.051	200	0.87	13.0	9.05	7.32	0.24	0.69	0.2
L-III	0.176	0.049	120	0.87	•••	5.56	3.66	1.43	0.043	0.1
S–11	0.165	f	300	0.87	5.18	3.92	2.82	0.063	0.096	0.02
L-I	0.123	0.034	200	0.34	4.39	3.34	2.46	0.19	0.25	0.08
L–I	0.149	0.035	160	0.34	3.74	3.34	2.44	0.17	0.14	0.05
S–I	0.144	0.007	40	0.67	3.00	2.46	1.77	0.08	0.12	•••
L-III	0.125	0.036	220	0.87	•••	0,60	0.40	0.12	0.0038	0.002
L–I	0.094	0.026	200	0.34	0.42	0.27	0.20	0.11	0.0080	•••
L–I	0.096	0.023	200	0.34	0.24	0.22	0.16	0.050	0.0047	•••
L-III	f	f	100	0.34	***	0.21	0.14	0.070	0.0016	***
S-I	0.090	f	720	0.44	0.10	0.089	0.062	0.008	0.0026	•••

<sup>a</sup>L denotes the 3.8 cm long cell and S the 0.9 cm short cell. Sample I is 4.9 Torr SiF<sub>4</sub>/0.37 Torr C<sub>2</sub>H<sub>5</sub>Cl/0.37 Torr CHCl<sub>2</sub>CH<sub>2</sub>Cl. Sample II is 5.2 Torr SiF<sub>4</sub>/0.26 Torr C<sub>2</sub>H<sub>5</sub>Cl/0.38 Torr CHCl<sub>2</sub>CH<sub>2</sub>Cl/0.14 Torr toluene. Sample III is 4.9 Torr SiF<sub>4</sub>/0.70 Torr CHCl<sub>5</sub>CH<sub>5</sub>Cl.

<sup>b</sup>P(40) line pulse energy with uncertainty  $< \pm 10\%$ .

<sup>c</sup>The per pulse yield has uncertainty of  $\pm 8\%$  of the measured yield except for C<sub>2</sub>HCl.

<sup>d</sup>C<sub>2</sub>HCl<sub>3</sub> was also observed in some pyrolyses. However, the amount was too small to allow meaningful measurement.

Very approximate from shoulder of C<sub>2</sub>H<sub>4</sub> GC peak.

<sup>f</sup>Not measured.

only be important during the first peak. The IR fluorescence rose to 80% of the first maximum during the 1.3  $\mu$ s laser pulse. Between 5 and 20  $\mu$ s the fluorescence decayed with roughly a 30  $\mu$ s time constant.

A search for fluorescence near 3.4  $\mu$ m was unsuccessful, presumably due to the combined effects of self absorption at the CH stretching fundamental, low concentration and low thermal excitation of levels at 3000 and 6000 cm<sup>-1</sup>.

## C. Pyrolysis yields

The gas chromatographic analysis gives the total decomposition yield  $(F_{t,i})$  of product *i* as a fraction of each initial reagent. The total decomposition per pulse is F $=1-(1-F_t)^{1/n}$ , where  $F_t = \sum_i F_{t,i}$  and *n* is the number of pulses. The per pulse yield of product i is then  $F_i = F \cdot F_{t,i}/$  $F_t$ . The yields per pulse in the irradiated column are then obtained by multiplying by the volume ratio of 50/1.3. Data are shown in detail in Tables I and II. Figure 3 shows the yield per pulse for EtCl decomposition, the  $C_2H_4$  product, from all of the pyrolyses. The dramatic increase in yield with incident laser energy combined with the uncertainty and shot-to-shot variability in laser energy causes considerable scatter. This clearly demonstrates the need for an internal temperature standard in quantitative pyrolysis work. Thus in Figs. 4 and 5 the product yields of 111-TCE and 112-TCE are plotted against those of EtCl. The reduced data scatter is apparent. CCl<sub>2</sub>CH<sub>2</sub> is the only major product from 111-TCE pyrolysis. 112-TCE yields mainly cis- and trans-CHClCHCl. The C<sub>2</sub>HCl is only roughly measured since it occurs as a shoulder on the much larger C<sub>2</sub>H<sub>4</sub> peak from EtCl dissociation.

A few pyrolysis yields were measured in a short cell

(0.9 cm vs 3.8 cm) of modestly larger diameter (4.8 cm vs 3.8 cm). At about 25 Torr, four times the normal pressure, this cell gave a similar fractional absorption and heating when excited by a less strongly absorbed



FIG. 3. Ethyl chloride dissociation yield per pulse in heated zone vs incident laser pulse energy. (o) indicate pyrolyses with the long (3.8 cm) cell, (**o**) the short (0.9 cm) cell, and (**o**) the short cell at four times higher pressure. Typical uncertainty of the data is shown for three points.



FIG. 4. The CCl<sub>2</sub>CH<sub>2</sub> yield from CCl<sub>3</sub>CH<sub>3</sub> dissociation vs the corresponding C<sub>2</sub>H<sub>4</sub> yield from ethyl chloride dissociation. (o)-long cell; ( $\bullet$ )- short cell at higher pressure. The solid line is the best fit from the gas dynamic model calculation with  $E_a = 49.5$  kcal/mol and log A = 13.1. The dashed lines are with  $E_a = 48$  and 51 kcal/mol and log A = 12.8 and 13.4, respectively.

 $CO_2$  laser line. Pyrolysis of EtCl/111-TCE mixtures (S-II in Table I and Figs. 3 and 4) gave per pulse dissociation yields falling on the same curves with the lower pressure data. Pyrolysis of EtCl/112-TCE mixtures at the normal pressure gave the same yields in the short and long cells (Table II, Figs. 3 and 5) for 1, 2-dichloroethenes and vinyl chloride. The 1, 1-dichloroethene yield was at least a factor of two lower in the short cell.

The role of radical reactions in 112-TCE pyrolysis was probed by addition of toluene as a scavenger to a sample (S-II, Table II) in the short cell. The 1, 2-dichloroethene yields were unaffected; however, both minor products  $CCl_2CH_2$  and  $CH_2CHCl$  were substantially decreased. Since EtCl also participates in the radical reactions, three samples (L-III, Table II) were pyrolyzed without EtCl. Data were plotted on Fig. 5 (solid points) according to the observed *cis*-CHClCHCl yields. The *trans*- and 1, 1-dichloroethenes are formed in normal yield relative to *cis*, while the  $CH_2CHCl$  yield is decreased nearly fivefold. Since  $CH_2CHCl$  is not a product of EtCl pyrolysis, it must arise not only from 112-TCE but also from the joint radical reactions of EtCl and 112-TCE.

In order to understand the origin of minor products, pyrolyses of major products were carried out, Table III.  $CCl_2CH_2$  pyrolysis at nearly the highest laser energy yielded only a trace ~0.1% of  $C_2HCl$ . There was no back reaction to TCE's when  $CCl_2CH_2$  was mixed with HCl and pyrolyzed. Pyrolysis of *cis*-CHClCHCl yielded 5% of *trans*- at the highest pulse energies of Table II.

TABLE III. Experimental results of some test pyrolyses.

Sample <sup>a</sup>	Pulses <sup>b</sup>	Product	Yield <sup>c</sup> (%)
0.76 Torr $cis-C_2H_2Cl_2$	50	$\begin{array}{c} trans-C_2H_2Cl_2\\C_2HCl\\CCl_2CH_2\end{array}$	5.0 0.14 ≤0.002
0.72 Torr CCl <sub>2</sub> CH <sub>2</sub>	100	C2HCl	0.10
0.36 Torr HCl+ 0.34 Torr CCl <sub>2</sub> CH <sub>2</sub>	150	CCl <sub>3</sub> CH <sub>3</sub> CHCl <sub>2</sub> CH <sub>2</sub> Cl	<0.001 <0.001

<sup>a</sup>In presence with 4.9±0.1 Torr SiF<sub>4</sub> in the 3.8 cm long cell. <sup>b</sup>Number of pulses with P(40) line with pulse energy ~ 0.19– 0.20 J at a repetition rate of 0.87 Hz.

<sup>c</sup>Yield per pulse.

For pyrolysis of a 112-TCE/EtCl mixture, a product molecule finds itself, on average, in the laser-heated zone once during the 39 pulses (cell volume/heated volume) following its formation. Thus for a 200 shot



FIG. 5. The product yield from 112-TCE dissociation vs EtCl dissociation yield. The circles are the sum of the measured *trans*-CHClCHCl and C<sub>2</sub>HCl products from Table II. Blank points ( $\diamond$  etc.) are results from pyrolyses with the 3.8 cm long cell. Filled points ( $\diamond$  etc.) denote the pyrolyses without ethyl chloride. (s) denotes the short (0.9 cm) cell pyrolyses at the same pressure and (t) the pyrolysis with toluene in the mixture. The curves are the best fits from the gas dynamic model calculation with  $E_a$  and A shown in Table V except for CCl<sub>2</sub>CH<sub>2</sub>, for which  $E_a = 27$  kcal/mol and log A = 6.9.

pyrolysis with a 20% per pulse decomposition of starting material, the average product molecule is pyrolyzed three times and about 15% of *cis*-CHClCHCl is converted to *trans*. The *trans*-*cis* rate constant is about equal to that of *cis*-*trans*.<sup>10,11</sup> Under these conditions the *cis* and *trans* product distribution is shifted about 30% from the initial pyrolysis product distribution toward the equilibrium distribution at the pyrolysis temperature. This alters the absolute product yields by 3-4% at the highest pyrolysis temperatures resulting in a negligible effect on the  $E_a$  and A derived. A small amount of  $C_2$ HCl may be formed in the pyrolysis of *cis*-CHClCHCl. No other products were detected.

# IV. CALCULATION OF RATE CONSTANTS FROM DISSOCIATION YIELDS

To deduce rate constants from yield data the temperature must be found as a function of position and time in the reacting gas. This requires the construction of a model for the gas dynamics (Sec. A) and a method for calculation of dissociation yields (Sec. B). Then yields must be calculated for assumed Arrhenius parameters until the calculated product yields match the observed (Sec. C).

## A. Gas dynamics

A cylindrically symmetric laser-heated gas mixture of infinite length and radial coordinate r is considered. In the absence of heat conduction and viscosity the fluid equations are<sup>12</sup>

continuity condition 
$$\frac{\partial \rho}{\partial t} + \frac{\rho u}{r} + \frac{\partial}{\partial r} (\rho u) = 0$$
, (1)

equation of motion  $\rho \frac{\partial u}{\partial t} + \rho u$ 

$$\frac{\partial u}{\partial r} + \frac{\partial P}{\partial r} = 0 , \qquad (2)$$

$$\frac{\partial P}{\partial t} + u \frac{\partial P}{\partial r} - a^2 \left( \frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial r} \right) = 0 , \quad (3)$$

where a, the sound speed, is defined as  $a = [(\partial P/\partial \rho)_S]^{1/2}$ and u, P,  $\rho$ , and S are the gas velocity, pressure, density, and entropy, respectively. The isentropic expansion of the gas can be studied by the method of characteristics.<sup>12</sup> The above partial differential equations are converted into ordinary differential equations along three sets of Mach lines. The Mach line  $C_1$  is given by dr/dt = u + a,  $C_2$  by dr/dt = u - a, and  $C_3$  by dr/dt = u. The equations along each line are

$$C_1: dP + \rho a \ du + \frac{\rho a^2 u}{r} \ dt = 0 , \qquad (4)$$

$$C_2: \ dP - \rho a \ du + \frac{\rho a^2 u}{r} \ dt = 0 \ , \tag{5}$$

$$C_3: dP - a^2 d\rho = 0 . (6)$$

For given initial conditions these equations can be solved iteratively on a computer and  $\rho(r)$ , P(r), and hence the gas temperature T(r) obtained.

The change of the gas state for each iteration of Eqs. (4)-(6) is kept small so that the effect of heat conduction may be added independently between iterations. The pressure change caused by heat conduction is, <sup>13</sup>



FIG. 6. Calculated temperature and gas density profiles at times following absorption of 0.044 J laser energy at 5.6 Torr. The initial centerline temperature is 1334 K.

$$\frac{\partial P}{\partial t} = \frac{2m}{3\sigma} \left(\frac{P}{\pi\rho}\right)^{1/2} \left[\frac{\partial^2}{\partial r^2} \left(\frac{P}{\rho}\right) + \frac{1}{r} \frac{\partial}{\partial r} \left(\frac{P}{\rho}\right)\right], \tag{7}$$

where *m*, the molecular weight, and  $\sigma = 39 \text{ Å}^2$ , the collisional cross section, <sup>14, 15</sup> are the values for SiF<sub>4</sub>.

The calculations were performed on an LSI-11 microcomputer with 23 000 bytes of program memory, sufficient to calculate the gas evolution using 250 points, 0.01 cm apart. Since the time interval between points is half the space interval divided by the sound speed, as determined by the intersection of Mach lines from neighboring points, points are at most 0.15  $\mu$ s apart. The calculation with a Tek-Basic program takes several hours for a period of 30  $\mu$ s. A more powerful computer is to be recommended. The initial state (t = 0) is calculated from the energy deposition profile in Fig. 1(b) and the heat capacity of the mixture.<sup>16</sup> The initial gas density is constant and the velocity zero. The mixture is assumed to thermalize on a submicrosecond time scale at each point. Results are shown in Fig. 6.

The fluid equations describe the continuous expansion of the heated column. When a shock front develops, these equations no longer apply. In Fig. 6, the shock wave formation can be identified at 16  $\mu$ s, from the dual values for the calculated gas state near r = 0.8 cm. The gas evolution after the formation of the shock front must be calculated with another set of equations.<sup>12</sup> However, this is unnecessary for computing the reaction yield since by the time this shock formation can perturb the temperature near r = 0 (t > 30  $\mu$ s) the gas has cooled sufficiently to quench the reaction (Sec. IV B). The fluid equations still give a good description of the reacting gas.

The temperature decrease in the heated zone primarily comes from isentropic expansion of the gas. Heat conduction through Eq. (7) contributes just a little more than 1% to the cooling in the 1400-900 K temperature range.

The calculated variation of temperature and density with time may be compared to the experimental IR fluorescence traces. The overtone fluorescence in-

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FIG. 7. SiF<sub>4</sub>  $v_3$  mode population multiplied by the quantum number dependence for  $\Delta v = 2$  fluorescence as a function of temperature.  $\sum_{v} N_v = 1$ .

tensity is approximately proportional to

$$\sum_{v} v(v-1)N_{v}(T) ,$$

where  $N_v$  is the population of level v of the 1022 cm<sup>-1</sup> mode, Fig. 7. The observed IR fluorescence intensity is then proportional to

$$\int_{\mathbf{v}} \rho(T, t) \sum_{v} v(v-1) N_v(T) dV,$$



FIG. 8. Decay of IR fluorescence. — Experimental. Expanded scale from Fig. 2. Fluorescence curves were calculated from the gas dynamic model for the detection focal point on the laser beam axis (....), and translated by 2 mm(---) and 3 mm(---) away. For comparison, the maxima of the curves were placed at the same height by multiplying the intensity of the 2 and 3 mm curves by 1.44 and 3.60, respectively.

where V is the region viewed by the IR detector and dVis weighted by the solid angle of fluorescence collection. Calculated curves are compared in Fig. 8 for several locations of the detector focal point along a line perpendicular to the laser beam and the viewing axis. The shape of experimental and calculated curves is similar for a translation of between 2 and 3 mm. The IR intensity of returning radial shock waves at 0.2 ms and later, shows that the temperature never rises above ~900 K after the initial decay from 1334 K.

## B. Dissociation yield calculation

The yield of a reaction with known  $E_a$  and A can be calculated. The molecules in the cell were divided into cylindrical layers of 0.2 mm thickness at t=0. The thickness of the layer was allowed to change with time so that it always contained the same number of molecules  $N_0$ . The calculation in Sec. IV A gives the temperature history T(t) of each layer. The number of molecules dissociated within a layer is then,

$$\Delta N = \sum_{i} \Delta N_{i} = N_{0} \left\{ 1 - \exp\left[ -\int_{0}^{\infty} \sum_{i} A_{i} \exp\left\{ -E_{a,i} / RT(t) \right\} dt \right] \right\}$$
(8)

The summation is over all dissociation products i. The dissociation yield is the sum for all layers divided by the number of molecules originally in the 0.32 cm radius irradiation column.

The integral in Eq. (8) was carried out until at least 30  $\mu$ s. To determine the effect of this approximation the dissociation yield per unit time was examined as a function of time. The calculated time dependence of the 111-TCE dissociation rate for pyrolysis with an 0.175 J laser pulse is shown in Fig. 9. The rate decreases more than 30-fold in the first 20  $\mu$ s. Although the model fails at the shock front, it gives an accurate description, until well after 30  $\mu$ s, of the heated zone where reaction occurs. Truncation of the dissociation yield causes an error much smaller than the experimental yield uncertainties. Errors introduced by the step



FIG. 9. Dissociation yield/ $\mu$ s for 111-TCE vs time calculated for  $T_{\text{max}} = 1334$  K (0.175 J/pulse), with  $E_a = 49.5$  kcal/mol, and log  $A(s^{-1}) = 13.1$ . The yield integrated to 24, 30, and 34  $\mu$ s is 22.6, 25.1, and 25.7%, respectively.

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TABLE IV. Rate constants for  $CCl_3CH_3 \rightarrow CCl_2CH_2 + HCl$ .

Method	Temperature (K)	E <sub>a</sub> (kcal/mol)	$\log[A(s^{-1})]$
Sensitized laser pyrolysis	1130-1350	49.5±1.3	<b>13.1 ± 0.3</b>
Thermal reactor <sup>a</sup>	678-715	54.0±?	14.0±?

<sup>2</sup>From Ref. 31.

sizes in r and t were similarly small.

# C. Extraction of $E_a$ and A

Since energy deposition measurements determine temperatures only roughly and since reaction rates depend exponentially on temperature, the extent of EtCl dissociation ( $E_a = 57.4 \pm 1.0$  kcal/mol and log A (s<sup>-1</sup>) = 13.8 \pm 0.2)<sup>17-19</sup> is used as an internal thermometer. Figure 10 shows the calculated EtCl dissociation yield as a function of the initial temperature at  $\gamma = 0$  for the energy deposition profile of Fig. 1(b).

 $E_a$  and A are then extracted from the data of Tables I and II by fixing the maximum initial temperatures as given by the measured EtCl dissociation yields and varying  $E_a$  and A in Eq. (8) to give a least-squares fit to each set of data points in Figs. 4 and 5. The curve fit sensitivity of the analysis is shown for 111-TCE in Fig. 4. The uncertainties quoted in Tables IV and V are the 50% confidence range given by a *chi*-square test.

The dissociation of 112-TCE yielded primarily transand cis-CHClCHCl. Yields of other products were at least one order of magnitude smaller. Therefore,  $E_a$ 's and A's for the production of trans- and cis-CHClCHCl were varied simultaneously to fit their experimental points. Then CCl<sub>2</sub>CH<sub>2</sub> and CH<sub>2</sub>CHCl were included in Eq. (8) one by one. For CH<sub>2</sub>CHCl, the yields from the



FIG. 10. Initial temperature at the center of the irradiation column calculated from the EtCl dissociation yield.

pyrolyses without EtCl were analyzed by using the cis-CHClCHCl yield to determine the temperature. The fits in Fig. 5 yield the rate constants in Table V.

#### V. LIMITATIONS OF THE METHOD AND ANALYSIS

The use of a temperature standard compensates for a multitude of small problems in the experimental design and in the model used to extract thermal rate constants from sensitized laser pyrolysis data. There are nonetheless several problems and features of the experimental design which must be carefully considered in these and similar experiments.

#### A. Heating and thermalization

The model of Secs. IV A and B presumes that the gas is heated instantaneously; more precisely it requires that neither the expansion nor the chemical reaction proceed significantly until all of the laser energy has been delivered. Since the expansion begins with the initial 70 ns spike and the final 5% of the laser energy is delivered 1  $\mu$ s later, the model is not perfect. For  $T_{max} = 1334$  K, T(r=0) decreases by only 4 K, and r increases less than 0.1 mm during the first 1  $\mu$ s of the calculation. The actual changes before the end of the

Tribilly, The constants for unmolecular decomposition of OnO1201120	TAF	BLE V.	Rate constants	for	unimolecular	decomposition	of	CHCl <sub>2</sub> CH <sub>2</sub> C	21.
---------------------------------------------------------------------	-----	--------	----------------	-----	--------------	---------------	----	-------------------------------------	-----

	Temperature	$E_a$ (kcal/mol), $\log[A(s^{-1})]$							
Method	range (K)	$cis-C_2H_2Cl_2^a$	trans-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub> <sup>a</sup>	CCl <sub>2</sub> CH <sub>2</sub> <sup>a</sup>	CHClCH <sub>2</sub> Cl <sup>b</sup>	Ref.			
Sensitized laser pyrolysis	1150-1400	58.5 $\pm$ 2, 14.1 $\pm$ 0.4	$59.5 \pm 2,$ 13.9 ± 0.4	<pre>&gt;60, &lt;13.2</pre>	$64 \pm 4$ , 12.8 $\pm 0.8$				
Chemical activation	~ 90 kcal/mol <sup>c</sup>	59-60, <sup>d</sup>	59-60, <sup>d</sup>	57, 	•••	10			
Flow pyrolysis	620-770	•••		38, 9.7 <sup>e</sup>	•••	32			
Flow pyrolysis	640-800			34, 9.9 <sup>e</sup>	 	33			

<sup>a</sup>Values are for the HCl molecular elimination reaction.

<sup>b</sup>Determined from the yield of vinyl chloride.

<sup>c</sup>Initial energy constant.

<sup>d</sup>59 kcal/mol is for the four-centered elimination and 60 kcal/mol for the three-centered elimination reaction threshold.

<sup>•</sup>Determined from the total HCl production rate.  $CCl_2CH_2$  was the major product and is primarily derived from radical chain reaction.

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laser pulse are even smaller, and have a negligible effect on the rate constants derived.

For the study of thermal pyrolysis kinetics it is essential that chemical reaction takes place under thermal conditions. The vibrational excitation delivered by the laser must be thermalized on a time scale short compared to the 5-10  $\mu$ s time scale of gas expansion and chemical reaction, Figs. 6 and 9. The vibration  $\rightarrow$  vibration (V - V) energy transfer between a highly excited  $SiF_4$  molecule and a cold reactant or another  $SiF_4$  molecule should occur at greater than one tenth the gas kinetic collisional rate.<sup>20,21</sup> Since there is no IR fluorescence peak or inflection during the laser pulse (Fig. 2), the laser-pumped mode of  $SiF_4$  is relaxed in less than 0.4  $\mu$ s risetime of the IR detection. For each reactant there are several vibrational modes with frequencies close enough to those of  $SiF_4$  to make near-resonant  $V \rightarrow V$  transfer likely. Vibration  $\rightarrow$  translation  $(V \rightarrow T)$ energy transfer rates in polyatomics are usually determined by the V - T transfer rate of the lowest frequency vibrational mode,<sup>22</sup> 260 cm<sup>-1</sup> for SiF<sub>4</sub>. From the Lambert-Salter  $plot^{22}$  V - T relaxation is estimated to occur in 65 collisions. The even lower frequencies of the reactants will speed up the overall relaxation and prevent overheating of the reactant vibrations. Complete thermalization of the absorbed energy should occur within about 1  $\mu$ s at 6 Torr. While this is a bit too close to the 5-10  $\mu$ s time scale of the chemical reaction for complete comfort it is important to note that the yields of EtCl and 111-TCE at 25 Torr agreed well with those at 6 Torr (Fig. 3 and Table I).

In the process of heating the gas mixture, direct, nonthermal multiphoton dissociation (MPD) of the sensitizer, reagent, or product molecules must be carefully avoided. Significant dissociation of  $SiF_4$  by MPD is not anticipated even at the highest fluence,  $1.7 \text{ J/cm}^2$ , used for pyrolysis. SiF<sub>4</sub> has a bond energy of 137 kcal/ mol.<sup>23</sup> The average number of photons absorbed per  $SiF_4$  molecule  $\langle n \rangle$  in the irradiation column was measured to be about 13 at 1.7 J/cm<sup>2</sup>. For SF<sub>6</sub>, which has a dissociation energy 44 kcal/mol lower, the MPD yield is < 0.01% for  $\langle n \rangle \approx 13$ .<sup>24</sup> Furthermore, no fluorinated hydrocarbon products were detected. Of the reagent and product molecules only ethylene and vinyl chloride absorb at 1027.4 cm<sup>-1</sup>. The threshold for MPD of vinyl chloride at the strong 940 cm<sup>-1</sup> band was estimated<sup>25</sup> to be  $20-40 \text{ J/cm}^2$ . Therefore irradiation at the weaker 1030 cm<sup>-1</sup> band with 1.7 J/cm<sup>2</sup> could not cause dissociation. For ethylene the MPD threshold close to the 950 cm<sup>-1</sup> band center was estimated<sup>26</sup> to be about 20 J/  $cm^2$ . At 1.7 J/cm<sup>2</sup> irradiation on the shoulder of the R branch could not cause dissociation of ethylene. Thus MPD does not contribute to any of the observed yields in this work

# B. Simple analysis of a limiting case

McMillen *et al.* have analyzed their laser pyrolysis experiments using a simple, approximate, linear equation to solve for the unknown activation energy and Afactor.<sup>9</sup> Their analysis is appropriate for a cylinder of gas heated to a uniform temperature  $T_m$  surrounded by gas at ambient temperature. Since the boundary is a discontinuous step, the gas dynamics are governed by shock wave propagation. The cylinder of hot gas expands and cools as a rarefaction wave moves in from the initial shock front. The reacting volume thus shrinks with time but remains at a constant high temperature. If the fraction of molecules reacted F is small, then  $F = k(T_m)\overline{\tau_r}$ , where  $\overline{\tau_r}$  is the average time during which a molecule remains hot. Then

$$\log F_{u} = \log A_{u} + \left(1 - \frac{E_{a_{1}u}}{E_{a_{s}s}}\right) \log \overline{\tau}_{\tau}$$
$$- \frac{E_{a_{1}u}}{E_{a_{s}s}} \log A_{s} + \frac{E_{a_{1}u}}{E_{a_{s}s}} \log F_{s} . \tag{9}$$

Thus the slope of a log-log plot of the fraction of unknown decomposed  $F_u$  versus standard  $F_s$  gives the activation energy ratio  $E_{a,u}/E_{a,s}$ ; the intercept gives the A factor. If this analysis is applied in Fig. 5, the activation energy and A factor derived from the curve for cis-dichlorethene are  $E_{\mu} = 57.7$  kcal/mol and log. A = 13.7 for  $10 < \overline{\tau_r} < 30 \ \mu s$ . The curve was produced by the gas dynamics program from  $E_a = 58.5$  kcal/mol and  $\log A = 14.1$ . Here the standard and unknown are nearly identical and no analysis can be far wrong. For the 1, 1-dichloroethene curve produced by the gas dynamic model with  $E_a = 27$  kcal/mol and log A = 6.9 the simple analysis underestimates  $E_a = 24.3$  kcal/mol and gives log A = 6.6 or 6.3 for  $\overline{\tau}_r$  = 10 or 30  $\mu$ s, respectively. The unknown and standard are badly mismatched and the relative yields depend strongly on the exact temperature-time profile. For 111-TCE in Fig. 4 the simple analysis gives  $E_a = 48.5 \pm 2.1 \text{ kcal/mol}$  and log  $A = 13.2 \pm 0.4$  rather than the  $49.5 \pm 1.5$  kcal/mol and  $13.1 \pm 0.3$  used to generate the curves. If 111-TCE is taken as the standard,  $E_{a,s} = 49.5$  kcal/mol, then Eq. (9) gives  $E_{a,\mu} = 58.6$  kcal/mol for EtCl rather than 57.4 kcal/mol. The source of these differences is discussed in detail in Sec. IV of Ref. 9(a).

### C. T(r, z, t) and the temperature standard

There are modest differences between the temperature distributions of the experiment and of the gas dynamic model (Secs. IV A and IV B). The simple model (Sec. B) requires a uniformly heated cylinder, which is substantially different from both. Nevertheless Eq. (9) allows reasonably accurate  $E_a$  and A values to be derived. Thus only an approximate knowledge of the dependence of temperature and density on spatial coordinates and time is needed; the temperature standard compensates well for the differences between the gas dynamic calculation and experiment.

It is clear from Fig. 1(b) that a substantial fraction of the molecules in the reacting zone is at temperatures lower than the center-line temperature. It is equally clear that this radial profile is experimentally uncertain. The simple form of the analysis in Sec. V D suggests that a laser beam with a perfectly uniform intensity and sharp edges be used. This situation can be approximated by overdriving the laser medium and forcing high order transverse modes to fill the entire cavity. Unfortunately, this produces a complicated intensity distribution with small, very hot spots. This problem is only partially mitigated by saturation of the sensitizer absorption. A smoothly varying intensity profile produced by careful aperturing of the beam should produce more reliable results.

The laser beam was significantly attenuated by the sample in these experiments (Sec. III A). The effect of temperature drop along the z axis, neglected in the gas dynamic model, can be estimated. For simplicity the radial and temporal variation of temperature is ignored; thus Eq. (9) is exact. For a linear temperature decrease from  $T_i$  at the entrance window to  $sT_i$  at the exit window z = L, the product yield is,

$$F = \int_0^L \tau_r A \exp\{-[E_a/RT][L/(L-sz)]\} dz .$$
 (10)

For the extreme case of  $E_{a,s} = 60 \text{ kcal/mol and } A_s = 10^{13} \text{ s}^{-1}$ ,  $E_{a,u} = 30 \text{ kcal/mol}$ , and  $A_u = 10^7 \text{ s}^{-1}$ ,  $T_i = 1100-1400 \text{ K}$  and s = 0.75, the slope of the log  $F_u$  vs log  $F_s$  plot is 0.515 instead of 0.500, and the  $E_{a,u}$  derived is only 0.9 kcal/mol higher than the 30 kcal/mol value used. The effect, as should be qualitatively clear, is much smaller than that of the radial variation of temperature.

The pulse-to-pulse fluctuation of laser energy may cause error in the  $E_a$  and A determined. A simple analysis using Eq. (9) shows that even with 1/3 of the pulses having energy 10% higher than the average and 1/3 being 10% lower the  $E_a$  obtained is only 0.7 kcal/ mol higher than the true value for the extreme case above of  $E_{a,u} = 30$  kcal/mol and  $E_{a,s} = 60$  kcal/mol.

The gas dynamic model gives the correct reaction rate only until the effect of shock front formation propagates back to the heated gas (~30  $\mu$ s). Significant yields (>10% of total yield) may occur beyond this time for activation energies below 40 kcal/mol since the gas cools about ten times less rapidly beyond 40-50  $\mu$ s than before (see Fig. 2 and Ref. 9a, Fig. 5). Treatment of reactions with activation energies near 30 kcal/mol would require a longer time calculation including shock wave propagation.

The models do not account for cooling of the gas by progress of the endothermic chemical reactions. This is computationally painful though certainly quite possible to do. Since in this work 25% dissociation of the chloroethanes  $(\Delta H \approx 15 \text{ kcal/mol})^{11}$  gives only a 20 K cooling, the effect has been left for compensation by the temperature standard.

The temperature standard brings with it the errors and possible problems associated with relative rate constant determinations. Equation (9) shows how any errors in the values of  $E_{a,s}$  and  $A_s$  are transferred to the unknown.

#### D. High pressure limit

The most serious systematic problem with the laser pyrolysis method is operation in the high pressure limit. RRKM calculations for EtCl and for 1, 1- and 1, 2-dichlorethane by Hassler and Setser<sup>18</sup> indicate that at 1500 K pressures in excess of 1 atm are required for the unimolecular decomposition rate to be within 10% of the high pressure limiting rate  $k_{\infty}$ . By contrast several Torr pressure is calculated to be sufficient at 600 K. Two values of transition pressure  $P_{1/2}$  have been reported for EtCl, 2.8 Torr at 521 K<sup>27</sup> and 0.15 Torr at 439 K; 28 both are higher than the calculated value  $P_{1/2} \approx 10^{-1}$  Torr at 600 K. An earlier report that at 922 K,  $k(20 \text{ Torr}) = 0.8 k_{\infty}$  agrees well with the calculation.<sup>29</sup> Hassler and Setser's calculation predicts  $k/k_{\infty}$ =0.8-0.9 for the normal pressure used here and gives about the same ratios for the mono and the dichloroethanes." The experimental pressure must be well above  $P_{1/2}$  since the EtCl pyrolysis yield data at four times normal pressure  $[(\bullet)$  in Fig. 3] fall nicely for % dissociation versus laser pulse energy curve and are certainly not a factor of four above. The higher pressure point for 111-TCE yield versus EtCl yield  $[(\bullet)$  in Fig. 4] also falls on the curve. It should also be noted that the similarity of unknown and standard insures that the rate ratios will be much closer to the high pressure limit than the rates themselves. Ideally studies should be made at several pressures of a chemically inert buffer gas. The buffer should be an efficient energy transfer partner in collisions with activated molecules (to reach the high pressure limit), it should have a fast  $V \leftrightarrow R$ , T relaxation rate (to insure thermalization in less than 1  $\mu$ s and it should have a small heat capacity (to improve the cooling by expansion and to require less laser energy for heating).

#### E. Heterogeneous reaction

One of the great virtues of sensitized laser pyrolysis experiments is that there are no hot surfaces to catalyze inhomogeneous reaction. There are, however, hot molecules in contact with the surfaces (NaCl) through which the laser beam enters and exits the sample gas. The reflection of the shock wave at the cylindrical walls of the cell produces significant heating if the cell diameter is not sufficiently larger than the laser beam diameter. The experiments in the short cell on 112-TCE (Table II, S-I, and Fig. 5 points labeled s) tested the effect of the NaCl window surfaces by decreasing the volume fourfold relative to that surface. The yields of cis- and trans-dichlorethene and of vinyl chloride fall on the curves for the long cell. The 1, 1-dichlorethene yield decreases by about  $2 \times$  near 1300 K and about 5×near 1100 K.

There should be little or no effect of cold surfaces on the unimolecular decomposition of stable molecules in a hot gas. Thermal accommodation should occur before catalytic decomposition. However, surfaces may be expected to trap radicals and promote radical-radical recombination with a consequent shortening of radical reaction chains. Reactions of radicals trapped on surfaces with molecules (perhaps hot) from the gas must also be considered. However, in this study polymerization reactions were not seen. Even at the highest laser energies no deposit was formed where the laser beam passed through the cell windows.

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# VI. REACTION RATES AND MECHANISMS

The unimolecular decompositions of alkyl halides have been studied in thermal reactors, in shock tubes, and by chemical activation. The homogeneous reaction of EtCl is known to be simple molecular elimination, <sup>19,30</sup>

$$C_2H_5Cl \rightarrow C_2H_4 + HCl \quad (11)$$

Other monochloroalkanes and 1, 1-dichloroethane have been shown to primarily eliminate HCl.<sup>30</sup> Another class of molecules, including TCE's is found to react primarily by radical chain propagation in thermal reactors.<sup>30-33</sup> Sensitized laser pyrolysis is biased against the observation of radical chain reactions because of the high temperature and short reaction time. The higher temperature increases the rates of molecular elimination and radical chain initiation with respect to those of chain propagation. The consequent higher radical concentrations also increase termination rates with respect to chain propagation rates.

In thermal reactors homogeneous chemistry is often obscured by heterogeneous reactions. Even with the optimum surface preparation techniques, the rates of homogeneous free radical chain reactions are extracted with difficulty. In sensitized laser pyrolysis, the chain initiation kinetics are well defined just as are the molecular elimination kinetics. However, if most of the chains are not terminated homogeneously while the gas is near its maximum temperature, analysis of the overall kinetics requires a complete knowledge of the chain reaction rate constants versus temperature and of T(r, t) until the radicals are completely gone.

#### A. 1, 1, 1-Trichloroethane

The pyrolysis of 111-TCE in a thermal reactor gives both molecular and radical decompositions<sup>31</sup>:

$$CCl_{3}CH_{3} \rightarrow CCl_{2}CH_{2} + HCl , \qquad (12)$$

$$- CCl_2CH_3 + Cl , \qquad (13)$$

$$Cl + CCl_3CH_3 \rightarrow CCl_3CH_2 + HCl$$
, (14)

$$CCl_3CH_2 \rightarrow CCl_2CH_2 + Cl$$
 (15)

In the EtCl/111-TCE mixture studied here the radical chain propagation, [Eqs. (14) and (15)] is stopped by EtC1:

$$Cl + C_2 H_5 Cl \rightarrow CH_3 CHCl + HCl ; \qquad (16)$$

 $k_{16}$  is 30-40 times faster than  $k_{14}$  for 1400-1100 K.<sup>34,35</sup> CH<sub>3</sub>CHCl does not dissociate without an H-atom transfer occurring first.<sup>30</sup> Radical-radical reactions of CCl<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CHCl finish the radical chemistry:

$$CH_3\dot{C}HC1 + \dot{C}C1_2CH_3 - CH_3CH_2C1 + CC1_2CH_2 , \qquad (17a)$$

$$\rightarrow CH_2CHCl + CHCl_2CH_3$$
, (17b)

$$2CH_3CHCl - CH_3CH_2Cl + CH_2CHCl , \qquad (18)$$

$$2CCl_2CH_3 \rightarrow CHCl_2CH_3 + CCl_2CH_2 . \tag{19}$$

Since the concentrations of CCl<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CHCl are about equal, comparable amounts of CCl<sub>2</sub>CH<sub>2</sub> and CH<sub>2</sub>CHCl should be produced. The overall reaction produced CCl<sub>2</sub>CH<sub>2</sub> with less than 2% vinyl chloride, thus

reaction (13) is 1.5-2 orders of magnitude slower than reaction (12). The activation energy of  $49.5 \pm 1.3$  kcal/ mol and  $\log A$  of 13.1±0.3 derived from Fig. 4 applies to reaction (12). The decrease in  $E_a$  from EtCl (57.4 kcal/mol) to CHCl<sub>2</sub>CH<sub>3</sub> (53.5 kcal/mol)<sup>18,19</sup> to 111-TCE is normally observed upon  $\alpha$  chlorination.<sup>19</sup> The results  $(E_a = 54 \text{ kcal/mol}, \log A = 14)$  of Barton and Onyon<sup>31</sup> using a radical inhibitor (Table IV) were obtained over a temperature range of only 678-715 K. Their measured rates are fit well enough by  $E_a = 51$  kcal/mol and log A = 13.1. Since the radical yield from reaction (13) is small and increases relative to the molecular yield as temperature increases (Table I), the activation energy for Eq. (13) must be significantly greater than 50 kcal/ mol.

#### B. 1, 1, 2-Trichloroethane

Unimolecular elimination of HCl from 112-TCE gives three distinguishable products:

$$CHCl_2CH_2Cl \rightarrow cis - CHClCHCl + HCl , \qquad (20)$$

$$- trans - CHC1CHC1 + HC1$$
, (21)

$$- CCl_2CH_2 + HCl . \qquad (22)$$

(02)

The most probable radical initiation reaction is

$$CHCl_2CH_2Cl \rightarrow CHClCH_2Cl + Cl , \qquad (23)$$

$$CHC1CH_2Cl \rightarrow CH_2CHCl + Cl .$$
 (24)

Dissociation of C(1)-Cl is not expected<sup>36</sup> and in any case gives the same products as reaction (24). The uninhibited radical chain propagates by

$$C1 + CHCl_2CH_2C1 \rightarrow CHCl_2CHC1 + HC1 , \qquad (25a)$$

$$- CCl_2CH_2Cl + HCl , \qquad (25b)$$

$$CHCl_2CHCl \rightarrow trans - or cis - CHClCHCl + Cl, (26)$$

$$CCl_2CH_2Cl \rightarrow CCl_2CH_2 + Cl$$
, (27)

and terminates by

$$C1 + CCl_2CH_2Cl - CCl_2CHCl + HCl , \qquad (28)$$

$$C_1 + CHC_{1_2}CHC_{1_2} - CC_{1_2}CHC_{1_2} + HC_{1_2}.$$
(29)

The radical initiation reactions yield vinyl chloride and all three dichloroethene isomers. Since  $k_{25a}$  and  $k_{25b}$  were determined to be similar, <sup>35</sup> the radical reaction yield of CCl<sub>2</sub>CH<sub>2</sub> and of trans - and cis-CHClCHCl should be comparable. The trichloroethene from the chain propagation was not measured quantitatively. In the presence of EtCl, the chain is inhibited by the faster reaction (13), though less completely than in 111-TCE, and terminates through reaction (18) and

$$C1 + CH_3CHC1 - CH_2CHC1 + HC1 , \qquad (30)$$

In both the initiation and the termination of the proposed radical reactions for the EtCl/112-TCE mixture, one vinyl chloride and no dichloroethenes are produced.

Cis- and trans-dichlorethene are the major products of the sensitized laser pyrolysis, Table II and Fig. 5. Their yields are insensitive to the presence or absence of radical inhibitors (EtCl or toluene) and to changes in cell geometry. These are simple products of unimolecular elimination of HCl. The chemical activation ex-

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periments of Kim and Setser<sup>10</sup> show that the energy thresholds for three-center (H and Cl from the same carbon) and four-center elimination are equal to within 1 kcal/mol. The laser pyrolysis experiments therefore measure a single activation energy. Table V shows excellent agreement between laser pyrolysis and chemical activation results for 1, 2-dichloroethene production.

1, 1-dichloroethene may be produced both by molecular elimination of HCl [reaction (22)] and by propagation of the radical chain [reaction (25b) and (27)]. The appearance of vinyl chloride demonstrates that radicals are formed. The fivefold increase of 1, 1-dichloroethene upon removal of the EtCl inhibitor at ~1300 K (7% EtCl dissociation) also indicates the importance of the radical channel. The rate parameters derived from the 1, 1-dichloroethene line,  $E_a = 27 \pm 5 \text{ kcal/mol}$  and  $\log A = 6.9 \pm 0.8$ , are completely wrong for the molecular reaction (22) by itself. Unfortunately, these parameters cannot safely be interpreted to give information on the radical channel rate constants either. That reaction (22) is at least 70 times slower than reaction (20) plus reaction (21) near 1300 K can be partly ascribed to the 7 times smaller statistical weight of 112-TCE geometries leading to CCl<sub>2</sub>CH<sub>2</sub> product. It must also be the case, as expected from generalizations of other HCl elimination data<sup>19,30</sup> and from the lowering of the C-Cl bond energy by  $\alpha$  chlorination, <sup>36</sup> that the activation energy is higher by some 5 kcal/mol or more. This is not consistent with the lower threshold from chemical activation results, Table V. However, in that work the production of CCl<sub>2</sub>CH<sub>2</sub> from 111-TCE had to be subtracted from the measured total and the radical reaction was completely neglected. In thermal reactor studies<sup>32,33</sup>  $CCl_2CH_2$  is the dominant product and the overall rate constant for HCl production Table V is appropriate for a radical chain process and cannot apply to reaction (22).

The vinyl chloride product results entirely from radical reactions. Reaction (24) produces one  $CH_2CHCl$ for each radical dissociation [reaction (23)]. Chain termination by EtCl, reactions (18) and (30), produces one  $CH_2CHCl$  per radical pair terminated. The  $CH_2CHCl$ yield is increased by a factor closer to 5 than 2 upon addition of EtCl, suggesting that reactions

$$CH_3CHCl + CHCl_2CH_2Cl \rightarrow CHCl_2CH_3 + CHClCH_2Cl$$
, (31a)

$$CHC1CH_2C1 - C1 + CH_2CHC1 , \qquad (32)$$

$$CHCl_2CH_2 \rightarrow Cl + CH_2CHCl$$
, (33)

produce  $CH_2CHCl$ . The small amount of  $CHCl_2CH_3$ , which came out late and broad on the GC trace, was difficult to detect. For the three experiments without EtCl the vinyl chloride yield should give precisely the radical initiation, reaction (23), yield. The activation energy derived,  $64 \pm 4$  kcal/mol, rests unsteadily on three points determined for a decidedly minor product. More thorough chemical studies are needed to confirm the radical reaction mechanism and subsequently the initiation rate. Nonetheless, it is clear that unimolecular decomposition to radicals has a high A factor (Table V) and an activation energy significantly higher than 60 kcal/mol, as expected from previous studies of C-Cl bond dissociation.<sup>36</sup>

# VII. CONCLUSIONS

Sensitized laser pyrolysis is a clean, efficient method for the measurement of high temperature homogeneous gas phase reaction rates. The application to molecular elimination reactions with activation energies in the range 50-60 kcal/mol has been demonstrated here. This work and that of McMillen *et al.*<sup>9</sup> show that considerably higher and lower  $E_a$ 's may be studied. Single bond rupture reactions which produce radicals may also be studied if chain reactions can be quantitatively controlled. Laser heating and pyrolysis should also provide high temperature samples in which fast reactions may be studied by laser flash kinetic spectroscopy.

The experimental arrangement is simple and flexible; there are enough physical variables under experimental control that a wide range of reactions may be studied. Consequently, for any given experiment the sample gases, the cell and the laser must be selected carefully in advance.

SiF<sub>4</sub> is an excellent but not unique choice of sensitizer. It provides a range of absorption strengths, some very large, for different CO<sub>2</sub> laser lines. Its  $V \rightarrow V$  and  $V \rightarrow R$ , T relaxation rates are fast and it is relatively inert chemically at high temperature even in the presence of  $CO_2$  laser radiation. A temperature standard should have  $E_a$  and A values within about  $\pm 10$ kcal/mol and a factor of 10, respectively, so that accurate and useful data may be collected over a wide temperature range. The standard should not interfere (unless in a well-defined, useful manner) chemically with the unknown reaction. In many cases addition of a buffer gas<sup>9</sup> will be desirable in order to ensure measurement of unimolecular rate constants in the high pressure limit. The buffer, too, must be chemically inert; it should also have a small heat capacity in order to maximize cooling upon expansion and any vibrations contributing to the heat capacity must relax on a submicrosecond time scale (or not at all). These conditions are best satisfied by the rare gases.

The geometry of the heated zone and its evolution in time are governed by the sample cell and laser as well as the sample gases. A laser beam with a cylindrically symmetric, and well-known intensity distribution is needed. In most cases the cell diameter should be much larger than the laser beam diameter (5 or 10 times) and the cell length much shorter than the absorption length of the gas for the laser light. Propagation of the beam off center may be useful to prevent significant reheating of the gas by shock waves reflected from the walls.<sup>9</sup> In circumstances which require a longer heating time scale it may be desirable to heat the entire cell volume.<sup>9a</sup>

The simple analytical data reduction of McMillen et al.<sup>9a</sup> may be used if the laser intensity profile is nearly uniform over the irradiated volume and  $E_a$  and A are quite close for the unknown and standard. Otherwise it is necessary to treat to first order the gas dynamic development of the gas temperature in the cell as a function of position and time. The computational analysis presented here will be sufficient for most purposes. When free radicals are produced which can chain react after the initial cooling to give the products being studied, quantitative data analysis will probably not be practical. The chains must be terminated rapidly at the high temperature.

As with all methods in chemical kinetics, considerable care and chemical ingenuity will be required in the application of laser pyrolysis. Nonetheless, it is reasonable to expect that much information of value for basic high temperature chemistry, for combustion, for hydrocarbon conversions, and for materials processing will be obtained using laser pyrolysis.

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