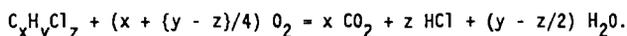


HIGH TEMPERATURE PYROLYSIS OF C₂-CHLOROCARBONS

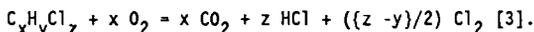
Barry Dellinger, Philip H. Taylor, and Debra A Tirey
Environmental Sciences Group
University of Dayton Research Institute
300 College Park
Dayton, Ohio 45469

Environmental concern over the safe disposal of toxic organic wastes has led to the emergence of the field of incineration as one of the more controversial and exciting applications of the combustion sciences [1]. A significant fraction of hazardous organic wastes are chlorinated hydrocarbons (CHCs) [2]. The presence of chlorine brings a number of complications to the understanding of the incineration process beyond that usually addressed in combustion research.

For a CHC designated by C_xH_yCl_z, the overall equilibrium combustion stoichiometry can be defined for y > z:



For y < z, the formation of molecular chlorine (Cl₂) must be considered:



Numerous full-scale tests and thermodynamic calculations have clearly indicated that the nature and quantity of organic compound emissions from toxic waste incinerators are not thermodynamically controlled, actual emissions being greater than 10⁶ times that predicted from equilibrium [4]. Due to their toxicity, there is particular concern over the emissions of chlorinated products of incomplete combustion (PICs).

Simple conceptual and more complex computer models suggest that kinetic factors including temperature, time at temperature, and reaction atmosphere in the post-flame, or thermal zones, of full-scale incinerators control the emission of organic compounds from such systems [5-7]. These models further indicate that hazardous wastes entering the flame zone are completely oxidized and only the small fraction that does not pass through this zone may undergo incomplete reaction. Various excursions may cause a small fraction of the waste to circumvent the flame zone [6,7]. Once in the post-flame zone, high-temperature thermal decomposition kinetics control the rate of waste destruction and the rate of formation and destruction of organic byproducts.

Emissions from full-scale incinerators are generally several orders of magnitude higher than those calculated using rate parameters obtained from laboratory-scale experiments simulating the oxidative reaction conditions in the post-flame zones of such systems [6,8]. This result suggests that oxygen-starved reaction pathways may be responsible for most organic emissions since the rate of destruction of the parent is significantly slowed and the rate of organic byproduct formation is substantially increased [8-10]. Thus, although incinerators operate under oxygen-rich conditions, oxygen-starved pockets may exist in the system due to locally poor mixing conditions. Consequently, laboratory-scale flow reactors appear to be particularly well suited for the evaluation of the fuel-rich thermal decomposition behavior of CHCs.

To build a database of the possible reaction mechanisms involved in the formation of CHC emissions under oxygen-starved reaction conditions, we have initiated a program to evaluate the high-temperature thermal decomposition behavior of different classes of CHCs using fused silica flow reactor thermal instrumentation. Our initial study involved an analysis of the simplest of CHCs, the chlorinated methanes, as pure compounds and as mixtures of varying elemental composition [11-13]. The most important finding was the observation of significant yields (≥ 0.1 mole %) of higher-molecular-weight, thermally stable, unsaturated CHCs, e.g., hexachlorobenzene (C_6Cl_6), for H:Cl ratios less than 1.0 under oxygen-starved ($\phi = 3.0$) reaction conditions.

As a consequence, we have begun a study of C_2 -CHCs, with particular interest on the analysis of pentachloroethane (C_2HCl_5), hexachloroethane (C_2Cl_6), trichloroethylene (C_2HCl_3), tetrachloroethylene (C_2Cl_4), and dichloroacetylene (C_2Cl_2). These saturated and unsaturated C_2 -chlorocarbons have been observed as intermediates in the high-temperature oxygen-starved decomposition of chloroform, carbon tetrachloride, and chloromethane mixtures (H:Cl = 0.2) [11,12]. The formation of these compounds has been hypothesized to be an important step in reaction channels leading to chlorinated aromatics and chlorinated polynuclear aromatic hydrocarbons (PNAs) [11-13]. These high-molecular-weight organic compounds have been detected in stack gases of full-scale incineration systems. Such emissions are unacceptable because of their potential toxic effects on human health and the environment.

EXPERIMENTAL

Kinetic studies were conducted using various isothermal fused silica flow reactors equipped with in-line GC and GC/MS analytical systems [14,15]. These closed continuous thermal instrumentation systems permit quantitative data to be obtained expediently without errors associated with batch sampling and lack of true quantitative transport. A block diagram of one such system, the System for Thermal Diagnostic Studies (STDS) is shown in Figure 1a; a cross-section view of the thermal reactor is shown in Figure 1b.

The reactor is geometrically configured as a helical tube 500 cm long with an internal diameter of 0.17 cm. The geometry of the reactor produces a laminar gaseous flow which exhibits a nearly square wave thermal pulse with a very narrow, near-Gaussian residence time distribution, thus making this reactor ideally suited for reaction kinetic studies. The thermal reactor consists of a relatively inert, high-temperature fused silica material. However, one of the compromises of the precise time/temperature control of this reactor is the corresponding large surface to volume ratio (23.5 cm^{-1}). Using gas collision theory, we have evaluated the relative importance of heterogeneous surface decomposition as compared to homogeneous thermal decomposition for several hydrocarbons and CHCs for which experimental rate data have been previously estimated. Activation energies for heterogeneous decomposition were estimated by assuming the wall reaction rate represented 100% of the experimental reaction rate at a temperature corresponding to the onset of chemical reaction.

Ratios of rate constants and destruction efficiencies (DE) were calculated at temperatures corresponding to 50%, 90%, and 99% decomposition for 2 hydrocarbons and 6 CHCs. With the exception of benzene (C_6H_6) and dichloromethane (CH_2Cl_2), the results indicated that heterogeneous decomposition accounted for less than 10% of the measured decomposition at overall decomposition levels of 90 and 99%. These calculations imply that, at low temperatures, wall collisions may initiate

the radical chain processes that likely dominate CHC decomposition. However, at higher temperatures, due to the much larger activation energies for homogeneous (-55.0 to -100 kcal/mole) as compared to heterogeneous (-25.0 to 35.0 kcal/mole) decomposition, gas-phase reactions dominate initiation processes and radical chain processes in general.

Following thermal exposure, the effluent is quenched in a heated (250°C) fused silica transfer conduit which connects the reactor to the thermal trapping/gas chromatographic assembly. Leading to and from this assembly are separate, thermally programmable transfer paths designed to produce nonreactive quantitative transport of organic substances. Migrating effluent species from the reactor are then trapped at -60°C and axially focused at the head of the GC column for subsequent analysis.

In this manuscript, we report the results of two different sets of experiments. Pure C_2Cl_4 thermal decomposition was studied under oxygen-starved conditions. The thermal decomposition behavior of the chlorinated ethanes and chlorinated ethenes was evaluated in multi-component organic mixtures of constant elemental composition (C_2H_nCl) under oxygen-starved conditions. The constant elemental composition produces in an essentially invariant radical pool which allows the evaluation of stability of the CHCs under realistic conditions. The experimental approach will be presented in more detail in future publications.

Results

The thermal stability data for the chlorinated ethane and chlorinated ethene mixture experiments are summarized in Figures 2 and 3 and Table 1. For the chlorinated ethanes, three initiation pathways are plausible: (1) concerted 4-center elimination of HCl, (except for C_2Cl_6); (2) carbon-chlorine bond rupture; and (3) carbon-carbon bond rupture. In addition, the reactive radicals formed by the latter two mechanisms can attack the parent compound and abstract available hydrogen atoms, resulting in an apparent decomposition rate as much as 2-3 times greater than the unimolecular initiation rate. In all cases, a major product is expected to be the olefin corresponding to loss of HCl by one of these mechanisms. This is even the case for C_2Cl_6 , with a hypothetical mechanism involving C-Cl β -bond rupture following initial C-Cl bond rupture. Our mixture studies generally result in a faster rate of decomposition compared with pure compound flow reactor and shock tube studies reported in the literature, presumably due to secondary chain reactions [16-20]. Important decomposition rate parameters which include data reported in the literature and thermochemical estimates are given in Table 2. Both theory and experiment suggest that for the homologous series, there is a trend of decreasing stability with increasing chlorination. Carbon-carbon and carbon-chlorine bond rupture become more favorable with increased chlorination due to weakening of these bonds while the rate of HCl elimination is less sensitive. When comparing isomers, (e.g., 1,1,1-trichloroethane vs 1,1,2-trichloroethane), the isomer with more chlorines on a single carbon decomposes more rapidly. This may be influenced by weaker C-Cl and C-C bonds and a greater reaction path degeneracy for HCl elimination.

The chlorinated ethylenes are 200-300°C more stable than the chlorinated ethanes. These compounds increase in stability as chlorine substitution increases (see Table 1 and Figure 3). This suggests a dominant decomposition mechanism involving hydrogen atom abstraction by reactive radicals such as Cl atoms. C_2Cl_4 , which contains no H atoms, is the most stable of the series, and decomposition by the

endothermic ($\Delta H_{298}^{\circ} = 27.5$ kcal/mole) pathway of Cl abstraction by Cl to form Cl_2 is not significant at the temperatures of our experiments.

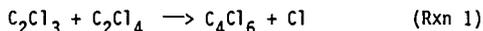
Alternative decomposition pathways for the chloroethenes include HCl elimination and chlorine displacement by hydrogen atoms. Shock tube data from the literature for $\text{C}_2\text{H}_3\text{Cl}$ suggest that HCl elimination is too slow to account for all of the observed rate of destruction [21]. Cl₂ elimination for tetrachloro-ethylene seems even more unlikely due to its greater endothermicity ($\Delta H_{298}^{\circ} = 53.5$ kcal/mole). Cl displacement by H has been experimentally demonstrated to be a viable mechanism for pyrolytic decomposition of chlorinated aromatics and is a potential destruction mechanism for chlorinated olefins [10]. However, the trend of increased stability with increasing chlorine content in our mixture studies does not support this pathway as the principal mechanism of destruction of the chloroethenes. The relative importance of H abstraction and Cl displacement mechanisms for these compounds has not yet been established.

These mixture studies have not addressed product formation; however, previous flow reactor studies of chloroform, carbon tetrachloride, and premixed flat-flame studies of trichloroethylene have shown that chlorinated olefins and olefinic radical species may be key intermediates in the formation of higher-molecular-weight chlorinated aromatic species [11-13,23]. As such, it appears important to study the chemistry of these intermediates more thoroughly.

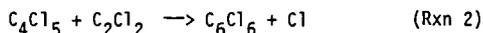
The oxygen-starved thermal decomposition profile of C_2Cl_4 is presented in Figure 4. The results indicate that this compound is very stable ($T_{99}(2) = 980^{\circ}\text{C}$) under the conditions studied with measurable quantities (0.007%) persisting at the highest temperatures studied (1050°C). Of the two compounds detected as PICs, hexachlorobenzene (C_6Cl_6) exhibited the greatest yields (~11% at 950 and 1050°C) and was the most thermally stable. Carbon tetrachloride (CCl_4) was produced in lower yields and was 99.9% destroyed at 950°C . It is probable that C_2Cl_4 and Cl_2 were produced as well in the thermal decomposition experiments; however, mass spectral data acquisition limitations precluded the detection of these products.

Comparison of the results of this pure compound study with previous flow reactor mixture experiments under fuel-rich conditions provides insight into possible C_2Cl_4 decomposition pathways. Under hydrogen-rich mixture conditions, the formation of high yields of C_2HCl_3 was observed indicating the importance of a mechanism involving H displacement of Cl atoms. Under pure compound conditions, the absence of hydrogen precludes such a mechanism. The types of products shown in Figure 4 suggest that C-Cl bond fission followed by reactions of C_2Cl_3 radicals plays important roles in destruction of C_2Cl_4 .

We have previously proposed a mechanism for formation of C_6Cl_6 from chloroform, which involves Cl displacement from C_2Cl_4 (formed as an intermediate from chloroform) via reaction 1 [11-13]:

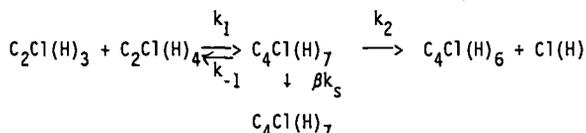


Hexachlorobutadiene (C_6Cl_6) has been shown in our lab to rapidly decompose via C-Cl bond rupture to form the resonance stabilized pentachlorobutadienyl radical (C_5Cl_5) which can then react with dichloroacetylene (C_2Cl_2) to form C_6Cl_6 via reaction 2.

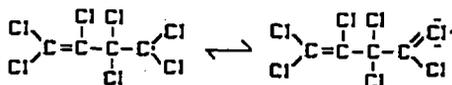


A possible route of formation of CCl_4 is chlorine addition to C_2Cl_4 to form C_2Cl_5 , followed by α -bond fission to form CCl_3 and CCl_2 , which can subsequently recombine with Cl atoms to form CCl_4 . β -bond fission of C_2Cl_5 to reform C_2Cl_4 is likely a faster reaction, and indeed there is evidence for reformation of C_2Cl_4 , as indicated by the knee in the decomposition curve at 950°C (see Figure 4).

We were intrigued by the possibility that reaction 1 may be faster than its hydrocarbon analogue which has been proposed as a key reaction in soot and PNA formation in fuel-rich hydrocarbon flames. [24] The general scheme for activated complex reactions was used to perform a Quantum RRK (QRRK) calculation [25]:



If k_2 is rate-limiting, the stabilization reaction involving the chlorinated species may be facilitated by the following resonance structure



which is not possible for the hydrocarbon analogue. If k_2 is rate-limiting, the chlorocarbon reaction is facilitated by the displacement of chlorine which has a lower bond energy ($D_0(\text{C}-\text{Cl}) \sim 85 \text{ kcal/mole}$) than hydrogen in the hydrocarbon ($D_0(\text{C}-\text{H}) = 108 \text{ kcal/mole}$).

Rate constants for the hydrocarbon reaction were estimated from the literature [25]. The rates for k_1 and k_{-1} were assumed to be the same for both hydrocarbon and chlorocarbon analogues. A_2 was estimated via transition state theory for the chlorocarbon reaction and E_2 was estimated by assuming a linear relationship between activation energy and bond dissociation energy. Using the same rate for k_1 and k_{-1} for the chlorocarbon and hydrocarbon was considered a conservative method of evaluating the effect of chlorine substitution in displacement reactions. One could argue that the chlorocarbon addition step, k_1 , is slower due to the inductive destabilizing effect of chlorine; however, since radicals are not charged species, they do not respond to inductive effects as fully as to electrophilic attack by cations. Thus, we feel that resonance stabilization effects of chlorine may dominate. The results in Figure 5 confirm that the displacement reaction is faster at all temperatures for the chlorocarbon system. This is consistent with our findings in the chloromethanes, where relatively large yields of C_4 and aromatic products were seen from chloroform (CHCl_3) and CCl_4 , but not observed at all from chloromethane (CH_3Cl) and dichloromethane (CH_2Cl_2).

The experimental and theoretical studies presented in this manuscript suggest that chlorinated hydrocarbons may be particularly prone to formation of complex, potentially toxic, reaction byproducts. A systematic, detailed kinetic and mechanistic study of the reactions of these compounds, particularly the C_2 -olefins and acetylenic compounds is indicated.

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TABLE 1

Temperature for 99% Destruction of Chlorinated Ethanes and Chlorinated Olefins in Mixtures at $\bar{t}_r = 2.0$ s, $\phi = 3.0$, $H:Cl = 3.0$

Chlorinated Ethanes		Chlorinated Olefins	
Compound	$T_{99}(2)$ (C°)	Compound	$T_{99}(2)$ (C°)
Chloroethane	620	Chloroethene	770
1,1-Dichloroethane	610	1,1-Dichloroethene	860
1,2-Dichloroethane	680	1,2-Dichloroethene	835
1,1,1-Trichloroethane	545	Trichloroethene	865
1,1,2-Trichloroethane	635	Tetrachloroethene	890
1,1,1,2-Tetrachloroethane	560		
1,1,2,2-Tetrachloroethane	690		
Pentachloroethane	640		
Hexachloroethane	580		

Table 2a. Decomposition Rate Parameters—Chloroethanes

Compound	$\Delta H^{\circ}300$ (kcal/mole) [b]						log k 300					
	C-Ci	C-C	HCl	Elim.	H abst.	(Ci)	C-Ci (1/s) [c]	C-C (1/s) [c]	HCl elim. (1/s) [d]	H abst. by Cl [e]	(cm ³ /mol-s)	
C2H5Cl	82.1	89.3	17.2	-	-	-	15.1-81.8/2.3RT	17.2-89.0/2.3RT	13.5-56.6/2.3RT	13.6-1.5/2.3RT	[29]	
1,1-C2H4Cl2	-	89.5	17.5	-	-	-	16.1-80.0/2.3RT	17.3-89.2/2.3RT	13.5-53.5/2.3RT	13.0-1.9/2.3RT	[29]	
1,2-C2H4Cl2	-	87.6	17.4	-	-	-	16.0-81.5/2.3RT	17.2-87.3/2.3RT	13.6-58.0/2.3RT	13.8-3.1/2.3RT	[29,30]	
1,1,1-C2H3Cl3	-	85.9	12.1	-	-	-	16.4-78.5/2.3RT	17.4-85.6/2.3RT	14.1-54.2/2.3RT	12.4-3.6/2.3RT	[30]	
1,1,2-C2H3Cl3	-	85.5	12.1	-	-	-	16.4-79.7/2.3RT	17.3-85.2/2.3RT	13.1-57.0/2.3RT	13.0-3.1/2.3RT	[29]	
1,1,2-C2H3Cl3 [f]	-	-	14.8	-	-	-	-	-	13.7-58.0/2.3RT	13.2-3.7/2.3RT	[g] [29]	
1,1,1,2-C2H2Cl4	-	83.3	13.1	-	-	-	16.6-78.2/2.3RT	17.4-83.0/2.3RT	14.1-54.0/2.3RT	12.2-2.5/2.3RT	[29]	
1,1,2,2-C2H2Cl4	-	84.7	10.6	-	-	-	17.3-84.4/2.3RT	17.3-84.4/2.3RT	14.1-58.0/2.3RT	12.6-2.5/2.3RT	[29]	
C2HCl5	68.3	76.6	6.7	-11.5	-	-	16.7-68.0/2.3RT	17.5-76.3/2.3RT	14.1-59.7/2.3RT	12.7-3.6/2.3RT	[29]	
C2Cl6	70.0	69.1	NA	NA	NA	NA	16.8-69.7/2.3RT	17.5-68.8/2.3RT	NA	NA	NA	

Table 2b. Decomposition Rate Parameters—Chloroethanes

Compound	$\Delta H^{\circ}300$ (kcal/mole) [b]						log k 300					
	C-Ci	HCl	Elim.	Cl Disp.	H abst.	(Ci)	C-Ci (1/s) [c]	HCl elim. (1/s) [d]	Cl disp. by H	H abst. by Cl	(cm ³ /mol-s)	
C2H3Cl	89.5	23.8	-19.1	-	-	-	14.9-89.2/2.3RT	14.0-69.3/2.3RT	[21]	-	-	
1,1-C2H2Cl2	-	28.8	-15.8	-	-	-	15.7-85.0/2.3RT	14.3-75.0/2.3RT	-	-	-	
1,2-C2H2Cl2	-	28.1	-15.1	-	-	-	15.6-85.0/2.3RT	14.0-75.0/2.3RT	-	-	-	
C2HCl3	-	27.6	-21.5	3.5	-	-	15.9-84.0/2.3RT	14.0-75.0/2.3RT	-	-	-	
C2Cl4	85.3	NA	-21.2	NA	NA	NA	14.7-80.0/2.3RT	[22]	-	-	NA	

Legend:

- [a] Decomposition pathways from left to right are unimolecular C-Cl bond fission, C-C bond fission (chloroethanes only), 4-center HCl elimination, and bimolecular H abstraction by OH, and Cl displacement by H (for the chloroethanes only).
- [b] Thermodynamic data were obtained from one of the following sources:
 1. Reference 27
 2. Reference 20
 3. Reference 28.
- [c] Except where noted, Arrhenius A factors were calculated by transition state theory. Arrhenius Ea's were calculated by subtracting 0.5RT from the reaction enthalpy. In the absence of reaction enthalpies, Ea's were estimated by comparison with similar compounds. For 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, and pentachloroethane, Arrhenius parameters reflect fission of the weaker C-Cl bonds.
- [d] Except where noted, Arrhenius A factors were calculated by transition state theory. Ea's were estimated by comparison with similar compounds.
- [e] Rate coefficients reflect H abstraction from highest chlorinated carbon unless otherwise noted.
- [f] 4-center HCl elimination from 1,1,2-trichloroethane can occur by two pathways, with different reaction enthalpies.
- [g] Beta-H abstraction.

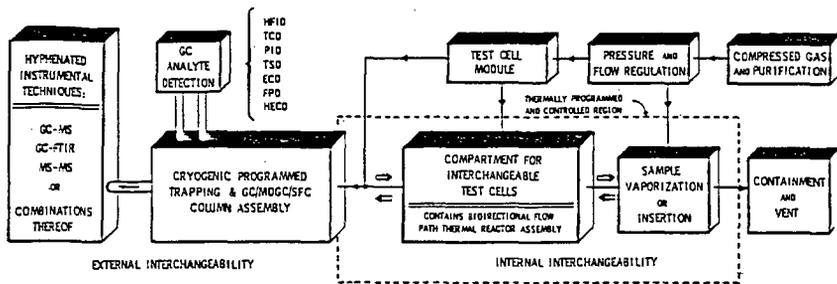


Figure 1a. Schematic Diagram of the System for Thermal Diagnostic Studies.

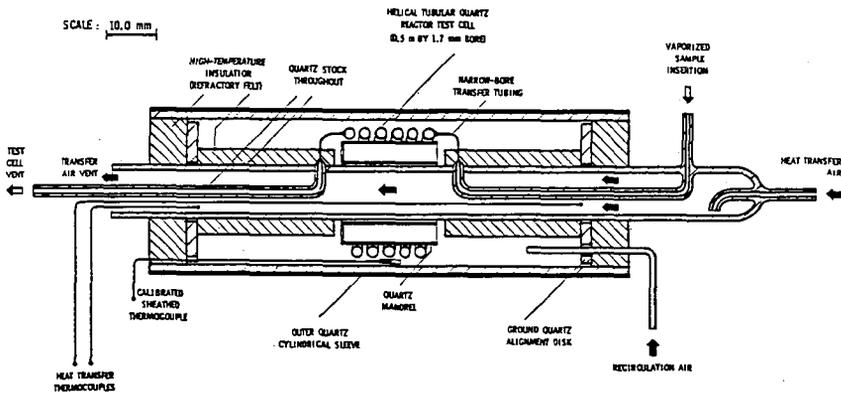


Figure 1b. Cross-sectional schematic of helical tubular reactor.

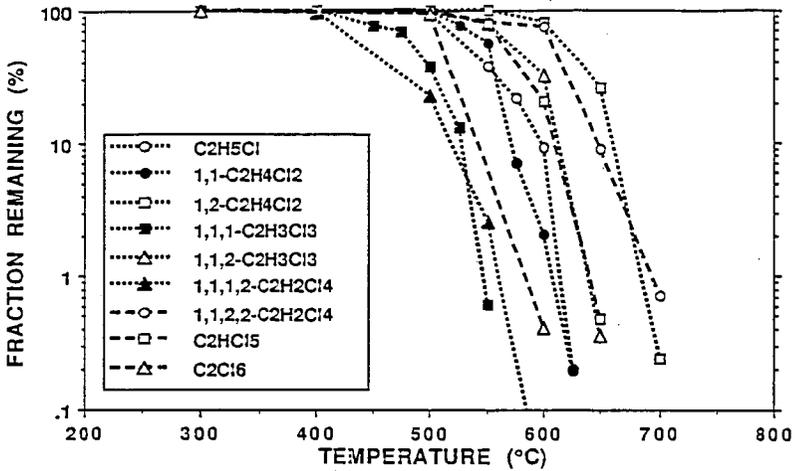


Figure 2. Thermal decomposition curves for the chlorinated ethanes. Fuel/oxygen equivalence ratio = 3.0, mixture elemental composition = C_2H_3Cl , $t_r = 2.0$ s, total organic concentration = 4×10^{-5} moles/ l_3H_3Cl .

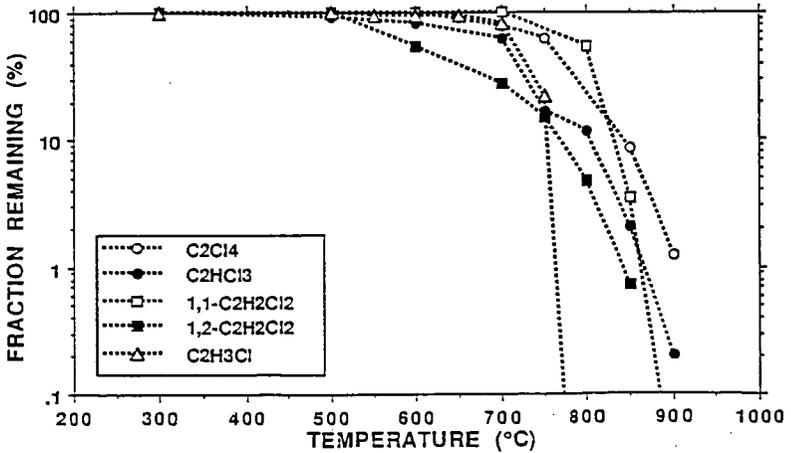


Figure 3. Thermal decomposition curves for the chlorinated ethenes. Fuel/oxygen equivalence ratio = 3.0, mixture elemental composition = C_2H_2Cl , $t_r = 2.0$ s, total organic concentration = 4×10^{-5} moles/L.

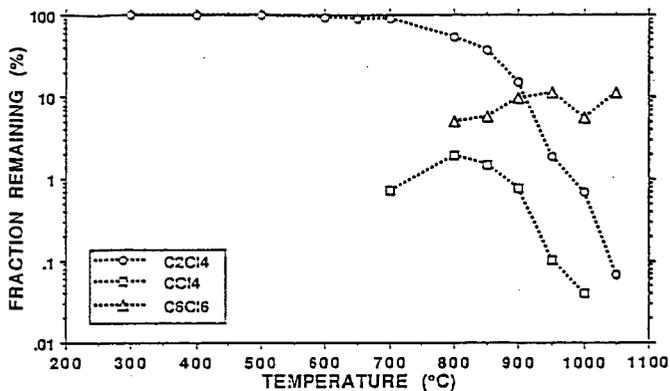


Figure 4. Thermal decomposition profile for tetrachloroethene. Fuel/oxygen equivalence ratio = 3.0, $t_r = 2.0$ s, $[C_2Cl_4] = 4 \times 10^{-5}$ moles/L.

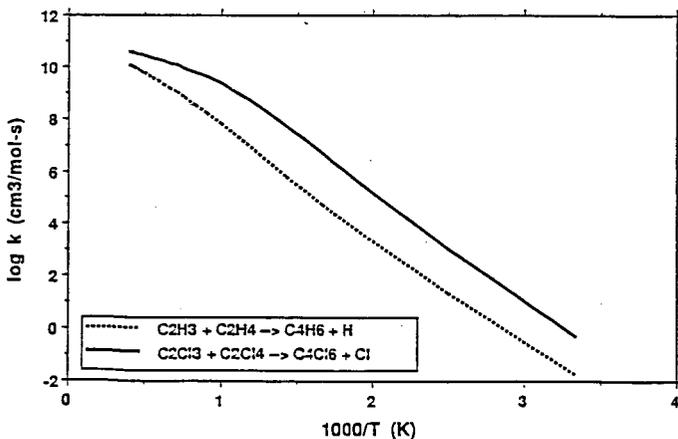


Figure 5. Predicted effect of temperature upon reaction 1 for both hydrogen and chlorine analogues. $P = 1$ atm, $\log A(H) = \log A(Cl) = 11.2$, $E_1(H) = E_1(Cl) = 7.3$, $\log A_1(H) = \log A_1(Cl) = 12.7$, $E_2(H) = E_2(Cl) = 27.8$, $\log A_2(H) = \log A_2(Cl) = 13.1$, $E_2(H) = 38.4$, $\log A_2(H) = 14.5$, $E_2(Cl) = 29.7$; units for rate parameters are cm^3 , mole, s, kcal. $V_{C_4H_7} = 1500$ cm^{-1} , $V_{C_4Cl_7} = 250$ cm^{-1} . Energy transfer media: air (21% O_2 , 79% N_2).