# CHEMICAL KINETIC MODELING OF CHLORINATED HYDROCARBONS UNDER STIRRED-REACTOR CONDITIONS

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## Abstract

The combustion of chloroethane is modeled as a stirred reactor so that we can study critical emission characteristics of the reactor as a function of residence time. We examine important operating conditions such as pressure, temperature, and equivalence ratio and their influence on destructive efficiency of chloroethane and production of other chlorinated products. The model uses a detailed chemical kinetic mechanism that we have developed previously for $C_3$ hydrocarbons. We have added to this mechanism the chemical kinetic mechanism for $C_2$ chlorinated hydrocarbons developed by Senkan and coworkers. Some reactions have been added to Senkan's mechanism and some of the reaction-rate expressions have been updated to reflect recent developments in the literature. In the modeling calculations, sensitivity coefficients are determined to find which reaction-rate constants have the largest effect on destructive efficiency.

## INTRODUCTION

Chlorinated hydrocarbons comprise a significant fraction of hazardous waste. Incineration is a commonly used method to dispose of chlorinated hydrocarbons. Some of the drawbacks of incineration are that the hazardous component may not be completely destroyed, other hazardous components may be produced during the combustion process and both may be released as a pollutants. Release of these hazardous components can potentially cause an incinerator to exceed present or future emission requirements and can raise public concerns about the associated health risks.

In this study, the chemical kinetics of the destruction of chlorinated hydrocarbons are examined. The combustion process is modeled as a perfectly-stirred reactor with the inclusion of detailed chemical kinetics. A perfectly-stirred reactor is a highly simplified physical model in which the hazardous component and oxidizer are assumed to mix very rapidly with combustion products. Practical combustors have highly turbulent regions where the chlorinated hydrocarbon is rapidly mixed with combustion products. Some of the physical and chemical processes occurring in these regions may be simulated as a stirred reactor with chemical kinetics controlling the extend of chlorinated hydrocarbon destruction and the production of any additional hazardous components. Lutz _et_ _al_. [1] have used a turbulent model which includes two stirred reactors to model the production of pollutants in a turbulent, reacting jet.

The numerical model considered allows the examination of a wide range of operating parameters such as temperature, pressure, residence time, and equivalence ratio. All these operating parameters are easily-specified, input parameters in a stirred reactor model. The model allows the examination of operating conditions not easily achievable in experimental studies, particularly high pressure. Our objective is to find conditions which achieve the maximum destruction of the chlorinated hydrocarbon and the minimum production of other hazardous components. Additionally, this study seeks to identify the chemical reactions which control destruction of the chlorinated hydrocarbon.

The chemical kinetic mechanism that we employed is based on one that we developed for $C_3$ hydrocarbons [2,3]. To this hydrocarbon mechanism, we added a submechanism that treats the reactions of chlorinated species and is based on the mechanism of Senkan and coworkers [4]. We modified the chlorinated hydrocarbon submechanism to reflect recent developments in the literature. For example, Fisher et al. [5] have modeled the site-specific abstraction of H-atoms from chloroethane. Tsang [6] has recently reviewed many reactions involving chlorinated species. Gutman and coworkers [7,8] have performed fundamental experimental studies on individual reactions involving chlorinated hydrocarbons.

Much previous work has been performed on the chemical kinetics of chlorinated hydrocarbons. Inhibition of flames by chlorinated hydrocarbons has been investigated [9]. The flame structure of chlorinated hydrocarbons has been experimentally measured and numerically simulated [4,10-12]. The thermal degradation of chlorinated hydrocarbons in a fused silica reactor has been studied by Dellinger [13]. Barat et al. [14] have examined the combustion of methyl chloride under jet-stirred reactor conditions. Koshland and Fisher [15] have performed a chemical kinetics modeling study of chlorinated hydrocarbons under flow reactor conditions and examined the relationships between destructive efficiency, carbon monoxide and other reaction intermediates. All these studies have furthered the development of the chemical kinetic mechanism of chlorinated hydrocarbons.

## NUMERICAL MODEL AND CHEMICAL KINETIC MECHANISM

### Chemical kinetic mechanism

The chemical kinetic model was based on a previous mechanism developed for the oxidation of hydrocarbon fuels which has been documented earlier [2,3]. We added a submechanism (see Appendix) for the oxidation of chlorinated hydrocarbons from Karra et al. [4]. For most of the reactions in the Appendix, the forward rate parameters are listed on one line, with the reverse rate parameters listed on the following line. In general, the reverse rate parameters are calculated from the forward rate parameters and thermochemistry. For those reactions listed with only an "=" sign in the reaction name, the reverse rate is not given specifically in the Appendix, but was calculated from a thermochemistry database.

Some modifications were made to the Karra et al. mechanism that are important to note. The species $Cl_2$ and two reactions involving it, which were not present in the original mechanism, were added. These reactions are

$$Cl + Cl + M = Cl_2 + M \tag{31}$$

$$Cl_2 + H = Cl + HCl \quad . \tag{32}$$

(Note that the reaction numbers listed on the right are from the Appendix.) The rate for Reaction 31 is $2.0 \times 10^{14} \exp(1.79 \text{ kcal/mole})$ $cm^6\text{-}mole^{-2}sec^{-1}$ from Lloyd [16]. The rate used for Reaction 32 is $8.6 \times 10^{13} \exp(-1.17 \text{ kcal/mole})$ $cm^3\text{-}mole^{-1}sec^{-1}$ from Atkinson et al. [17].

Some of the reaction rate expressions were updated to reflect recent results in the literature. For the reaction between HCl and OH radicals,

$$HCl + OH \Rightarrow H_2O + Cl \quad , \qquad (7)$$

we used Ravishankara's rate [18], $k = 2.71 \times 10^7 T^{1.65} \exp(0.222 \text{ kcal/mole})$ $cm^3\text{-mole}^{-1}\text{-sec}^{-1}$, which gives a description of the non-Arrhenius behavior. This rate is about a factor of two faster than Baulch's rate [19] at 1100 K. The recent laser photolysis/laser-induced fluorescence measurements by Taylor et al. [13] have been used to update the rate parameters for

$$CH_3Cl + OH \Rightarrow CH_2Cl + H_2O \quad . \qquad (91)$$

The updated rate is about two times more rapid at 1100 K than the previous rate given in Reference 4. Russell et al. [8] recently studied the rate of

$$CH_2CCl + O_2 \Rightarrow CClHO + HCO \quad . \qquad (105)$$

We have employed their measured rate expression which is very similar to the one estimated in Reference 4. Fisher et al. [5] considered site-specific rates of abstraction of H-atoms from chloroethane to explain the presence of $C_2H_3Cl$ in their flow reactor. We have adopted their rates for the reactions of chloroethane and dichloroethane with radical species.

For the rate of the thermal decomposition of HCl,

$$HCl + M = H + Cl + M \qquad (1,2)$$

Reference 4 specified the forward rate, and the reverse rate was calculated by thermochemistry. Under the stirred reactor conditions examined here, this leads to a much too rapid rate of recombination of H and Cl atoms. The rate exceeds gas-kinetic collision rates for temperatures below 800 K. Alternatively, we specified the reverse rate (Reaction 2) and calculated the forward rate from thermochemistry. To specify the reverse rate, we assumed a curvature of $T^{-2}$ as in Wagner [20]. We chose a rate expression of $7.2 \times 10^{21} T^{-2}$ $cm^6\text{-mole}^{-2}\text{-sec}^{-1}$ so that the forward rate (Reaction 1) would agree with Baulch's [19] rate at 2900 K (the lowest temperature he examined). This rate expression gives reasonable recombination rates for temperatures of 300 K and above. Calculations showed significant sensitivity to this rate constant, particularly before the reverse rate was reduced to the above value. Because of the lack of information on this reaction, there is a real need to examine this recombination rate constant experimentally and theoretically. Finally, note that for reactions involving chlorinated species that were not discussed above, their rate expressions were taken directly from Reference 4.

### Numerical model

The oxidation of chlorinated hydrocarbons was examined under conditions of a perfectly-stirred reactor where the reactants, intermediate species and products were assumed to be perfectly mixed and react for a specified residence time, $\tau$. The PSR (Perfectly Stirred Reactor) code by Glarborg et. al [21] and CHEMKIN [22] were used to perform the calculations. The temperature of the reactor was specified so that we could determine some interesting features such as the residence time required to achieve 99.99% destruction of the chlorinated hydrocarbon. Alternatively, the energy equation can be solved and behavior such as extinction of chlorinated-hydrocarbon/air mixtures can be examined [e.g. 14].

## RESULTS AND DISCUSSION

Calculations were performed over a wide range of temperature, residence time, equivalence ratio, and pressure to examine the effect of these parameters on destructive efficiency and production of additional chlorinated hydrocarbons. The chlorinated hydrocarbon chloroethane was considered in this initial investigation because its chemical kinetics are probably the least complicated to treat of the $C_2$ chlorinated hydrocarbons.

Regulatory requirements in the United States dictate that 99.99% of the hazardous component be destroyed by incineration [23]. We performed calculations to determine the relationship between residence time and temperature at 99.99% destructive efficiency (DE). Destructive efficiency (also called destructive and removal efficiency) is defined as the percent of the hazardous component that is removed by the treatment process. For $C_2H_5Cl$,

$$DE = 100 \left( 1 - [C_2H_5Cl]_{final}/[C_2H_5Cl]_{initial} \right) .$$

Figure 1 shows the residence time and temperature at 99.99 % DE for a stoichiometric mixture of chloroethane-air at 1 atm. To obtain each point, we performed a series of calculations in which the residence time was fixed and the reactor temperature was varied to achieve a DE of 99.99%. It is interesting to note from the plot that a residence time of 1 sec requires a temperature of 1110 K to achieve 99.99% DE. The plot also shows that if one wants to reduce in residence time by a factor of 10 and still have 99.99% DE, the reactor temperature must be raised by about 85 K. It is useful to plot the calculated results in Arrhenius form to determine an overall activation energy (Fig. 2). The activation energy is quite high, about 66 kcal/mole (the temperature dependences of the ignition delay time for most hydrocarbons exhibit activation energies of around 40 kcal/mole).

We used a constant residence time for the rest of the calculations, which was chosen by considering experimental residence times given in the literature. For a typical liquid injection combustion chamber [24], the mean combustion gas residence times range from 0.3 to 2.0 sec. The residence time of the fuel-air mixture in the high temperature region of

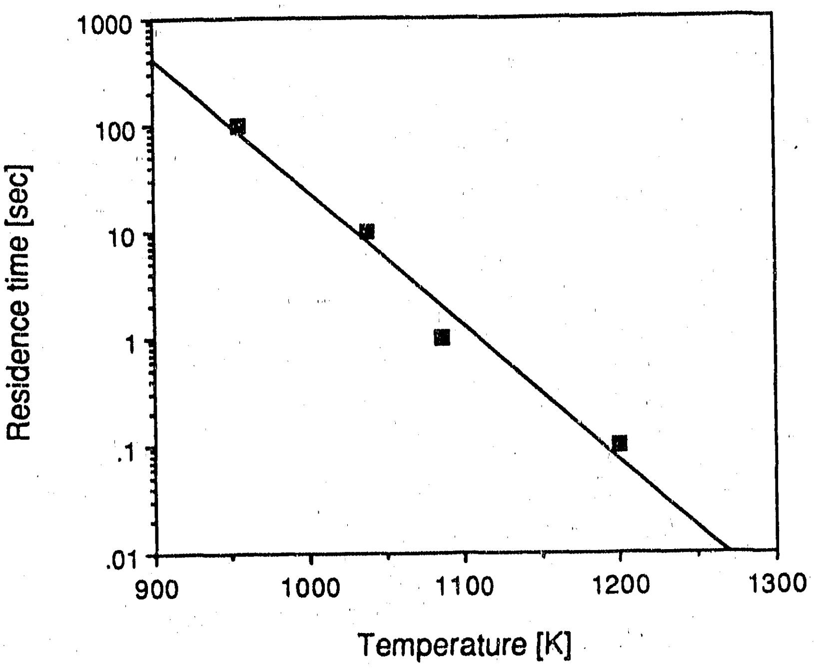

Fig. 1. The residence time and temperature at 99.99% destructive efficiency in the reactor. ($\Phi$=1, P=1atm, $C_2H_5Cl$/air mixtures).

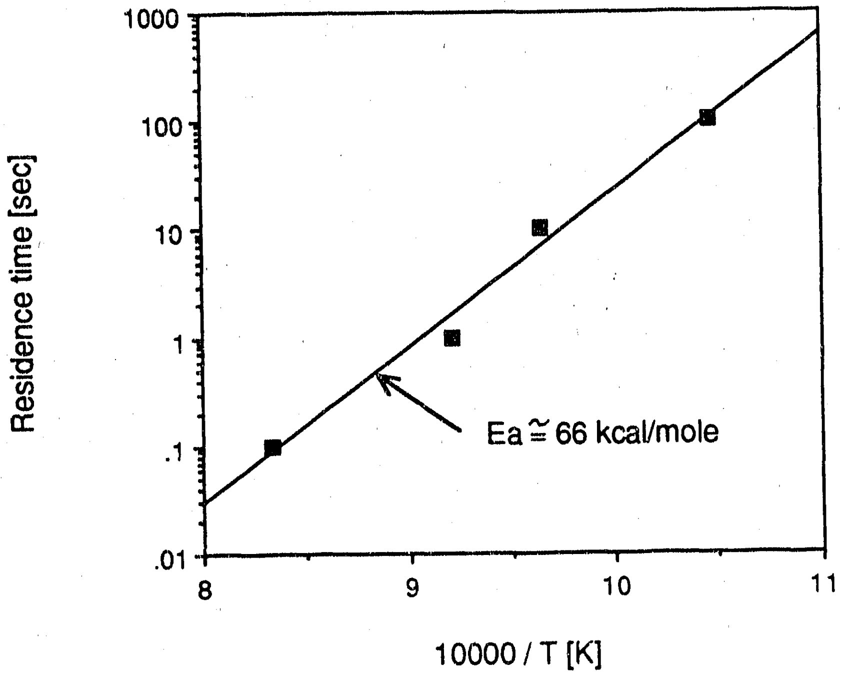

Fig. 2. Arrhenius plot of residence time and temperature at 99.99% destructive efficiency in the reactor. ($\Phi$=1, P=1atm, $C_2H_5Cl$/air mixtures).

the combustion chamber should be less than the mean residence time, so we chose 0.1 sec as a baseline residence time.

Species concentrations in the stirred reactor for a baseline case of $\tau = 0.1$ sec, $\Phi = 1$, and 1200 K is given in Table 1. We chose this set of conditions because they gave the required destructive efficiency of 99.990 %. The $C_3$ species that were below $10^{-8}$ mole fraction are omitted in Table 1. The radicals that are in the highest concentration are Cl, H, OH, $CH_3$ and $CH_2Cl$ (in descending order). Note that the Cl atoms are in very high concentration ($8.4 \times 10^{-4}$ mole fraction). It is a much higher concentration than any of the other radical species, and exceeds the concentration of any of the chlorinated hydrocarbons listed. Further calculations need to be performed to assess the final fate of these Cl atoms when this high temperature mixture is cooled to ambient temperatures. During this cooling, there will probably be a significant amount of chlorinated products formed due to recombination of Cl atoms.

The stable intermediate species in the highest concentration are CO, $H_2$, $C_2H_2$, and $C_2H_4$ (in descending order). The chlorinated, stable intermediate species in highest concentration are $C_2H_5Cl$, HOCl, $C_2H_3Cl$, and $Cl_2$. In an actual combustor, this high temperature mixture would be cooled before being emitted to the atmosphere. It is likely that these species concentrations would change and further calculations need to be performed to assess this effect.

The effect of equivalence ratio ($\Phi$) on destructive efficiency (DE) and on production of additional chlorinated hydrocarbons ($CH_3Cl$ and $C_2H_3Cl$) is shown in Fig. 3. The equivalence ratio was defined assuming that the final combustion products are carbon dioxide, water, and hydrogen chloride. As seen from Fig. 3, the equivalence ratio must be near stoichiometric to maximize the destructive efficiency. The

Table 1

Species Mole Fractions in the Reactor.
(C2H5Cl-air, stoichiometric mixture, 1200 K, 1 atm, 0.1 sec residence time)

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h          =  3.63E-05     h2          =  2.24E-03     o          =  7.78E-07
o2         =  1.35E-02     oh          =  1.50E-05     h2o        =  1.19E-01
n2         =  6.84E-01     co          =  2.06E-02     hco        =  2.52E-07
co2        =  9.89E-02     ch3         =  3.19E-06     ch4        =  9.19E-06
ho2        =  2.00E-06     h2o2        =  3.36E-08     ch2o       =  1.16E-06
ch3o       =  3.23E-09     c2h6        =  1.24E-07     c2h4       =  1.87E-05
c2h5       =  8.73E-08     ch2         =  4.17E-08     ch         =  9.16E-11
c2h        =  7.79E-07     c2h2        =  8.84E-04     c2h3       =  5.88E-07
ch3oh      =  3.27E-06     ch2oh       =  3.64E-09     ch2co      =  6.21E-06
hcco       =  8.61E-07     c2h5oh      =  2.09E-11     pc2h4oh    =  2.39E-14
sc2h4oh    =  6.58E-15     ch3o2       =  7.83E-09     c2h5o2     =  4.98E-11
ch3o2h     =  7.74E-15     c2h5o2h     =  1.65E-17     c2h5o      =  4.89E-16
c2h3o      =  1.08E-17     c2h4o       =  1.99E-08     c2h4o2h    =  4.19E-13
o2c2h4oh   =  2.24E-21     ch3co       =  2.29E-12     ch2cho     =  4.10E-11
ch3cho     =  2.18E-08     c2h3cho     =  5.82E-10     c3h6       =  3.51E-07
cl         =  8.36E-04     hcl         =  5.98E-02     clo        =  2.92E-07
hocl       =  3.03E-06     cl2         =  1.57E-06     cclho      =  1.42E-07
ch2cl      =  1.18E-06     ch3cl       =  3.32E-07     chclch     =  3.93E-09
ch2ccl     =  1.41E-07     c2h3cl      =  2.50E-06     ch3chcl    =  7.94E-07
ch2clch2   =  1.35E-08     c2h5cl      =  6.87E-06     ch3ccl2    =  7.86E-18
chcl2ch2   =  4.56E-13     ch2clchcl   =  4.58E-13     chcl2ch3   =  3.46E-12
ch2clch2cl=  2.75E-10
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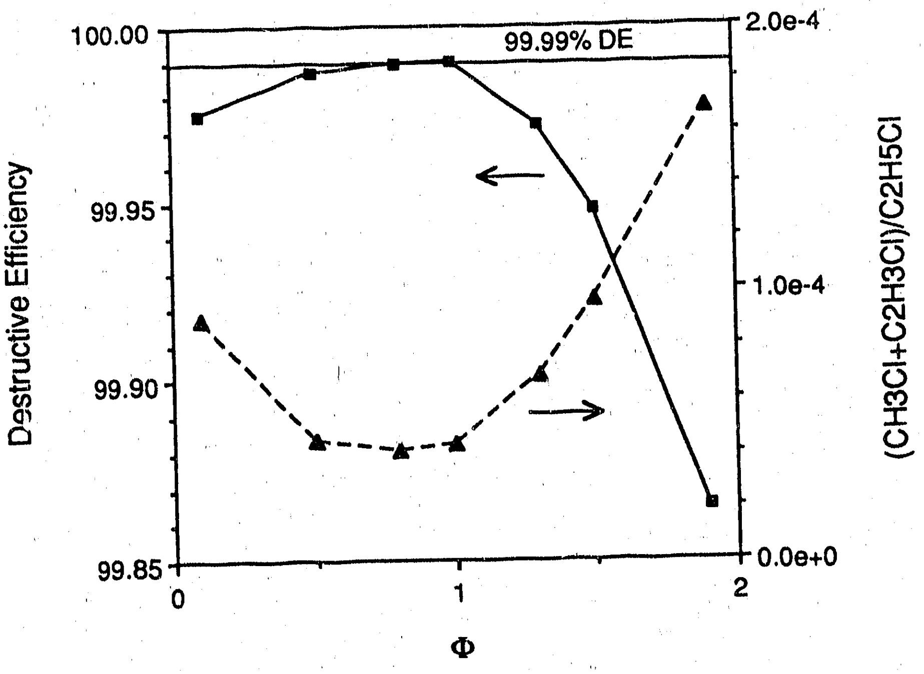

Fig. 3. Effect of equivalence ratio on destructive efficiency (DE) of $C_2H_5Cl$ and production of $CH_3Cl + C_2H_3Cl$. The sum $CH_3Cl + C_2H_3Cl$ is normalized by the initial chloroethane concentration. (T=1200K, P=1atm, $\tau$=0.1 sec, $C_2H_5Cl$/air mixtures).

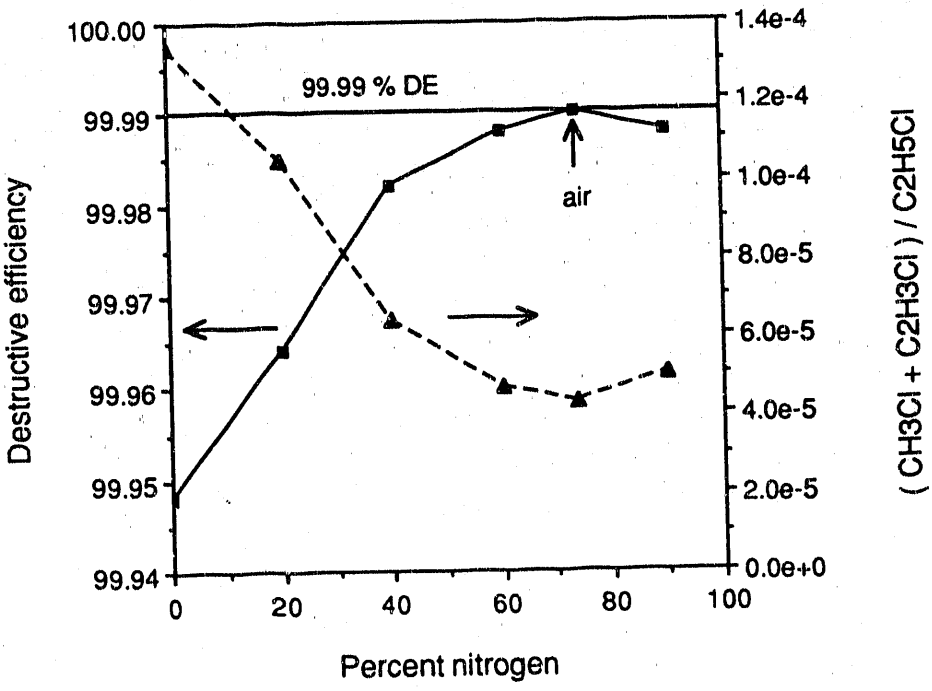

Fig. 4. Effect of dilution by nitrogen on destructive efficiency (DE) of $C_2H_5Cl$ and production of $CH_3Cl + C_2H_3Cl$. The sum $CH_3Cl + C_2H_3Cl$ is normalized by the initial chloroethane concentration. (T=1200K, Φ=1, P=1atm, $\tau$=0.1 sec).

destructive efficiency decreases rapidly for rich equivalence ratios ($\Phi > 1$) since there is insufficient oxygen to oxidize the chloroethane. Also shown in Fig. 3 is the concentration of two other chlorinated hydrocarbons, chloromethane and vinyl chloride. These were the chlorinated hydrocarbons that were produced in the highest concentrations during the oxidation of chloroethane under the present conditions. We plotted the sum of their concentration normalized by the initial chloroethane concentration since the initial amount of chloroethane changes with equivalence ratio. These results show that the normalized sum of chloromethane and vinyl chloride is minimized at slightly fuel-lean equivalence ratios.

Changing the equivalence ratio has the complicating effect of changing both the chloroethane to $O_2$ ratio and the chloroethane to $N_2$ ratio. For example as the equivalence ratio is reduced, the ratio of oxygen to chloroethane is increased and the chloroethane is further diluted by nitrogen. To separate these two effects, we investigated the effect of dilution alone in Fig. 4, varying the dilution from 0 to 90% nitrogen. Note that a dilution of 0% nitrogen corresponds to a chloroethane-$O_2$ mixture. The results show that the destructive efficiency (DE) increases significantly with increasing dilution until the dilution reaches that corresponding to air. The normalized sum of $CH_3Cl$ and $C_2H_3Cl$ shows the opposite trend. The sum of these chlorinated hydrocarbons was normalized since the initial amount of $C_2H_5Cl$ reactant changes with amount of dilution.

It is very interesting to use the model to investigate the effects of pressure which can be difficult to examine experimentally (Fig. 5). For this set of calculations, the residence time was 0.1 sec, the reactor temperature was 1200 K, and the equivalence ratio was one. The results

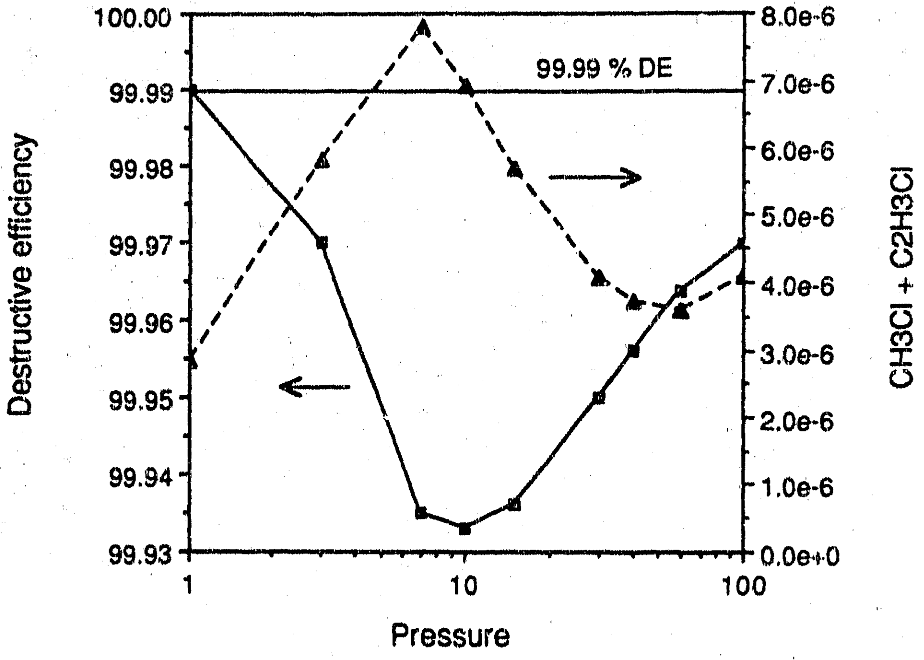

Fig. 5. Effect of pressure on the on destructive efficiency (DE) of $C_2H_5Cl$ and production of $CH_3Cl$ + $C_2H_3Cl$ (in mole fraction). (T=1200K, Φ=1, τ=0.1 sec, $C_2H_5Cl$/air mixtures).

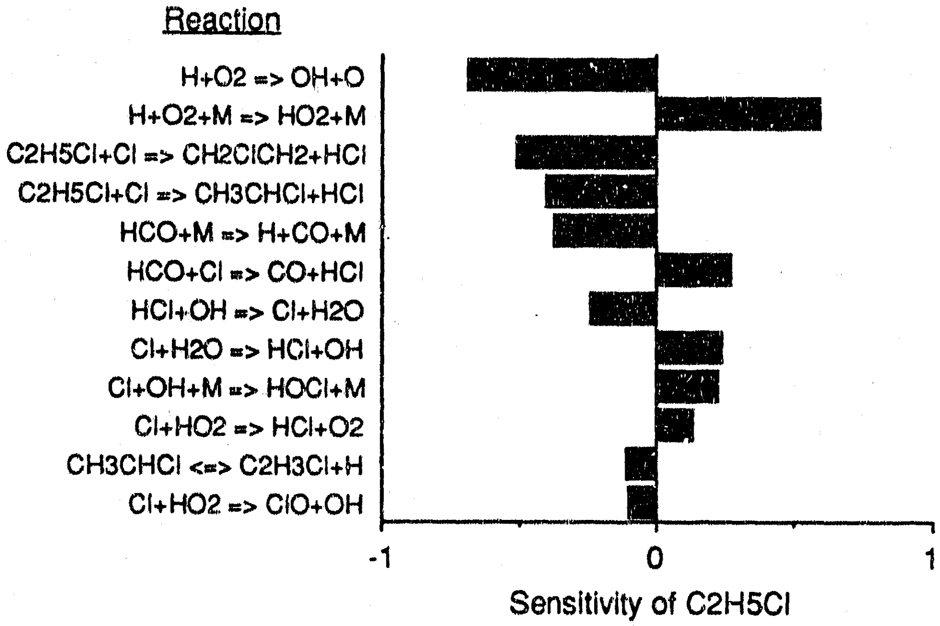

Fig. 6. Sensitivity of $C_2H_5Cl$ concentration to changes in reaction rate (T=1200K, P=1atm, Φ=1, τ=0.1 sec, $C_2H_5Cl$/air mixtures).

show that as the pressure is increased, the destructive efficiency decreases for pressures up to about 10 atm and then increases (100 atm was the highest pressure considered). These stirred reactor calculations do not indicate any advantage in improved destructive efficiency of operating at high pressures (at least up to 100 atm). The effect of pressure on the production of other chlorinated hydrocarbons is also shown in Fig. 5. The primary chlorinated hydrocarbons produced were chloromethane and vinyl chloride. Over the pressure range considered, their sum is minimum at 1 atm. From 1 to 50 atm, the sum reflects mainly the concentration of $C_2H_3Cl$. From 50 to 100 atm, the sum increases due to an increase in $CH_3Cl$ concentration. Note that the predictions of the model at high pressure are tentative since many of the pressure dependencies of reaction rates involving chlorinated species have not been investigated.

We investigated the addition of methane and ethane to the chloroethane-air mixture and its effect on destructive efficiency. The addition of methane is of interest because it constitutes a large fraction of natural gas that can be used to help incinerate chlorinated hydrocarbons. We performed calculations of chloroethane reacting with an equal amount of either methane or ethane in air. The calculations assumed a stoichiometry of one, a residence time of 0.1 sec, a pressure of 1 atm, and a temperature of 1200 K. With the addition of methane-air, the destructive efficiency was reduced from 99.989 to 99.979%. With the addition of ethane-air, the destructive efficiency decreased significantly from 99.989% to 99.916%. Thus, these preliminary stirred reactor calculations did not indicate any benefit of adding methane-air or ethane-air with respect to the destructive efficiency of chloroethane.

## Sensitivity

We used sensitivity analysis to provide insight into how individual reaction rate constants affect the destructive efficiency of chloroethane. The PSR code provides first-order sensitivity coefficients of species concentration with respect to rate constants. The sensitivity of the chloroethane concentration (and thus the destructive efficiency) to the rate constants is given for the most sensitive reactions in Fig. 6. These results show that the reactions that exhibit the highest sensitivity are those associated with the $H_2/CO$ submechanism. This finding is not too surprising because Warnatz has shown that hydrocarbon flames give similar sensitivity results [25]. It is interesting to examine the sensitivities of reactions involving chlorinated species. Almost all the reactions that give large sensitivities involve the fate of the Cl atom. The most highly ranked of these reactions are

$$C_2H_5Cl + Cl \Rightarrow CH_2ClCH_2 + HCl \qquad (189)$$

$$C_2H_5Cl + Cl \Rightarrow CH_3CHCl + HCl \quad . \qquad (191)$$

These reactions exhibit negative sensitivities (Fig. 6) which means that increasing their rate decreases the concentration of $C_2H_5Cl$ (and increases the destructive efficiency). They are the primary reactions consuming chloroethane under conditions near an equivalence ratio of one. In general, reactions which compete with the above reactions for Cl atoms give positive sensitivities and decrease the destructive efficiency. This trend can be seen in the sensitivities for the following reactions (Fig. 6):

$$HCO + Cl \Rightarrow CO + HCl \qquad (35)$$

$$Cl + H_2O \Rightarrow HCl + OH \qquad (8)$$

$$Cl + OH + M \Rightarrow ClOH + M \qquad (28)$$

$$Cl + HO_2 \Rightarrow HCl + O_2 \quad . \qquad (9)$$

All these reactions consume Cl atoms that would otherwise react with $C_2H_5Cl$ (via Reaction 189 and 191) and give positive sensitivities.

Note that Reaction 7,

$$HCl + OH \Rightarrow Cl + H_2O \qquad (7)$$

and Reaction 8 are the forward and reverse rate of the same reversible reaction and give sensitivities of nearly equal magnitude (Fig. 6), but opposite signs. This means that the high sensitivity shown in Fig. 6 is a sensitivity to a change in the equilibrium constant of the reaction. The sensitivity to a change in the magnitude of the rate constant (which would alter the forward and reverse rate by the same amount and keep the equilibrium constant for the reaction unchanged) is small. This result indicates that the concentration of OH and Cl atoms are in partial equilibrium at the present conditions and their relative concentration is controlled by the value of the equilibrium constant of the reaction. Our results show that the related reaction,

$$HCl + H = Cl + H_2 \qquad (3,4)$$

is also nearly in partial equilibrium, so that the relative concentrations of Cl, H and OH radicals are all controlled by equilibrium constants under the present conditions. By analyzing reaction rates with HCl, Tsang [6] predicted that Cl, H and OH radicals would be in partial equilibrium, and these calculations confirm this. The partial equilibrium is heavily weighted toward the production of Cl atoms. The ratio of Cl:H:OH radicals is 56:2.4:1 at the baseline conditions of 1200 K, $\Phi=1$, $\tau=0.1$ sec and 1 atm. Thus, any OH or H radicals that are produced are rapidly converted into Cl atoms. Subsequently, the Cl atoms can react with the chloroethane and intermediate products. Our results show that these Cl atoms are generally the main radicals responsible for the consumption of chloroethane and intermediate products under the present conditions.

## CONCLUSIONS

A stirred-reactor model was used to gain insight into the chemical kinetics of combustion of chloroethane. The operating conditions that maximized the destruction efficiency are high temperature, long residence times, equivalence ratios near one, and high dilution. The effect of pressure was more complex, with a minimum in destructive efficiency found near 10 atm. The reaction-rate constants that exhibited the largest sensitivity with respect to destructive efficiency were related to the $H_2/CO$ reaction submechanism. In the chlorinated hydrocarbon submechanism, the reactions that exhibited the highest sensitivities were concerned with the fate of the Cl atom. If the Cl atom reacted with chloroethane, the destructive efficiency was increased. If Cl atom reacted with other species, the destructive efficiency was usually reduced.

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## References

1. Lutz, A.E., Kee, R.J., Dibble, R.W., and Broadwell, J.E.: A model for detailed chemical kinetics in a turbulent nonpremixed jet flame. To be presented at the 29th AIAA Aerospace Sciences Meeting, Reno, Nevada, January 7-10, 1991.

2. Wilk, R.D., Green, R.M., Pitz, W.J., Westbrook, C.K., Addagarla, S., Miller, D.L., Cernansky, N.P.: SAE Trans. 99 (1990). SAE paper #900028.

3. Wilk, R.D., Cernansky, N.P., Pitz, W.J., and Westbrook, C.K.: Comb. Flame 77, 145 (1989).

4. Karra, S.B., Gutman, D., and Senkan, S.M. Combust. Sci. Tech.: 60, 45 (1988).

5. Fisher, E.M., Koshland, C.P., Hall, M.J., Sawyer, R.F., and Lucas, D.: Experimental and numerical study of the thermal destruction of $C_2H_5Cl$. The Twenty-third International Symposium on Combustion, Orleans, France, July, 1990.

6. Tsang, W.: Mechanisms for the Formation and Destruction of Chlorinated Organic Products of Incomplete Combustion. To appear in Comb. Sci. Tech., 1990.

7. Russell, J.J., Senkan, S.M., Seetula, J.A. and Gutman, D.: J. Phys. Chem. 93, 5184 (1989).

8. Russell, J.J., Seetula, D., Gutman, D., and Senkan, S.M.: J. Phys. Chem. 93, 1934 (1989).

9. Westbrook, C. K.: Inhibition of hydrocarbon oxidation in laminar flames and detonations by halogenated compounds. Nineteenth Symposium (International) on Combustion, p. 127, The Combustion Institute, Pittsburgh, 1983.

10. Bose, D. and Senkan, S.M.: Combust. Sci. Tech. 35, 187 (1983).

11. Chang, W.D. an Senkan, S.M.: Environ. Sci. Tech. 23, 442 (1983).

12. Miller, G.P., Lester, T.W., and Cundy, V.A.: A computational simulation of carbon tetrachloride/methane/air flames. Presented to the American Chemical Society, Dallas, TX, April, 1989.

13. Taylor, P.H., and Dellinger, B. Environ. Sci. Technol.: 22, 438 (1988).

14. Barat, R.B., Sarofim, A.F., Longwell, J.P., and Bozzelli, J.W.: Effects of chlorocarbons on flame intermittency and stability in a jet stirred combustor, To appear in Comb. Sci. Tech., 1990.

15. Koshland, C.P. and Fisher, E.M.: Relationships among CO, byproducts and destruction efficiences: A numerical simulation of chlorinated hydrocarbon combustion. Joint Western States Section and Canadian Section of the Combustion Institute, Banff, Canada, May 1990.

16. Lloyd, A.C.: Int. J. Chem. Kinet. 3, 39 (1971).

17. Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.F., Jr, Kerr, J.A., and Troe, J.: J. Phys. Chem. Ref. Data 18, 881 (1989).

18. Ravishankara, A.R., Wine, P.H., Wells , J.R. and Thompson, R.L: Int. J. Chem. Kinet. 17, 1281 (1985).

19. Baulch, D.L., Duxbury, J., Grant, S.J., and Montogue, D.C.: J. Phys. Chem. Ref. Data 10, Suppl. 1 (1981).

20. Wagner, H. Gg.: Proc. 8th Int. Shock Tube Symp., paper 4 (1971).

21. Glarborg, P., Kee, R.J., Grcar, J.F., and Miller, J.A.: PSR: A fortran program for modeling well-stirred reactors. Sandia report # SAND-8209, 1986.

22. Kee, R.J., Miller, J.A., Jefferson, T.H.: CHEMKIN: A general-purpose, problem-independent, transportable, fortran chemical kinetics code package. Sandia Report # SAND80-8003, 1980.

23. Code of Federal Regulations (CFR) under 40 CFR 264.343.

24. Oppelt, E.T., JAPCA 37, 558 (1987).

25. Warnatz, J.: Rate Coefficients in the C/H/O System, in <u>Combustion Chemistry</u> (W.C. Gardiner, ed.), p. 197, Springer-Verlag Inc., 1984.

## Appendix

### Reaction submechanism for the oxidation of chlorinated C2 hydrocarbons

Reaction rate parameters are in cm**3-mole-sec-cal units. Reaction rate constants are described by the three-parameter expression k=(A)(T**n)exp(-Ea/RT).

| | Reaction | Rate | | |
|---|---|---|---|---|
| | | A | n | Ea |
| 1. | hcl+m=>cl+h+m | 7.90E+25 | -3.0 | 106500.0 |
| 2. | cl+h+m=>hcl+m | 7.20E+21 | -2.0 | 0.0 |
| 3. | hcl+h=>cl+h2 | 7.94E+12 | 0.0 | 3400.0 |
| 4. | cl+h2=>hcl+h | 1.36E+13 | 0.0 | 4320.0 |
| 5. | hcl+o=>cl+oh | 3.16E+13 | 0.0 | 6700.0 |
| 6. | cl+oh=>hcl+o | 2.38E+13 | 0.0 | 5525.0 |
| 7. | hcl+oh=>cl+h2o | 2.71E+07 | 1.6 | -222.5 |
| 8. | cl+h2o=>hcl+oh | 2.01E+08 | 1.6 | 15850.0 |
| 9. | cl+ho2=>hcl+o2 | 1.08E+13 | 0.0 | -338.0 |
| 10. | hcl+o2=>cl+ho2 | 2.35E+13 | 0.0 | 54490.0 |
| 11. | cl+ho2=>clo+oh | 2.47E+13 | 0.0 | 894.0 |
| 12. | clo+oh=>cl+ho2 | 3.89E+12 | 0.0 | -487.0 |
| 13. | clo+o=>cl+o2 | 9.70E+12 | 0.0 | 507.0 |
| 14. | cl+o2=>clo+o | 1.01E+14 | 0.0 | 55540.0 |
| 15. | clo+ho2=>hocl+o2 | 3.55E+11 | 0.0 | 1410.0 |
| 16. | hocl+o2=>clo+ho2 | 2.26E+12 | 0.0 | 46350.0 |
| 17. | clo+h2=>hocl+h | 1.00E+13 | 0.0 | 13500.0 |
| 18. | hocl+h=>clo+h2 | 1.71E+13 | 0.0 | 2700.0 |
| 19. | hocl+h=>hcl+oh | 1.00E+13 | 0.0 | 1000.0 |
| 20. | hcl+oh=>hocl+h | 2.81E+12 | 0.0 | 49790.0 |
| 21. | cl+hocl=>hcl+clo | 1.00E+13 | 0.0 | 2000.0 |
| 22. | hcl+clo=>cl+hocl | 3.42E+12 | 0.0 | 11880.0 |
| 23. | hocl+o=>clo+oh | 5.00E+13 | 0.0 | 1500.0 |
| 24. | clo+oh=>hocl+o | 1.29E+13 | 0.0 | 10200.0 |
| 25. | hocl+oh=>clo+h2o | 1.80E+12 | 0.0 | 3000.0 |
| 26. | clo+h2o=>hocl+oh | 4.57E+12 | 0.0 | 28950.0 |
| 27. | hocl+m=>cl+oh+m | 1.00E+18 | 0.0 | 55000.0 |
| 28. | cl+oh+m=>hocl+m | 2.55E+13 | 1.0 | -2725.0 |
| 29. | h2o2+cl=>hcl+ho2 | 1.26E+13 | 0.0 | 2000.0 |
| 30. | hcl+ho2=>h2o2+cl | 4.22E+12 | 0.0 | 19130.0 |
| 31. | cl+cl+m=cl2+m | 2.00E+14 | 0.0 | -1790.0 |
| 32. | cl2+h=cl+hcl | 8.60E+13 | 0.0 | 1172.0 |
| 33. | co+clo=>co2+cl | 1.00E+13 | 0.0 | 1000.0 |
| 34. | co2+cl=>co+clo | 9.21E+14 | 0.0 | 62250.0 |
| 35. | hco+cl=>co+hcl | 1.00E+14 | 0.0 | 0.0 |
| 36. | co+hcl=>hco+cl | 3.83E+14 | 0.0 | 89080.0 |
| 37. | ch2o+cl=>hco+hcl | 5.00E+13 | 0.0 | 500.0 |
| 38. | hco+hcl=>ch2o+cl | 2.33E+12 | 0.0 | 14250.0 |
| 39. | cclho+m=>co+hcl+m | 1.00E+17 | 0.0 | 40000.0 |
| 40. | co+hcl+m=>cclho+m | 1.40E+12 | 1.0 | 59960.0 |
| 41. | cclho+h=>hco+hcl | 2.00E+13 | 0.0 | 4500.0 |
| 42. | hco+hcl=>cclho+h | 8.04E+11 | 0.0 | 41900.0 |
| 43. | cclho+o=>co+cl+oh | 1.00E+13 | 0.0 | 1000.0 |
| 44. | co+cl+oh=>cclho+o | 0.00E+00 | 0.0 | 0.0 |
| 45. | cclho+oh=>co+cl+h2o | 1.00E+13 | 0.0 | 2000.0 |
| 46. | co+cl+h2o=>cclho+oh | 0.00E+00 | 0.0 | 0.0 |
| 47. | cclho+cl=>co+cl+hcl | 1.00E+13 | 0.0 | 1000.0 |

| | | | | |
|---|---|---|---|---|
| 48. | co+cl+hcl=>cclho+cl | 0.00E+00 | 0.0 | 0.0 |
| 49. | ch2cl+o2=>ch2o+cl+o | 1.50E+13 | 0.0 | 30300.0 |
| 50. | ch2o+cl+o=>ch2cl+o2 | 0.00E+00 | 0.0 | 0.0 |
| 51. | ch2cl+o2=>cclho+oh | 4.00E+13 | 0.0 | 34000.0 |
| 52. | cclho+oh=>ch2cl+o2 | 4.16E+13 | 0.0 | 87520.0 |
| 53. | ch2cl+o=>ch2o+cl | 1.00E+14 | 0.0 | 1000.0 |
| 54. | ch2o+cl=>ch2cl+o | 1.14E+15 | 0.0 | 94280.0 |
| 55. | ch2cl+oh=>ch2o+hcl | 6.31E+12 | 0.0 | 0.0 |
| 56. | ch2o+hcl=>ch2cl+oh | 9.54E+13 | 0.0 | 94460.0 |
| 57. | ch2cl+oh=>ch2o+cl+h | 5.00E+14 | 0.0 | 15000.0 |
| 58. | ch2o+cl+h=>ch2cl+oh | 0.00E+00 | 0.0 | 0.0 |
| 59. | ch2cl+clo=>cclho+hcl | 6.31E+12 | 0.0 | 0.0 |
| 60. | cclho+hcl=>ch2cl+clo | 9.10E+13 | 0.0 | 109700.0 |
| 61. | ch2cl+ho2=>ch2o+cl+oh | 1.00E+13 | 0.0 | 0.0 |
| 62. | ch2o+cl+oh=>ch2cl+ho2 | 0.00E+00 | 0.0 | 0.0 |
| 63. | ch2cl+ch2o=>ch3cl+hco | 3.16E+11 | 0.0 | 5000.0 |
| 64. | ch3cl+hco=>ch2cl+ch2o | 2.37E+11 | 0.0 | 21230.0 |
| 65. | c2h5cl=>ch2cl+ch3 | 9.30E+41 | -7.9 | 97190.0 |
| 66. | ch2cl+ch3=>c2h5cl | 2.98E+35 | -6.9 | 7694.0 |
| 67. | ch2cl+ch3=>c2h4+hcl | 1.48E+12 | -2.2 | 5207.0 |
| 68. | c2h4+hcl=>ch2cl+ch3 | 1.64E+13 | -2.2 | 82190.0 |
| 69. | ch2cl+ch3=>c2h5+cl | 3.21E+10 | 1.0 | 4696.0 |
| 70. | c2h5+cl=>ch2cl+ch3 | 1.57E+12 | 1.0 | 16190.0 |
| 71. | ch2cl+ch2cl=ch2clch2cl | 1.10E+36 | -7.2 | 8600.0 |
| 72. | c2h3cl+hcl=>ch2cl+ch2cl | 1.69E+25 | -3.2 | 86400.0 |
| 73. | ch2cl+ch2cl=>c2h3cl+hcl | 1.31E+24 | -3.2 | 8172.0 |
| 74. | ch2cl+ch2cl=ch2clch2+cl | 1.91E+17 | -1.0 | 9655.0 |
| 75. | ch2cl+ch2=>c2h4+cl | 5.00E+13 | 0.0 | 0.0 |
| 76. | c2h4+cl=>ch2cl+ch2 | 4.71E+15 | 0.0 | 82600.0 |
| 77. | ch4+cl=>ch3+hcl | 5.16E+06 | 2.1 | 1580.0 |
| 78. | ch3+hcl=>ch4+cl | 1.15E+05 | 2.1 | 180.0 |
| 79. | ch4+clo=>ch3+hocl | 1.00E+12 | 0.0 | 7500.0 |
| 80. | ch3+hocl=>ch4+clo | 6.53E+10 | 0.0 | -3780.0 |
| 81. | ch3cl=>ch3+cl | 3.42E+32 | -5.9 | 99370.0 |
| 82. | ch3+cl=>ch3cl | 1.66E+27 | -4.9 | 14010.0 |
| 83. | ch3cl+o2=>ch2cl+ho2 | 6.31E+13 | 0.0 | 54000.0 |
| 84. | ch2cl+ho2=>ch3cl+o2 | 1.80E+12 | 0.0 | -3304.0 |
| 85. | ch3cl+h=>ch3+hcl | 7.00E+13 | 0.0 | 5000.0 |
| 86. | ch3+hcl=>ch3cl+h | 3.75E+12 | 0.0 | 26170.0 |
| 87. | ch3cl+h=>ch2cl+h2 | 3.00E+13 | 0.0 | 11000.0 |
| 88. | ch2cl+h2=>ch3cl+h | 1.34E+12 | 0.0 | 16680.0 |
| 89. | ch3cl+o=>ch2cl+oh | 1.30E+13 | 0.0 | 6900.0 |
| 90. | ch2cl+oh=>ch3cl+o | 6.08E+11 | 0.0 | 3245.0 |
| 91. | ch3cl+oh=>ch2cl+h2o | 5.05E+08 | 1.4 | 2387.0 |
| 92. | ch2cl+h2o=>ch3cl+oh | 6.61E+07 | 1.4 | 22980.0 |
| 93. | ch3cl+ho2=>ch2cl+h2o2 | 3.00E+13 | 0.0 | 16000.0 |
| 94. | ch2cl+h2o2=>ch3cl+ho2 | 5.56E+12 | 0.0 | -3606.0 |
| 95. | ch3cl+ch3=>ch2cl+ch4 | 1.00E+12 | 0.0 | 9400.0 |
| 96. | ch2cl+ch4=>ch3cl+ch3 | 2.78E+12 | 0.0 | 8320.0 |
| 97. | ch3cl+cl=>ch2cl+hcl | 3.16E+13 | 0.0 | 3300.0 |
| 98. | ch2cl+hcl=>ch3cl+cl | 9.02E+11 | 0.0 | 7950.0 |
| 99. | ch3cl+clo=>ch2cl+hocl | 2.00E+12 | 0.0 | 12000.0 |
| 100. | ch2cl+hocl=>ch3cl+clo | 3.63E+11 | 0.0 | -360.0 |
| 101. | chclch=>c2h2+cl | 3.88E+22 | -3.7 | 16440.0 |
| 102. | c2h2+cl=>chclch | 5.13E+18 | -2.7 | -1779.0 |
| 103. | chclch+o2=>cclho+hco | 6.00E+11 | 0.0 | -330.0 |
| 104. | cclho+hco=>chclch+o2 | 1.95E+12 | 0.0 | 86550.0 |
| 105. | ch2ccl+o2=>cclho+hco | 6.00E+11 | 0.0 | -330.0 |
| 106. | cclho+hco=>ch2ccl+o2 | 1.95E+12 | 0.0 | 86550.0 |
| 107. | chclch+o=>ch2co+cl | 3.00E+13 | 0.0 | 0.0 |

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|---|---|---|---|---|
| 108. | ch2co+cl=>chclch+o | 3.24E+14 | 0.0 | 107800.0 |
| 109. | ch2ccl+o=>ch2co+cl | 3.00E+13 | 0.0 | 0.0 |
| 110. | ch2co+cl=>ch2ccl+o | 3.24E+14 | 0.0 | 107800.0 |
| 111. | c2h3+cl=>c2h2+hcl | 1.00E+13 | 0.0 | 0.0 |
| 112. | c2h2+hcl=>c2h3+cl | 1.69E+13 | 0.0 | 64650.0 |
| 113. | c2h4+cl=>c2h3+hcl | 5.90E+12 | 0.0 | 1140.0 |
| 114. | c2h3+hcl=>c2h4+cl | 4.00E+11 | 0.0 | -670.0 |
| 115. | c2h4+clo=>ch2cl+ch2o | 5.00E+12 | 0.0 | 0.0 |
| 116. | ch2cl+ch2o=>c2h4+clo | 6.48E+12 | 0.0 | 32740.0 |
| 117. | c2h4+ch2cl=>c2h3+ch3cl | 2.00E+12 | 0.0 | 12000.0 |
| 118. | c2h3+ch3cl=>c2h4+ch2cl | 2.18E+12 | 0.0 | 12670.0 |
| 119. | c2h3cl=>c2h2+hcl | 2.75E+17 | -1.3 | 69310.0 |
| 120. | c2h2+hcl=>c2h3cl | 2.12E+12 | -0.3 | 48030.0 |
| 121. | c2h3cl+h=>c2h3+hcl | 1.00E+14 | 0.0 | 4500.0 |
| 122. | c2h3+hcl=>c2h3cl+h | 5.04E+12 | 0.0 | 25090.0 |
| 123. | c2h3cl+h=>chclch+h2 | 6.67E+13 | 0.0 | 10000.0 |
| 124. | chclch+h2=>c2h3cl+h | 6.67E+12 | 0.0 | 7860.0 |
| 125. | c2h3cl+h=>ch2ccl+h2 | 3.33E+13 | 0.0 | 10000.0 |
| 126. | ch2ccl+h2=>c2h3cl+h | 3.33E+12 | 0.0 | 7860.0 |
| 127. | c2h3cl+o=>cclho+ch2 | 5.24E+11 | 0.0 | 0.0 |
| 128. | cclho+ch2=>c2h3cl+o | 5.45E+10 | 0.0 | 9430.0 |
| 129. | c2h3cl+oh=>cclho+ch3 | 5.00E+12 | 0.0 | 0.0 |
| 130. | cclho+ch3=>c2h3cl+oh | 5.86E+12 | 0.0 | 16220.0 |
| 131. | c2h3cl+oh=>chclch+h2o | 3.33E+13 | 0.0 | 3000.0 |
| 132. | chclch+h2o=>c2h3cl+oh | 1.44E+13 | 0.0 | 16010.0 |
| 133. | c2h3cl+oh=>ch2ccl+h2o | 1.67E+13 | 0.0 | 3000.0 |
| 134. | ch2ccl+h2o=>c2h3cl+oh | 7.22E+12 | 0.0 | 16010.0 |
| 135. | c2h3cl+ch3=>chclch+ch4 | 6.67E+11 | 0.0 | 11000.0 |
| 136. | chclch+ch4=>c2h3cl+ch3 | 1.74E+12 | 0.0 | 9340.0 |
| 137. | c2h3cl+ch3=>ch2ccl+ch4 | 3.33E+11 | 0.0 | 11000.0 |
| 138. | ch2ccl+ch4=>c2h3cl+ch3 | 8.71E+11 | 0.0 | 9340.0 |
| 139. | c2h3cl+cl=>chclch+hcl | 6.67E+13 | 0.0 | 5000.0 |
| 140. | chclch+hcl=>c2h3cl+cl | 3.89E+12 | 0.0 | 1940.0 |
| 141. | c2h3cl+cl=>ch2ccl+hcl | 3.33E+13 | 0.0 | 5000.0 |
| 142. | ch2ccl+hcl=>c2h3cl+cl | 1.95E+12 | 0.0 | 1940.0 |
| 143. | c2h3cl+clo=>ch2cl+cclho | 5.00E+12 | 0.0 | 0.0 |
| 144. | ch2cl+cclho=>c2h3cl+clo | 5.59E+12 | 0.0 | 31490.0 |
| 145. | c2h3cl+ch2cl=>chclch+ch3cl | 6.67E+11 | 0.0 | 12000.0 |
| 146. | chclch+ch3cl=>c2h3cl+ch2cl | 6.26E+11 | 0.0 | 11420.0 |
| 147. | c2h3cl+ch2cl=>ch2ccl+ch3cl | 3.33E+11 | 0.0 | 12000.0 |
| 148. | ch2ccl+ch3cl=>c2h3cl+ch2cl | 3.13E+11 | 0.0 | 11420.0 |
| 149. | c2h5+cl=>c2h4+hcl | 2.00E+12 | 0.0 | 0.0 |
| 150. | c2h4+hcl=>c2h5+cl | 4.55E+11 | 0.0 | 65490.0 |
| 151. | ch2clch2=>c2h4+cl | 1.05E+20 | -2.4 | 22000.0 |
| 152. | c2h4+cl=>ch2clch2 | 4.50E+13 | 0.0 | 0.0 |
| 153. | ch3ccl2=>c2h3cl+cl | 4.95E+20 | -2.4 | 20000.0 |
| 154. | ch3chcl=c2h3cl+h | 7.00E+25 | -4.1 | 42984.0 |
| 155. | ch2clch2+h=>c2h4+hcl | 3.16E+12 | 0.0 | 0.0 |
| 156. | c2h4+hcl=>ch2clch2+h | 6.19E+11 | 0.0 | 89140.0 |
| 157. | ch2clch2+cl=>c2h3cl+hcl | 1.00E+13 | 0.0 | 3000.0 |
| 158. | c2h3cl+hcl=>ch2clch2+cl | 2.64E+12 | 0.0 | 69740.0 |
| 159. | ch3chcl+cl=>c2h3cl+hcl | 1.00E+13 | 0.0 | 3000.0 |
| 160. | c2h3cl+hcl=>ch3chcl+cl | 2.64E+12 | 0.0 | 69740.0 |
| 161. | ch2clchcl=>c2h3cl+cl | 4.95E+20 | -2.4 | 20000.0 |
| 162. | c2h3cl+cl=>ch2clchcl | 1.02E+16 | -1.4 | 3870.0 |
| 163. | chcl2ch2=>c2h3cl+cl | 4.95E+20 | -2.4 | 20000.0 |
| 164. | c2h3cl+cl=>chcl2ch2 | 1.02E+16 | -1.4 | 3870.0 |
| 165. | chcl2ch2+h=>c2h3cl+hcl | 1.00E+13 | 0.0 | 1000.0 |
| 166. | c2h3cl+hcl=>chcl2ch2+h | 2.27E+12 | 0.0 | 91390.0 |
| 167. | ch2clchcl+h=>c2h3cl+hcl | 1.00E+13 | 0.0 | 1000.0 |

| | | | | |
|---|---|---|---|---|
| 168. | c2h3cl+hcl=>ch2clchcl+h | 2.27E+12 | 0.0 | 91390.0 |
| 169. | c2h6+cl=>c2h5+hcl | 4.64E+13 | 0.0 | 179.0 |
| 170. | c2h5+hcl=>c2h6+cl | 1.13E+13 | 0.0 | 6229.0 |
| 171. | c2h6+ch2cl=>c2h5+ch3cl | 1.00E+12 | 0.0 | 8500.0 |
| 172. | c2h5+ch3cl=>c2h6+ch2cl | 3.93E+12 | 0.0 | 17030.0 |
| 173. | c2h5cl=>c2h4+hcl | 1.11E+14 | -0.1 | 57790.0 |
| 174. | c2h4+hcl=>c2h5cl | 3.95E+08 | 0.9 | 45270.0 |
| 175. | c2h5cl+h=>c2h5+hcl | 6.31E+13 | 0.0 | 8600.0 |
| 176. | c2h5+hcl=>c2h5cl+h | 1.09E+13 | 0.0 | 37110.0 |
| 177. | c2h5cl+h=>ch2clch2+h2 | 3.00E+13 | 0.0 | 10000.0 |
| 178. | ch2clch2+h2=>c2h5cl+h | 1.03E+13 | 0.0 | 15780.0 |
| 179. | c2h5cl+h=>ch3chcl+h2 | 2.00E+13 | 0.0 | 10000.0 |
| 180. | ch3chcl+h2=>c2h5cl+h | 6.84E+12 | 0.0 | 15780.0 |
| 181. | c2h5cl+o=>ch2clch2+oh | 4.66E+13 | 0.0 | 6600.0 |
| 182. | ch2clch2+oh=>c2h5cl+o | 7.02E+12 | 0.0 | 10290.0 |
| 183. | c2h5cl+o=>ch3chcl+oh | 3.10E+13 | 0.0 | 6600.0 |
| 184. | ch3chcl+oh=>c2h5cl+o | 4.68E+13 | 0.0 | 10290.0 |
| 185. | c2h5cl+oh=>ch2clch2+h2o | 3.00E+13 | 0.0 | 4000.0 |
| 186. | ch2clch2+h2o=>c2h5cl+oh | 4.45E+13 | 0.0 | 24930.0 |
| 187. | c2h5cl+oh=>ch3chcl+h2o | 2.00E+13 | 0.0 | 4000.0 |
| 188. | ch3chcl+h2o=>c2h5cl+oh | 2.97E+13 | 0.0 | 24930.0 |
| 189. | c2h5cl+cl=>ch2clch2+hcl | 8.46E+12 | 0.0 | 616.0 |
| 190. | ch2clch2+hcl=>c2h5cl+cl | 1.69E+12 | 0.0 | 5476.0 |
| 191. | c2h5cl+cl=>ch3chcl+hcl | 5.64E+12 | 0.0 | 616.0 |
| 192. | ch3chcl+hcl=>c2h5cl+cl | 1.13E+12 | 0.0 | 5476.0 |
| 193. | c2h5cl+ch3=>ch2clch2+ch4 | 6.00E+11 | 0.0 | 8500.0 |
| 194. | ch2clch2+ch4=>c2h5cl+ch3 | 5.37E+12 | 0.0 | 14760.0 |
| 195. | c2h5cl+ch3=>ch3chcl+ch4 | 4.00E+11 | 0.0 | 8500.0 |
| 196. | ch3chcl+ch4=>c2h5cl+ch3 | 3.58E+12 | 0.0 | 14760.0 |
| 197. | c2h5cl+ch2cl=>ch2clch2+ch3cl | 1.90E+12 | 0.0 | 9000.0 |
| 198. | ch2clch2+ch3cl=>c2h5cl+ch2cl | 6.12E+12 | 0.0 | 16340.0 |
| 199. | c2h5cl+ch2cl=>ch3chcl+ch3cl | 1.26E+12 | 0.0 | 9000.0 |
| 200. | ch3chcl+ch3cl=>c2h5cl+ch2cl | 4.08E+12 | 0.0 | 16340.0 |
| 201. | chcl2ch3=c2h3cl+hcl | 6.61E+13 | -0.1 | 58000.0 |
| 202. | ch2clch2cl=c2h3cl+hcl | 6.61E+13 | -0.1 | 58000.0 |
| 203. | ch2clch2cl+h=ch2clch2+hcl | 6.31E+13 | 0.0 | 8400.0 |
| 204. | chcl2ch3+h=ch3chcl+hcl | 6.31E+13 | 0.0 | 8400.0 |
| 205. | chcl2ch3+h=ch3ccl2+h2 | 1.25E+13 | 0.0 | 10000.0 |
| 206. | chcl2ch3+h=chcl2ch2+h2 | 3.75E+13 | 0.0 | 10000.0 |
| 207. | ch2clch2cl+h=ch2clchcl+h2 | 5.00E+13 | 0.0 | 10000.0 |
| 208. | chcl2ch3+cl=ch3ccl2+hcl | 6.28E+12 | 0.0 | 3100.0 |
| 209. | chcl2ch3+cl=chcl2ch2+hcl | 1.88E+13 | 0.0 | 3100.0 |
| 210. | ch2clch2cl+cl=ch2clchcl+hcl | 2.51E+13 | 0.0 | 3100.0 |
| 211. | chcl2ch3+o=ch3ccl2+oh | 1.25E+13 | 0.0 | 7000.0 |
| 212. | chcl2ch3+o=chcl2ch2+oh | 3.75E+13 | 0.0 | 7000.0 |
| 213. | ch2clch2cl+o=ch2clchcl+oh | 5.00E+13 | 0.0 | 7000.0 |
| 214. | chcl2ch3+oh=ch3ccl2+h2o | 9.95E+12 | 0.0 | 4000.0 |
| 215. | chcl2ch3+oh=chcl2ch2+h2o | 2.98E+13 | 0.0 | 4000.0 |
| 216. | ch2clch2cl+oh=ch2clchcl+h2o | 3.98E+13 | 0.0 | 4000.0 |
| 217. | chcl2ch3+ch3=ch3ccl2+ch4 | 2.50E+11 | 0.0 | 8500.0 |
| 218. | chcl2ch3+ch3=chcl2ch2+ch4 | 7.50E+11 | 0.0 | 8500.0 |
| 219. | ch2clch2cl+ch3=ch2clchcl+ch4 | 1.00E+12 | 0.0 | 8500.0 |
| 220. | chcl2ch3+ch2cl=ch3ccl2+ch3cl | 7.90E+11 | 0.0 | 9000.0 |
| 221. | chcl2ch3+ch2cl=chcl2ch2+ch3cl | 2.37E+12 | 0.0 | 9000.0 |
| 222. | ch2clch2cl+ch2cl=ch2clchcl+ch3cl | 3.16E+12 | 0.0 | 9000.0 |

---

Third bodies are designated by "m".

# END

DATE FILMED

11 / 27 / 90