

CONF-9010197--1

UCRL-JC-104065
PREPRINT

Received by DE91
OCT 04 1990

**A Chemical Kinetic Modeling Study of
Chlorinated Hydrocarbon Combustion**

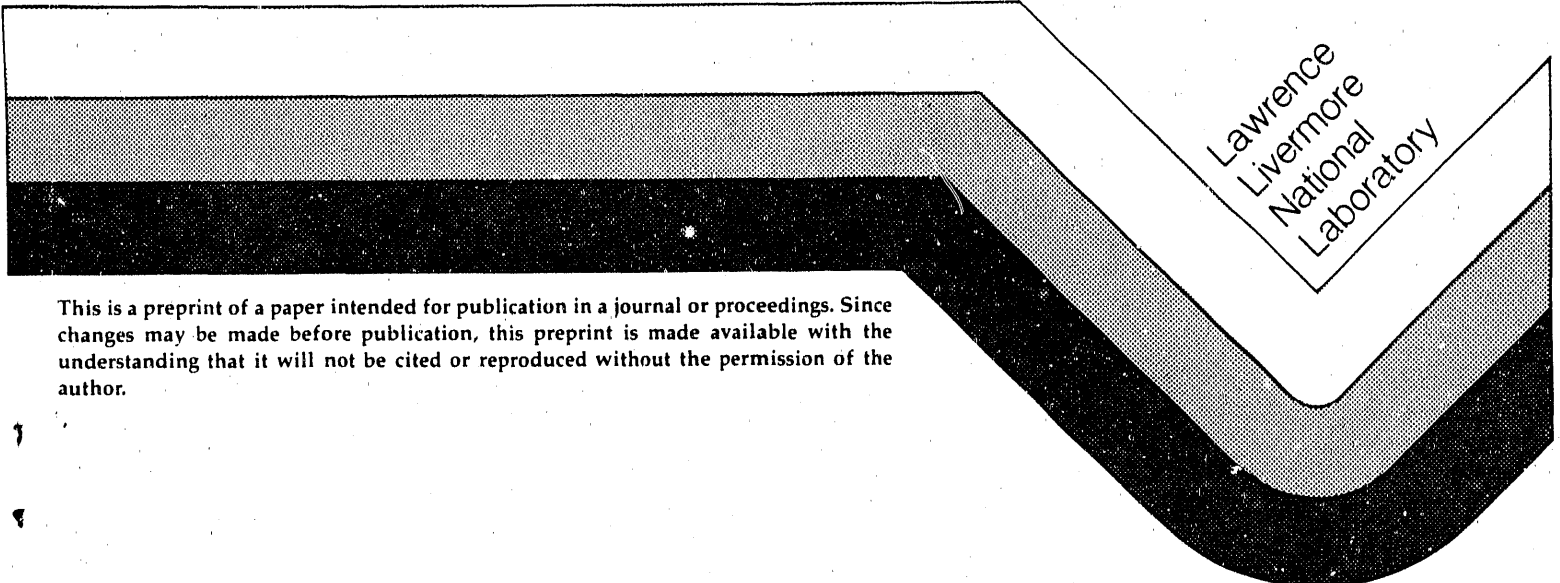
UCRL-JC--104065

DE91 000261

**William J. Pitz
Charles K. Westbrook
University of California
Lawrence Livermore National Laboratory
Livermore, CA 94550**

**This paper was prepared for submittal to
American Flame Research Committee
1990 Fall International Symposium
San Francisco, CA
October 8-10, 1990**

September 5, 1990



Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

MASTER *dk*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

A CHEMICAL KINETIC MODELING STUDY OF CHLORINATED HYDROCARBON COMBUSTION

William J. Pitz and Charles K. Westbrook

Lawrence Livermore National Laboratory
Livermore, CA 94550

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. The model uses a detailed chemical kinetic mechanism that we have developed previously for C₃ hydrocarbons. We have added to this mechanism the chemical kinetic mechanism for C₂ chlorinated hydrocarbons developed by Senkan and coworkers. 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 these 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 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. This is a highly simplified physical model in which the hazardous component and oxidizer are assumed to mix very rapidly with combustion products. However, this treatment has an attractive feature. Practical combustors have highly turbulent regions where the chlorinated hydrocarbon is rapidly mixed with combustion products. These regions may be simulated as a stirred reactor with chemical kinetics controlling the extent 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 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 us to examine operating conditions not easily achieved in experimental studies, particularly high pressure. Our objective is to find conditions under which the maximum destruction of the chlorinated hydrocarbon is obtained and the minimum amount of other hazardous components are produced.

Additionally, this study seeks to identify the reactions that control the extent to which the chlorinated hydrocarbon is destroyed.

The chemical kinetic mechanism that we employed is based on one that we developed for C₃ 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 considered the site-specific abstraction of H-atoms from chloroethane. Tsang [6] has recently reviewed many of the reactions involving chlorinated species. Gutman and coworkers [7,8] have performed fundamental studies on individual reactions involving chlorinated hydrocarbons.

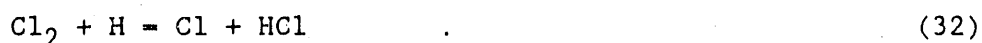
Much previous work has been performed on the chemical kinetics of chlorinated hydrocarbons. The inhibition of flames by chlorinated hydrocarbons has been investigated [9]. The flame structure of chlorinated hydrocarbons has been experimentally measured and numerically simulated [4,10-12]. The thermal degradation of chlorinated hydrocarbons in a fused silica reactor has been investigated by Dellinger [13]. Barat et al. [14] have studied 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. 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 (Table I) for the oxidation of chlorinated hydrocarbons from Karra et al. [4]. For most of the reactions in Table I, 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 a "-" sign in the reaction name, the reverse rate is not given specifically in the table, but was calculated from the thermochemistry database.

Some modifications were made to the Karra et al. mechanism that are important to note. The species Cl₂ and two reactions involving it, which were not present in the original mechanism, were added. These reactions are



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



we used Ravishankara's rate [18], $k = 2.71 \times 10^7 T^{1.65} \exp(0.222 \text{ kcal/mole}) \text{ cm}^3 \text{-mole}^{-1} \text{-sec}^{-1}$, 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



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



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 $\text{C}_2\text{H}_3\text{Cl}$ 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,



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 $7.2 \times 10^{21} T^{-2} \text{ cm}^6 \text{-mole}^{-2} \text{-sec}^{-1}$ 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, τ . 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

react for a specified residence time, τ . 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. 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). 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 85K. 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 an activation energies of around 40 kcal/mole).

The effect of equivalence ratio (Φ) on destructive efficiency (DE) 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 the plot, the equivalence ratio must be near stoichiometric to maximize the destructive efficiency. The destructive efficiency decreases rapidly for rich equivalence ratios ($\Phi > 1$) since there is insufficient oxygen to oxidize the chloroethane.

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. 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.

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

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 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 might 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 H₂/CO submechanism. This finding is not surprising because Warnatz has shown that hydrocarbon flames give similar sensitivity results [24]. Almost all the reactions involving chlorinated species that give large sensitivities involve the fate of the Cl atom. The most highly ranked of these reactions are



These reactions exhibit negative sensitivities which means that increasing their rate decreases the concentration of C₂H₅Cl (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):



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

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.

ACKNOWLEDGMENTS

The authors thank E. M. Fisher for sending us her chemical kinetic mechanism and paper prior to publication. We also thank Prof. R. F. Sawyer, Prof. Kathy Koshland, Dr. M. J. Hall, Dr. D. Lucas for very useful discussions. We greatly appreciate Dr. W. Tsang sending us his paper prior to publication. This work was supported by Internal Research and Development program of Lawrence Livermore National Laboratory and by the U. S. Department of Energy, Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences. This work was carried out under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

REFERENCES

1. Lutz, A.E., Kee, R.J., Dibble, R.W., and Broadwell, J.E.: A model for detailed chemical kinetics is 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. and 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 destructive efficiencies: 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. Warnatz, J.: Rate Coefficients in the C/H/O System, in Combustion Chemistry (W.C. Gardiner, ed), p. 197, Springer-Verlag Inc., 1984.

Table I
Reaction submechanism for the oxidation of
chlorinated C2 hydrocarbons

Reaction rate parameters are in cm³-mole-sec-cal units.
Reaction rate constants are described by the three-parameter
expression $k = (A) (T^n) \exp(-E_a/RT)$.

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=>cl+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	3.19E+12	0.0	9440.0
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	2.33E+08	1.4	15980.0
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	1.96E+12	0.0	820.0
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
108.	ch2co+cl=>chclch+o	3.24E+14	0.0	107800.0

109.	ch2cc1+o=>ch2co+cl	3.00E+13	0.0	0.0
110.	ch2co+cl=>ch2cc1+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=>ch2cc1+h2	3.33E+13	0.0	10000.0
126.	ch2cc1+h2=>c2h3cl+h	3.33E+12	0.0	7860.0
127.	c2h3cl+o=>cc1ho+ch2	5.24E+11	0.0	0.0
128.	cc1ho+ch2=>c2h3cl+o	5.45E+10	0.0	9430.0
129.	c2h3cl+oh=>cc1ho+ch3	5.00E+12	0.0	0.0
130.	cc1ho+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=>ch2cc1+h2o	1.67E+13	0.0	3000.0
134.	ch2cc1+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=>ch2cc1+ch4	3.33E+11	0.0	11000.0
138.	ch2cc1+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=>ch2cc1+hcl	3.33E+13	0.0	5000.0
142.	ch2cc1+hcl=>c2h3cl+cl	1.95E+12	0.0	1940.0
143.	c2h3cl+clo=>ch2cl+cc1ho	5.00E+12	0.0	0.0
144.	ch2cl+cc1ho=>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=>ch2cc1+ch3cl	3.33E+11	0.0	12000.0
148.	ch2cc1+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.	ch3cc12=>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=ch3cc12+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=ch3cc12+hcl	6.28E+12	0.0	3100.0
209.	chcl2ch3+cl=chcl2ch2+hcl	1.88E+13	0.0	3100.0
210.	ch2clch2cl+cl=ch2clchcl+ 1	2.51E+13	0.0	3100.0
211.	chcl2ch3+o=ch3cc12+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=ch3cc12+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=ch3cc12+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=ch3cc12+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".

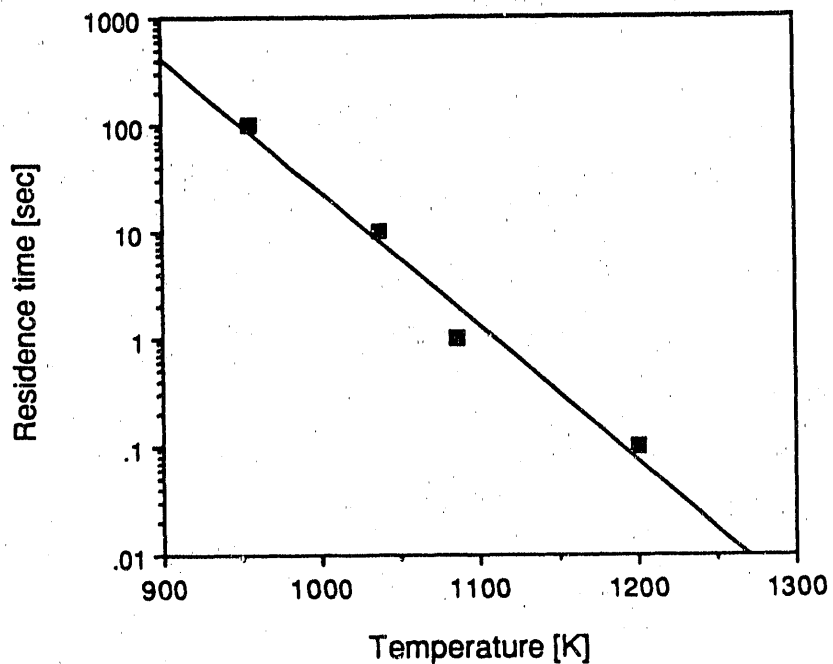


Figure 1. The residence time and temperature at 99.99% destructive efficiency in the reactor. ($T=1200\text{K}$, $\Phi=1$, $P=1\text{atm}$, $\text{C}_2\text{H}_5\text{Cl}/\text{air}$ mixtures).

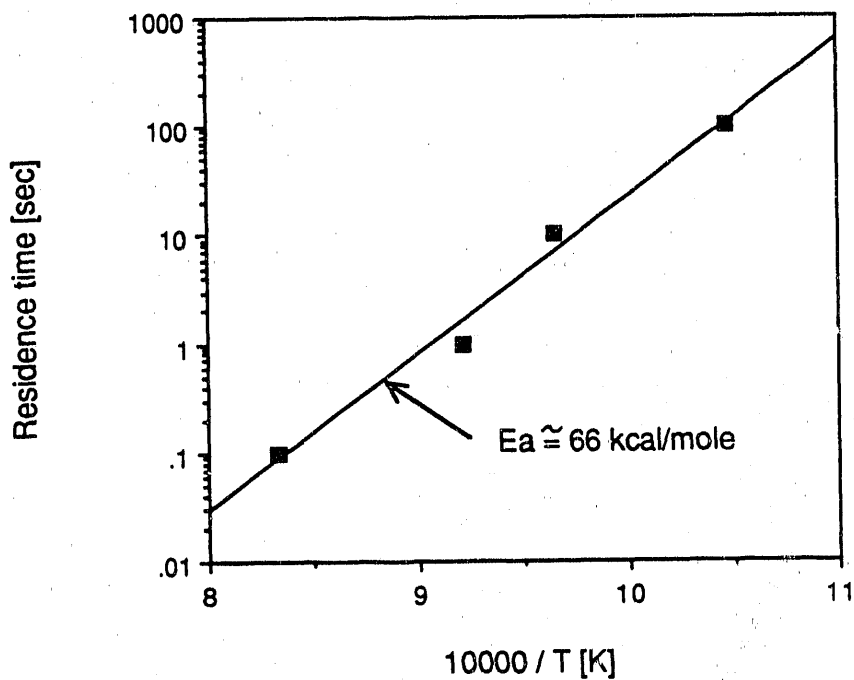


Figure 2. Arrhenius plot of residence time and temperature at 99.99% destructive efficiency in the reactor. ($\Phi=1$, $P=1\text{atm}$, $\text{C}_2\text{H}_5\text{Cl}/\text{air}$ mixtures).

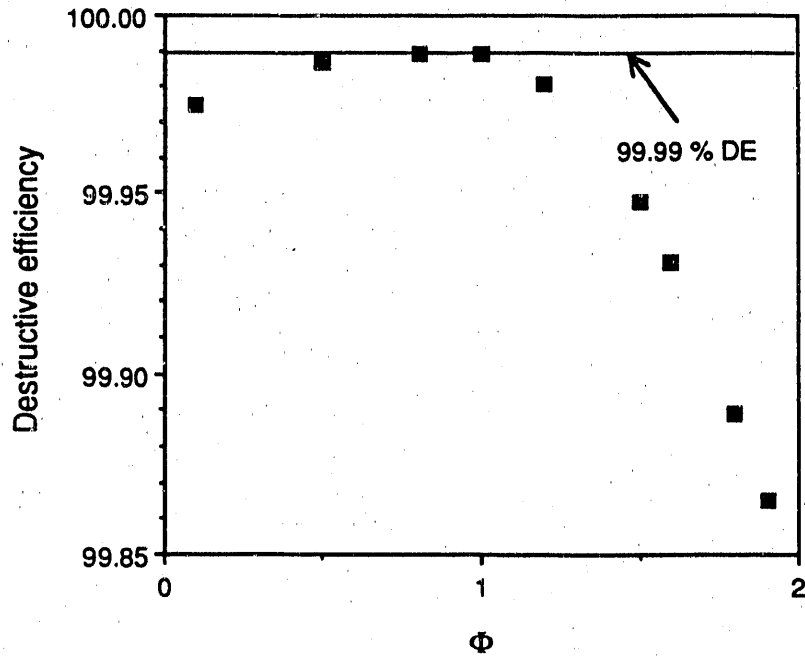


Figure 3. Effect of equivalence ratio on destructive efficiency (DE) of C_2H_5Cl . ($T=1200K$, $P=1atm$, $\tau=0.1$ sec, C_2H_5Cl /air mixtures).

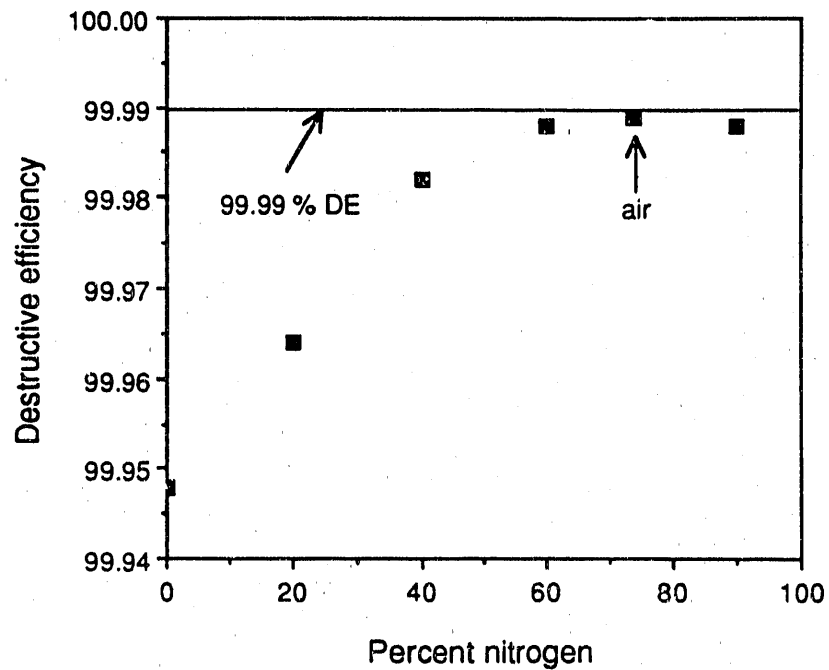


Figure 4. Effect of dilution by nitrogen on destructive efficiency (DE) of C_2H_5Cl . ($T=1200K$, $\Phi=1$, $P=1atm$, $\tau=0.1$ sec).

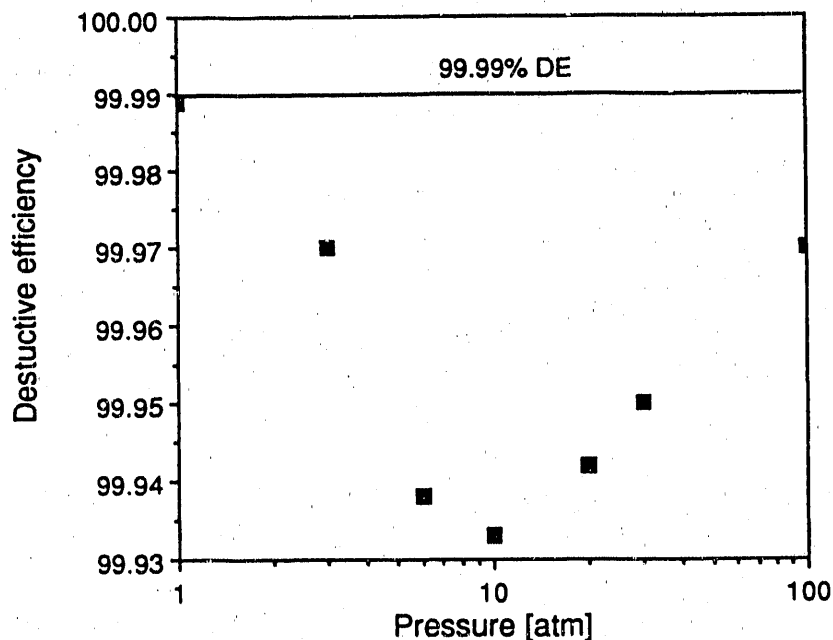


Figure 5. Effect of pressure on the on destructive efficiency (DE) of C_2H_5Cl . ($T=1200K$, $\Phi=1$, $\tau=0.1$ sec, C_2H_5Cl /air mixtures).

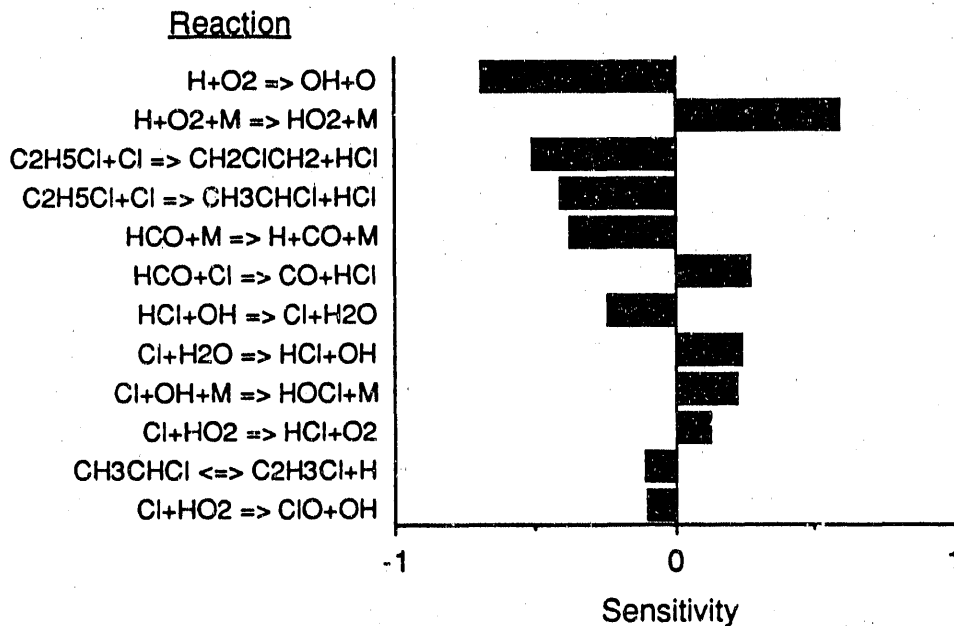


Figure 6. Sensitivity of the C_2H_5Cl concentration to changes in reaction rate ($T=1200K$, $P=1atm$, $\Phi=1$, $\tau=0.1$ sec, C_2H_5Cl /air mixtures).

END

DATE FILMED

10 / 26 / 90

