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EXPERIMENTAL STUDY ON THE THERMAL OXIDATION OF CHLOROBENZENE AT 575-825 °C

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ABSTRACT

The thermal degradation processes of chlorobenzene were investigated using a tubular flow reactor at 1 atm. over the range 575-825°C in reaction atmospheres in which oxygen was in excess (equivalence ratio $\Phi = 0.035$). The concentration profiles of C_6H_5Cl, CO_2, HCl and Cl_2 as well as the major intermediate byproducts (CO, CH_4, C_2H_2, C_2H_4 ,vinyl chloride, vinylacetylene, furane and benzene) were determined as a function of temperature for a residence time of 2 seconds. More seventy organics as trace species were also identified. Most of them are aromatics substituted by Cl (1 to 4), OH (1 or 2) or alkyl groups. Some precursors of dioxins (benzofuranes and chlorophenols) were also observed. Experimental results showed that the ring breaking processes were preponderant over the studied temperature range. Reaction pathways explaining the formation of mainly observed products are presented and discussed.

INTRODUCTION

Chlorinated hydrocarbons represent the major toxic components of hazardous wastes [1]. The thermal destruction of these toxic components via high temperature oxidation processes can release gas effluents containing stable toxic by-products with adverse effects on the human health and the environment if incinerators or other used devices are not very well designed or regulated for their disposal. So it is of great importance to identify all intermediates and determining parameters involved in the oxidation processes in order to optimize their destruction and reduce harmful effluents.

Chlorobenzene is the simplest species of chlorinated aromatic compounds. The knowledge of the formation mechanism of its oxidation products and the one of operative conditions under which they can be completely destroyed, can contribute to a better understanding of the fate of higher molecular weight aromatics such as polychlorinated benzene, phenols, biphenyls, dibenzo-dioxins (PCDD) and dibenzofuranes (PCDF) which are often associated with the incineration of chlorinated hydrocarbons containing hazardous chemical wastes [2].

Numerous laboratory studies were devoted to oxidation processes of chlorobenzene under different experimental conditions. Dellinger et al. [3] reported thermal decomposition data for 20 selected hazardous organics compounds determined using a 1 mm ID flow reactor and 10 ppmV of organics in air. For a 2 s residence time, 99% of C_6H_5Cl are destroyed at 710°C. Thermal reactions of chlorobenzene in H_2 and H_2-O_2 mixtures were studied by Ritter and Bozzelli [4] in tubular flow reactors at 1 atm. and temperatures between 560-1000°C. Major products in both reaction systems were benzene, carbon solids and HCl, with CH_4, and C_2H_6 in low concentrations. When O_2 was present, minor products included toluene, cyclopentadiene, biphenyl, C_2H_4, C_2H_2 with CO and CO_2. It was shown that H_2 accelerates the destruction of chlorobenzene via a catalytic gas phase process. A detailed chemical mechanism was developed for the thermal decomposition of chlorobenzene diluted in H_2 [5]. Sethuraman et al. [6] studied the gas-phase, flameless oxidation of chlorobenzene at 1 atm pressure in the range 630-850°C, reaction times 0.4-1.94 s using a 2.1 cm ID flow reactor and O_2 concentrations in the range 1.8- 3.3% (fuel rich). The role of analysed species (CO, CO_2, HCl, CH_4, C_2H_2, C_2H_4, C_4H_4 , C_6H_6, $C_{10}H_8$) was discussed in view of the understanding of the oxidation mechanism of chlorobenzene. Chemical structures of atmospheric pressure, fuel rich (sooting) premixed, flat flames of $C_6H_5Cl/CH_4/O_2/Ar$ and $C_6H_5Cl/O_2/Ar$ mixtures were investigated by Cicek and Senkan [7]. Mole fraction profiles were determined for a great number of molecular species and their role in view of the combustion mechanism of C_6H_5Cl was also discussed. High temperature thermal-photolytic oxidation of chlorobenzene was investigated by Graham et al. [8] to assess potential applications including hazardous waste destruction, chemical synthesis and materials processing.

In this paper, we report experimental results obtained on the thermal degradation of chlorobenzene over the range 575-825°C for a residence time of 2 seconds in reaction atmospheres in which oxygen was in excess (equivalence ratio $\Phi = 0.035$). A detailed analysis of products observed at 700°C illustrates the great diversity of produced intermediates. The concentration profiles of initial and final species as well as the major intermediate byproducts are determined as a function of temperature for a residence time of 2 seconds. Reaction pathways explaining the formation of major observed products was presented and discussed .

EXPERIMENTAL

Description of the experimental set-up

High temperature oxidation of chlorobenzene was performed at 1 atm. in a flow reactor. The experimental set-up has been described in detail elsewhere [9]. Only specific information is given here.

Synthetic air was purified by passage through a molecular sieve trap. The gas flows were measured using a Tylan mass flowmeter. The liquid chlorobenzene, from Aldrich, 99.9% purety, was injected by a syringe pump into the controlled flowing air through a vaporization chamber similar to a gas chromatograph injector. The chamber was heated at 200°C. To improve the homogeneity, the mixture passed through a 8 cm ID, 10 cm long tube also heated at 200°C prior to the reactor. All experiments were carried out using a C_6H_5Cl/air mixture containing 1000 ppmV of C_6H_5Cl (equivalence ratio $\Phi = 0.035$). The reactor, a cylindric quartz tube 3 cm ID and 10 cm long, was located in the middle part of an electric furnace. The variation of temperature along the axis of the reactor did not exceed 5°C at 1000°C.

Exhaust gas sampling was achieved by withdrawing gases through a glass line heated at 300 °C to the analytical instruments. Both chemical and chromatographic methods were used for analysing reaction products. Organics were quantified by using an on line gas chromatograph. Relative concentrations of carbon oxides were measured using a non dispersive IR analyser. Before entering the analyser, water and hydrogen chloride were removed by passing the effluents through cold traps (-30°C) and a trap filled with chips of Zn. Dichlore and hydrogen chloride were analysed by passing the effluents through impingers filled with appropriate solutions : aqueous KI solution for Cl_2 and H_2SO_4 solution for HCl (acidic medium prevents hydrolysis of Cl_2). Cl_2 was quantified by iodometric method and HCl by argentimetric method.

Identification of organics

Organics were identified using a gas chromatograph / mass spectrometer (GC/MS) system (Hewlett-Packard 5890/5971) or a gas chromatograph equipped with an ionization flame detector where known compounds were injected to compare their retention time with that of the corresponding supposed compounds. As the GC/MS system was not connected to the effluent line, gaseous products were withdrawn from the line with a gas syringe and injected into the system. Due to the large dilution of organic products in air, the GC/MS analysis revealed only major organic compounds. To make the concentration level of non major species suited to the detection limit of the system, the gaseous reaction products were accumulated in a cold trap at -100°C. After heating the trapped products to room temperature, a fraction of the obtained liquid phase (0.5µl) was injected into the GC/MS to be separated and identified. The chromatographic conditions were as follows : column, a HP5 fused silica capillary (0.32 mm ID, 30 m long), 35°C hold for 10 minutes then ramped to 250°C at 5°/min ; injector split mode, 1/10 ratio, 200°C ; detector quadripole, 280°C, 70 eV, scan mode. Identification was achieved by comparing the experimental spectra to reference mass spectra of the data base (NBS 49 K) and, when possible, to spectra of purchased reference compounds. Retention times of chromatographic peaks were also compared with the ones of purchased compounds when available. Figures 1a and 1b show typical total ionic chromatograms of products collected during the treatment of chlorobenzene at 700°C for a 2 s residence time. The captions give the list of identified peaks : ** indicates a complete identification, no asterisk corresponds to a relatively good confidence of the identification.

The thermal oxidation of chlorobenzene lead to the formation of a hundred intermediate reaction products among which about 74 of them were identified. Dichlorodibenzofurane ($C_{12}H_6Cl_2O$, MW 236) was the highest molecular weight species detected. Benzenic compounds may be substituted by Cl (1 to 4) or OH (1 or 2), or alkyl groups. Compounds with molecular weight lighter than the one of chlorobenzene are not as numerous as heavier species formed via addition reactions. As shown in Figures 1a and 1b, phenol (chromatographic peak 33), 2-H-pyran-2-one (peak 34), 3-chlorophenol (peak 60), 2-chloro 1,4-dihydroxybenzene (peak 75), and 2,5-dichloro 1,4-dihydroxybenzene (peak 76) are major compounds.

Precursors of dioxins were also observed, for example substituted furanes (peaks 31, 36, 42), chlorobenzofuranes (peak 58), or chlorophenols (peaks 35, 59, 60, 61). The dichlorodibenzofuranes (peaks 108, 110, 111, 112, and 114) have stuctures similar to dioxins.

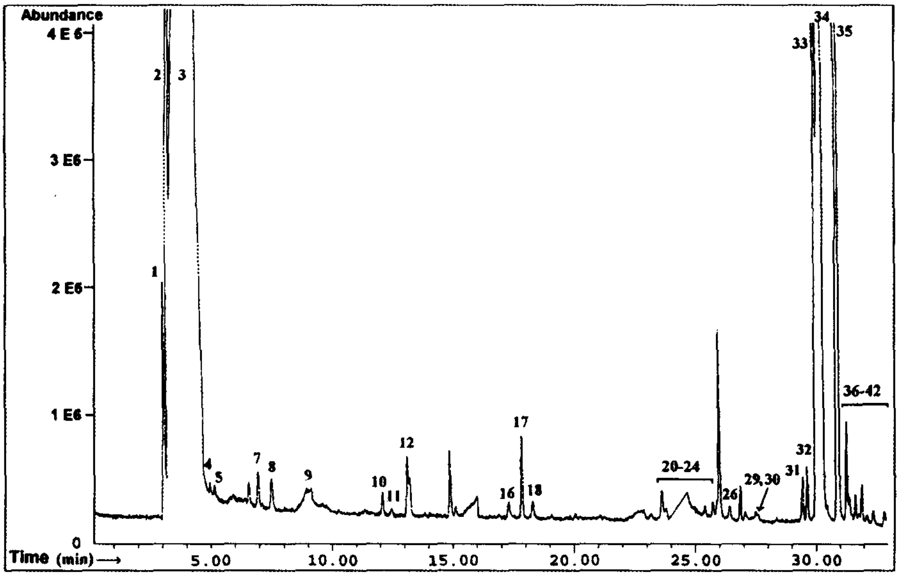


Figure 1a : Typical total ionic chromatogram of the condensed effluents, (cold trap at -100°C) collected during the oxidative degradation C_6H_5Cl at 700°C, 2 s residence time. Peaks : **1-** air ; **2-**water ; **3-** Hydrogen choride (HCl); **4-** 2-propenal (C_3H_4O); **5-** propanal (C_3H_6O); 7- 3 methyl,1pentene (C_6H_{12}); **8-** chloroacetaldehyde (C_2H_3ClO); **9-** acetic acid ($C_2H_4O_2$) ; **10-** chloromethoxyethane(C_3H_7ClO) ; **11-** 3methyl 1,3 pentadiene (C_6H_{10}); **12-** benzene** (C_6H_6) ; **16-** 1,1dichloro, 2 ethenyl cyclopropane ($C_5H_6Cl_2$) ; **17-** 1-chloroacetone (C_3H_5ClO) ; **18-** isomer of species 16 ($C_5H_6Cl_2$) ; **20-** 2-furanecarboxaldehyde ($C_5H_4O_2$) ; **21-** 3 methylfurane (C_5H_6O) ; **22-** chlorobenzene** (C_6H_5Cl) ; **23-** 1,4 dimethylbenzene (C_8H_{10}) ; **24-** ethynylbenzene (C_8H_6) ; **26-** ethenylbenzene (C_8H_8); **29-** 3,4 dihydro-2H-pyrane (C_5H_8O) ; **30-** methoxybenzene(C_7H_8O) ; **31-** 2 carbonylfuranechloride ($C_5H_3ClO_2$) ;

32- benzaldehyde (C_7H_6O) ; **33-** phenol (C_6H_6O) ; **34-** 2H-pyran-2-one ($C_5H_4O_2$) ; **35-** 2 chlorophenol** (C_6H_5ClO) ; **36-** benzofurane** (C_6H_8O) ; **37-** 4 hydroxybenzaldehyde ($C_7H_6O_2$) ; **38-** 1,3 dichlorobenzene** ($C_6H_4Cl_2$) ; **39-** 1,4 dichlorobenzene** ($C_6H_4Cl_2$) ; **41-** 1,1 dichloro, 2 ethenylcyclopropane ($C_5H_6Cl_2$) ; **42-** 3 methylfurane (C_5H_6O). Missing numbers correspond to non identified peaks.

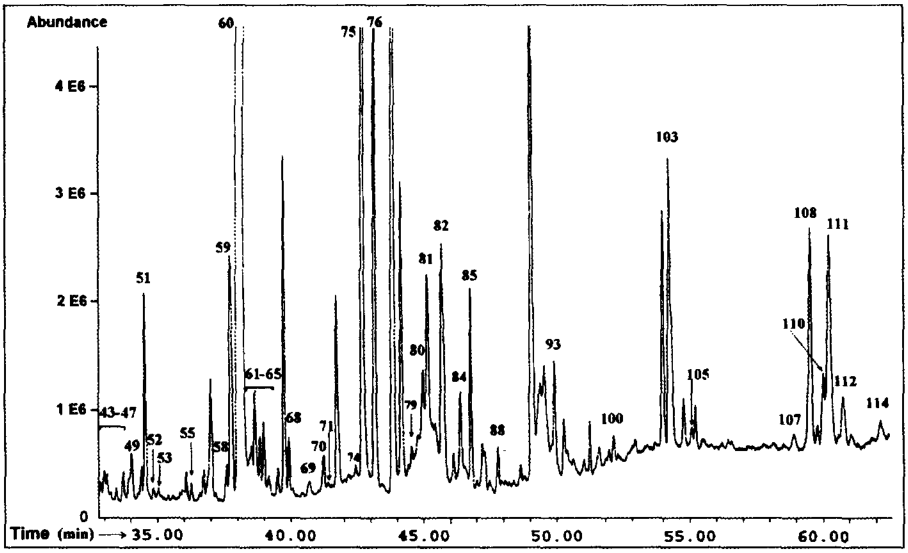


Figure 1b : Same conditions as for fig. 1a. Peaks : **43-** 1,2 dichlorobenzene** ($C_6H_4Cl_2$) ; **44-** 2 or 3 or 4 methylphenol (C_7H_8O) ; **45-** 2 hydroxybenzaldehyde ($C_7H_6O_2$) ; **46-** 1,2 propadienylbenzene (C_9H_8) ; **47-** phenylethanoate ($C_8H_8O_2$) ; **49-** benzoyl chloride (C_7H_5ClO) ; **51-** 2 chloro cyclohexa 2,5 diene (C_6H_7Cl) ; **52-** 2 butenoyl dichloride ($C_4H_2Cl_2O_2$) ; **53-** 1 chloro, 3 methoxybenzene (C_7H_7ClO) ; **55-** 3(or 4) chlorobenzaldehyde (C_7H_5ClO) ; **58-** 5(or 7) chlorobenzofurane (C_8H_5ClO) ; **59-** 2,4 dichlorophenol** ($C_6H_4Cl_2O$) ; **60-** 3 chlorophenol **(C_6H_5ClO) ; **61-** 4 chlorophenol **(C_6H_5ClO) ; **62-** naphtalene ($C_{10}H_8$) ; **63-** naphtalene 1,2 dione ($C_{10}H_6O_2$) ; **64-** isomer of 59 species ($C_6H_4Cl_2O$) ; **65-** 5 chloro, 2 hydroxybenzaldehyde ($C_7H_5ClO_2$) ; **68-** 2,5 cyclohexadiene-1,4-dione-2,6 dichloro ($C_6H_2Cl_2O_2$) ; **69-** 2(or 4) chloro,6(or 3) methylphenol (C_7H_7ClO) ; **70-** 2 chloro, 5(or 6) methylphenol (C_7H_7ClO) ; **71-** dichloro 4 methylphenol ($C_7H_6Cl_2O$) ; **74-** chlorobenzoic acid ($C_7H_5ClO_2$) : **75-** 2 chloro 1,4 dihydroxybenzene ($C_6H_5ClO_2$) ; **76-** 2,5 dichloro 1,4 dihydroxybenzene ($C_6H_4Cl_2O_2$) ; **79-** 2,3,4 (or 2,3,6 or 2,4,6) trichlorophenol ($C_6H_3Cl_3O$); **80-** 1 chloronaphtalene** ($C_{10}H_7Cl$) ; **81-** 3,4 dichlorophenol ($C_6H_4Cl_2O$) , **82-** 3 phenyl propenyl chloride** (C_9H_7ClO) ; **84-** 1 chloro 4 ethenylbenzene (C_8H_7Cl) ;

85- 2H-1 benzopyrone ** ($C_9H_6O_2$) ; **88-** 3 chloromethyl, 1methoxy, 2,4,6 trimethylbenzene ($C_{11}H_{15}ClO$) ; **93-** 2,3,5,6 tetrachlorophenol ($C_6H_2Cl_4O$) ; **100-** 4 hydroxy[1,1'-biphenyle] ($C_{12}H_{10}O$) , **103-** 4 ,4' oxybis phenol ($C_{12}H_{10}O_3$) ; **105-** 2,3 dimethylnaphtalene 1,2 dione ($C_{12}H_{10}O_2$) , **107-** xanthone** ($C_{13}H_8O_2$) ;**108-** dichlorodibenzofurane ($C_{12}H_6Cl_2O$) ; **110-112, 114-** isomers of 108 species ($C_{12}H_6Cl_2O$)
Missing numbers correspond to non identified peaks.

Quantification of organics

Only a few identified products have a sufficient concentration in the gaseous effluents to be quantified on line. The chromatograph (Shimadzu GC-14A) was equipped with a gas sampling valve. The gaseous effluents go through a loop of 2 cm^3 volume heated at 150°C. A HP5 fused silica capillary column (0.32 mm ID, 50 m long) was used to analyse the aromatic compounds : furane, benzene, chlorobenzene, 2-chlorophenol and benzofuranes . The chromatographic conditions were as follows : initial temperature of 35°C during 10 min then linear programmation of 5°/min up to 250°C. The lightest compounds, (not analysed by GC/MS system), CH_4, C_2H_2 , C_2H_4, vinyl chloride, and vinylacetylene were separated and quantified by using an Al_2O_3/KCl column (0.53mm ID, 50 m long). The GC temperature program started at 70°C and was ramped to 200°C at 3°C/min. The temperature of the flame ionization detector was 250°C. Helium was used as a carrier gas. Calibrations of the identified species (except vinylacetylene) were accomplished with pure commercial compounds. The response factor used for vinylacetylene was calculated from the one of C_2H_2, according to the method proposed by Grob [10].

RESULTS AND DISCUSSION

Figure 2 shows the concentration profile of C_6H_5Cl determined as a function of temperature for a 2 seconds residence time. No consumption was observed until 575°C. At 650 °C, about 7% of the initial chlorobenzene were destroyed. The reaction rate was maximum between 650 and 700°C. At 725°C, C_6H_5Cl is no more detectable in the exhaust effluents.

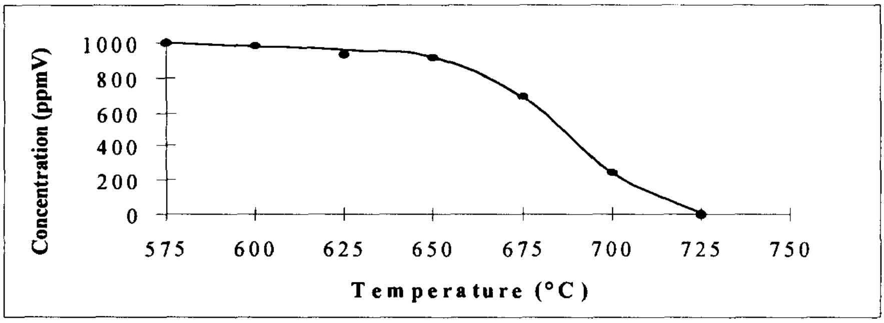


Figure 2. Thermal decomposition profile for C_6H_5Cl. 1000 ppmV C_6H_5Cl in air and 2s residence time.

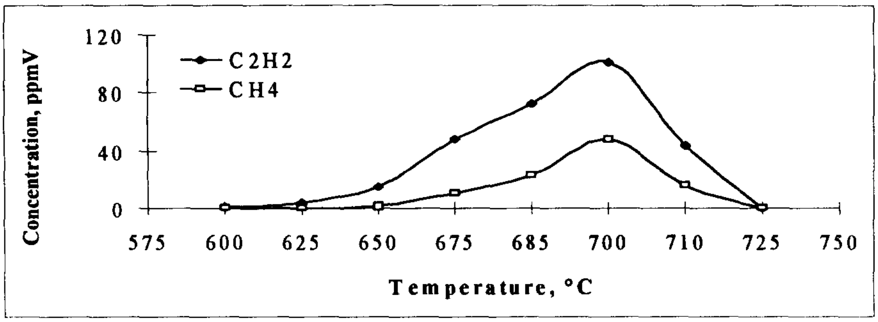


Figure 3 : Concentration profiles of C_2H_2 and CH_4 as a function of temperature observed for the thermal degradation of 1000 ppmV C_6H_5Cl in air ($\Phi = 0.035$) for a 2 s residence time.

This result is in concordance with the values of the litterature, $T_{99/2} = 710$ °C [3] and 730°C [8]. Figures 3 and 4 depict the concentration profiles of organic intermediate products. C_2H_2 and CH_4 are the major compounds, and their concentration profile as a function of temperature were quite similar (Fig.3). Formation of C_2H_2 proceeds at a lower temperature than the one of CH_4 (600°C instead of 650°C) but their concentrations go through a maximum value at the same temperature of 700°C. At this temperature, concentrations of 48 and 102 ppmV were measured for CH_4 and C_2H_2 respectively. Maximum concentration of acetylene represents about 3% of the initial carbon arising from chlorobenzene. This value is similar to that observed by Sethuraman et al. [6]. Maximum concentrations of the other analysed organics (C_4H_4, C_2H_4, furan, benzene and C_2H_3Cl) are clearly lower, about 3 to 15 ppmV (Fig.4). C_2H_4 and C_2H_3Cl show similar profiles, with maximum concentrations of 9 ppm at 700°C. To our knowledge, it is the first time that the presence of vinyl chloride is mentioned as a product of the thermal degradation of chlorobenzene. The concentration of vinylacetylene is maximum at 675°C, about 15 ppmV. Maximum concentrations of furane and benzene are quite similar, about 4 ppmV at 675°C and 700°C respectively, that represents less than 0.5% of the initial carbon. The observed percentage of benzene is in relatively good concordance with the work of Sethuraman et al. [6]. At 725 °C, all these compounds have been completely destroyed.

The concentration profiles of carbon oxides are shown in Figure 5. Carbon monoxide is the most important byproduct of all intermediates. Its concentration passes through a maximum of 3500 ppmV at about 710-715 °C. 100 ppmV of CO are still produced at 850°C for a 2 s residence time. Carbon dioxide formation occurs at higher temperatures. Its concentration becomes significant from 700°C. Beyond 725°C, its formation is only due to CO oxidation since all organic intermediates have been completely destroyed. Its final concentration is very close to 6000 ppmV, indicating complete oxidation of chlorobenzene.

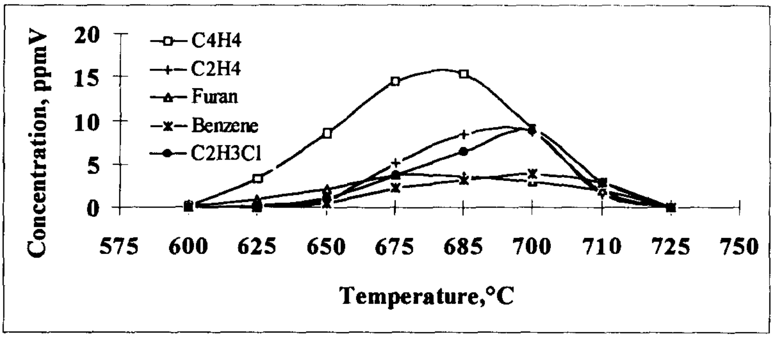


Figure 4 : Concentration profiles of some organic intermediates as a function of temperature for the thermal degradation of 1000 ppmV C_6H_5Cl in air (Φ = 0.035) for a 2 s residence time.

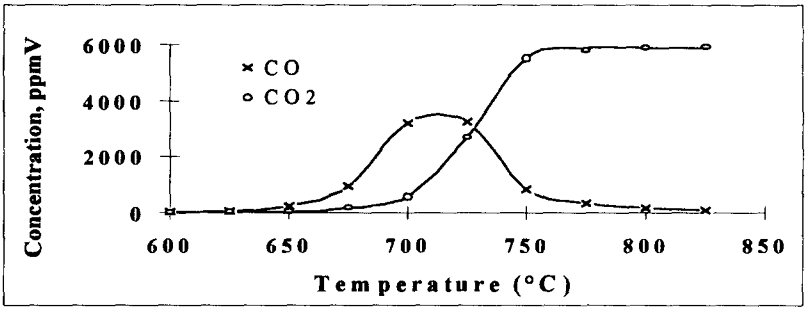


Figure 5 : Concentration profiles of CO and CO_2 as a function of temperature for the thermal degradation of 1000 ppmV C_6H_5Cl in air (Φ = 0.035) for a 2 s residence time.

Figure 6 exhibits the concentration profiles of non organic chlorinated species (HCl and Cl_2) as a function of temperature. HCl concentration in the exhaust gases is about 40 ppmV at 650°C. At lower temperatures, the chemical method used for the quantification of HCl was not accurate enough to access to low concentrations (< 20 ppmV). The formed amounts of HCl and Cl_2 sharply increase from 650 and 725°C respectively. A maximum concentration of about 800 ppmV is obtained at 750°C for HCl. Cl_2 production is observed at 50°C higher than HCl.

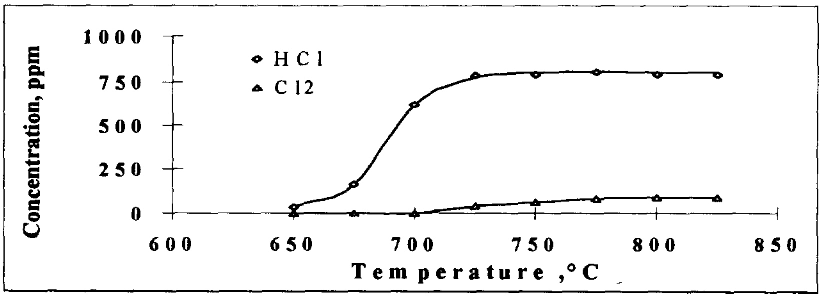


Figure 6 : Concentration profiles of HCl and Cl_2 as a function of temperature for the thermal degradation of 1000 ppmV C_6H_5Cl in air (Φ = 0.035) for a 2 s residence time.

Carbon and chlorine balances.

Carbon or chlorine balance is defined by the following ratio :

Carbon (or Cl) in gas phase species / Carbon (or Cl) fed in C_6H_5Cl

The initial relative concentration of C_6H_5Cl provides 6000 ppmV elemental carbon and 1000 ppmV elemental chlorine. Balances were calculated to ascertain the fidelity and accuracy of the experiments. Table 1 shows the results obtained by considering the participation of C and Cl atoms contained in all quantified species at each temperature.

T. (°C)	575	600	625	650	675	700	725	750	775	800	825
$(C) / (C)_0$	1.01	0.99	0.96	0.99	0.94	0.90	0.97	1.03	1.01	1.00	1.01
$(Cl) / (Cl)_0$	1.01	0.98	0.94	0.97	0.89	0.85	0.89	0.94	0.96	0.97	0.98

Table 1 : Carbon and chlorine balances from the degradation of monochlorobenzene in air (Φ = 0.035), 700°C, 2 s residence time, between 575 and 825°C.

As shown in Table 1, C and Cl balances are relatively good. The best results are obtained at the lowest and hightest studied temperatures. The largest deviation occurs at around 700°C, though 2-chlorophenol and benzofurane have been measured at this temperature, about 3 and 0.5 ppmV respectively. The GC/MS analysis of products observed at 700°C has highlighted the great number of species having molecular weight superior to that of chlorobenzene. Although their concentrations are very small, their carbon and chlorine content is large enough to induce discrepancies observed. The deviation is more important for chlorine than for carbon, probably due to experimental uncertainties from the HCl and Cl_2 quantitative determinations. Figures 7 and 8 present the contribution of all the species to C and Cl balances.

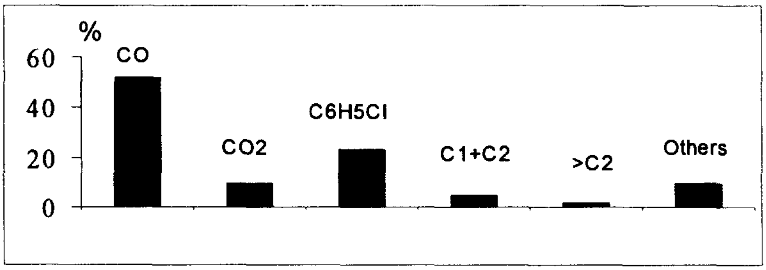


Figure 7 : Carbon balance, contribution of species issued from 1000 ppmV of chlorobenzene treated in air (Φ = 0.035), at 700°C, 2s residence time.

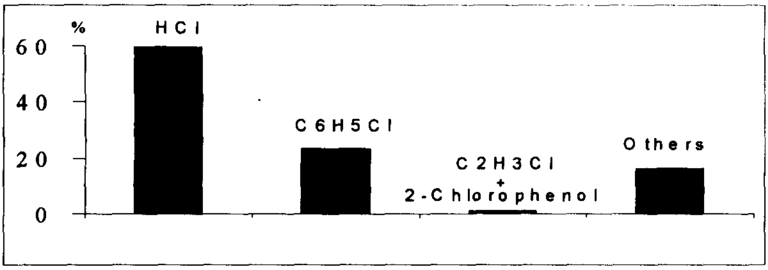


Figure 8 : Chlorine balance, contribution of species issued from 1000 ppmV of chlorobenzene treated in air ($\Phi = 0.035$), at 700°C, 2s residence time.

A detailed chemical kinetic mechanism will be necessary for explaining the partitioning of products as a function of temperature. However, kinetic parameters of only few reactions concerning chlorobenzene or related compounds can be found in the literature. Nevertheless preliminary remarks can be made with regard to the major reaction pathways based on thermochemical properties. The computer program THERM developed by Ritter and Bozzellli [11] was used to calculate thermodynamic parameters of molecules and radicals according to the group additivity method of Benson [12].

Destruction of chlorobenzene

Three reaction pathways can initiate the thermal oxidation of chlorobenzene :

- the breakdown of C-Cl bond to produce phenyl radicals and chlorine atoms :

$C_6H_5Cl \rightarrow Cl + C_6H_5(cy)$ $\Delta_rH°(298K) = 97.2\ kcal.mol^{-1}$

or, the one of C-H bonds to give C_6H_4Cl radicals and H atoms :

$C_6H_5Cl \rightarrow H + C_6H_4Cl$ $\Delta_rH°(298K) = 112.1\ kcal.mol^{-1}$

- the breakdown of the aromatic ring to generate CHCCl and C_2H_2 :

$C_6H_5Cl \rightarrow [C_6H_5Cl](l) \rightarrow CHCCl + 2\ C_2H_2$ $\Delta_rH°(298K) = 146.4\ kcal.mol^{-1}$

- the reactions of H-abstraction (or Cl-abstraction) by O_2 :

$C_6H_5Cl + O_2 \rightarrow C_6H_4Cl^{\bullet} + HO_2$ $\Delta_rH°(298K) = 62.5\ kcal.mol^{-1}$

$C_6H_5Cl + O_2 \rightarrow {}^{\bullet}C_6H_5(cy) + ClO_2$ $\Delta_rH°(298K) = 93.3\ kcal.mol^{-1}$

HO_2 can generate H and OH radicals via the following reactions where M represents any collision partner :

$HO_2 + M \rightarrow H + O_2 + M$ $\Delta_rH°(298K) = 48.6\ kcal.mol^{-1}$.

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ $\Delta_rH°(298K) = 5.0\ kcal.mol^{-1}$.

$H_2O_2 + M \rightarrow OH + OH + M$ $\Delta_rH°(298K) = 51.5\ kcal.mol^{-1}$

H and OH radicals play an important role as chain carriers in the conversion reaction of CO to CO_2

$CO + OH \rightarrow CO_2 + H$ $\Delta_rH°(298K) = -25$ kcal.mol^{-1}

and in the branching reaction

$H + O_2 \rightarrow OH + O$ $\Delta_rH°(298K) = 52.14$ kcal.mol^{-1}

All these radicals can react with chlorobenzene, leading to its consumption via various reaction pathways depending on the temperature range and the residence time. For example, we can have :

- H abstraction by Cl, H, OH, HO_2, etc....radicals (X):

$C_6H_5Cl + X \rightarrow C_6H_4Cl + HX$

- Cl abstraction or substitution by H atoms :

$C_6H_5Cl + H \rightarrow {}^{\bullet}C_6H_5(cy) + HCl$ $\Delta_rH°(298K) = -5.8$ kcal.mol^{-1}

$C_6H_5Cl + H \rightarrow C_6H_6Cl^* = C_6H_6 + Cl$ $\Delta_rH°(298K) = -15.5$ kcal.mol^{-1}.

- H (or Cl) substitution by OH radicals :

$C_6H_5Cl + OH \rightarrow (OH\ C_6H_5Cl)^* = C_6H_5OH + Cl$ $\Delta_rH°(298K) = -16.3$ kcal.mol^{-1}

$C_6H_5Cl + OH \rightarrow (OH\ C_6H_5Cl)^* = OHC_6H_4Cl + H$ $\Delta_rH°(298K) = 5.8$ kcal.mol^{-1}

$OHC_6H_4Cl + OH \rightarrow (OH)_2C_6H_3Cl + H$ $\Delta_rH°(298K) = -16.55$ kcal.mol^{-1}

These last three reactions can explain the formation of phenol, chlorophenol and chlorodihydroxybenzene, all identified by GC/MS. Formation of chlorophenol may be also explained from the reaction between primary radicals (C_6H_4Cl) and molecular oxygen [7].

Formation of the most important intermediates

C_2H_2 and CO are the most important by products of the thermal degradation of chlorobenzene. They are mainly produced from phenyl radicals by isomerization to give a linear (l) species, then decomposition :

$C_6H_5(cy) \rightarrow C_6H_5\ (l)$ $\Delta_rH°(298K) = 60.3$ kcal.mol^{-1}

$C_6H_5\ (l) \rightarrow C_4H_3 + C_2H_2$ $\Delta_rH°(298K) = 40.3$ kcal.mol^{-1}

-or by reaction with oxygen molecule and decomposition [13]

$C_6H_5(cy) + O_2 \rightarrow C_6H_5O + O$ $\Delta_rH°(298K) = -9.1$ kcal.mol^{-1}

$C_6H_5O \rightarrow C_5H_5 + CO$ $\Delta_rH°(298K) = 18.7$ kcal.mol^{-1}

where C_5H_5 represents the cyclopentadienyl radical.

From [6], phenyl radicals can also react via oxygen addition/decomposition processes :

$C_6H_5(cy) + O_2 \rightarrow (C_6H_5O_2)^* \rightarrow$ O=C-CH=CH-CH=CH-CHO (A) $\Delta_rH°(298K) = -89.4$ kcal.mol^{-1}

(A) $\rightarrow$ CH=CH-CH=CH (B) + CO + CHO $\Delta_rH°(298K) = 137$ kcal.mol^{-1}

(B) → 2 C_2H_2 $\Delta_rH°(298K) = -36.6\ kcal.mol^{-1}$

(A) → CO + CH=CH-CH=CH-CHO (C) $\Delta_rH°(298K) = 34.6\ kcal.mol^{-1}$.

(C) → CO + CH=CH-CH=CH_2 (D) $\Delta_rH°(298K) = 6.4\ kcal.mol^{-1}$

(D) → $C_2H_2 + C_2H_3$ $\Delta_rH°(298K) = 40.3\ kcal.mol^{-1}$

(D) → C_4H_4 +H $\Delta_rH°(298K) = 35.1\ kcal.mol^{-1}$

This reaction pathway can also explain the C_4H_4 formation. Besides C_2H_2 can also be formed [7] from C_2H_3 radical via the following reaction :

$C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$ $\Delta_rH°(298K) = -15.3\ kcal.mol^{-1}$

Formation of the other intermediate by products

Methane :

Formation of CH_4 takes place via methyl radicals CH_3 as precursors : $CH_3 + RH \rightarrow R + CH_4$

Under our experimental conditions, quantities of CH_4 in the reaction effluents are relatively important , then the reaction of methyl radicals with chlorobenzene might occur [7] :

$CH_3 + C_6H_5Cl \rightarrow C_6H_4Cl + CH_4$ $\Delta_rH°(298K) = 7.3\ kcal.mol^{-1}$

To explain the CH_3 formation, several reaction pathways are possible via C_2H_2 oxidation [6]:

$C_2H_2 + OH \rightarrow CH_2CO + H$ $\Delta_rH°(298K) = -22.9\ kcal.mol^{-1}$

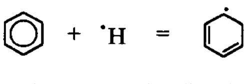
$C_2H_2 + O \rightarrow CH_2 + CO$ $\Delta_rH°(298K) = -55.6\ kcal.mol^{-1}$

$CH_2CO + H \rightarrow CH_3 + CO$ $\Delta_rH°(298K) = -32\ kcal.mol^{-1}$

$CH_2CO + M \rightarrow CH_2 + CO + M$ $\Delta_rH°(298K) = 76.6\ kcal.mol^{-1}$

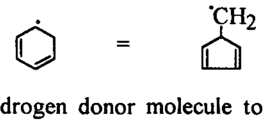
$CH_2 + RH \rightarrow CH_3 + R$

where RH is any hydrocarbonated compound. As shown above, these reactions can also contribute to the formation of CO. Another reaction pathway via the cyclohexadienyl and methylenecyclopentadienyl radicals was proposed by Louw et al. [14] to interpret the formation of CH_3 in the oxidation of chlorobenzene :



$\Delta_rH°(298K) = -22\ kcal.mol^{-1}$

then isomerization of the cyclohexadienyl radical into methylenecyclopentadienyl radical :



$\Delta_rH°(298K) = 22.1\ kcal.mol^{-1}$

that reacts with any hydrogen donor molecule to give methyl cyclopentadiene which decomposes into cyclopentadienyl and methyl radicals.

Benzene

Benzene can be produced from chlorobenzene [7] :

$C_6H_5Cl + H \rightarrow [C_6H_6Cl]^* \rightarrow C_6H_6 + Cl$ $\Delta_rH°(298K) = -15.5\ kcal.mol^{-1}$

or, from the reaction between vinylacetylene and acetylene [13]

$C_4H_4 + C_2H_2 \rightarrow C_6H_6$ $\Delta_rH°(298K) = -102.2\ kcal.mol^{-1}$

Ethylene :

Formation of ethylene results from the vinyl radical C_2H_3 hydrogenation. Formation of ethylene from ethane deshydrogenation seems unlikely because ethane was not detected in the reaction effluents.

Vinyl chloride

Vinyl chloride could be formed from C_2H_3 radical, or C_2H_4 and C_2H_2 molecules as follows :

$C_2H_3 + Cl \rightarrow C_2H_3Cl$ $\Delta_rH°(298K) = -95.5\ kcal.mol^{-1}$

$C_2H_3 + HCl \rightarrow C_2H_3Cl + H$ $\Delta_rH°(298K) = -8.23\ kcal.mol^{-1}$

$C_2H_4 + {}^{\bullet}Cl \rightarrow C_2H_3Cl + H$ $\Delta_rH°(298K) = 15.7\ kcal.mol^{-1}$

$C_2H_2 + HCl \rightarrow C_2H_3Cl$ $\Delta_rH°(298K) = -26.97\ kcal.mol^{-1}$

Formation of final compounds

Carbon dioxide is mainly produced by CO oxidation via the well known reactions :

$CO + OH \rightarrow CO_2 + H$ $\Delta_rH°(298K) = -25\ kcal.mol^{-1}$

$CO + HO_2 \rightarrow CO_2 + OH$ $\Delta_rH°(298K) = -60.6\ kcal.mol^{-1}$

$CO + O_2 \rightarrow CO_2 + O$ $\Delta_rH°(298K) = -8.1\ kcal.mol^{-1}$

$CO + ClO \rightarrow CO_2 + Cl$ $\Delta_rH°(298K) = -62.8\ kcal.mol^{-1}$

The main reactions concerning the HCl formation could involve as a hydrogen donor :

$C_6H_5Cl + Cl \rightarrow HCl + C_6H_4Cl$ $\Delta_rH°(298K) = 9.1\ kcal.mol^{-1}$

$C_6H_5Cl + H \rightarrow HCl + C_6H_5(cy)$ $\Delta_rH°(298K) = -5.8\ kcal.mol^{-1}$

Recombination of Cl atoms represents the main pathway to Cl_2 formation :

$Cl + Cl + M \rightarrow Cl_2 + M$ $\Delta_rH°(298K) = -57.8\ kcal.mol^{-1}$

Cl_2 is only formed at T>725°C and for a 2 s residence time, i.e when all organic compounds been destroyed.

CONCLUSION

Experimental flow reactor studies of the thermal oxidation processes of chlorobenzene in air for residence time of 2 seconds over the range 575-825°C were reported. More than seventy intermediate organics were identified by GC/MS as trace species. Most of them were substituted aromatics. Some precursors of dioxins such as benzofuranes and chlorophenols were also observed. Concentration profiles of major intermediates (C1 to C6) and final products (HCl, Cl_2 and CO_2) were determined as a function of temperature. Experimental results showed that the ring breaking processes were preponderant over the studied temperature range. Reaction pathways leading to the formation of the main products were proposed and corresponding reaction enthalpies estimated. Most kinetic parameters governing the reactions as a function of temperature are unknown and consequently, must be estimated for modelling the products partitioning experimentally observed. Developement of such a chemical mechanism is underway.

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