

## OXYCHLORINATION AND OXIDATION OF ETHYLENE ON FLY ASH SURFACE

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### ABSTRACT

The fly ash catalyzed oxychlorination of ethylene, using hydrogen chloride and molecular oxygen produced a wide range of chlorinated C<sub>1</sub> and C<sub>2</sub> compounds in the temperature range 250-500 °C. Apart from chlorination, oxidation is an important pathway as well, especially above 350 °C. The latter process primarily produces carbon monoxide.

### KEYWORDS

Fly ash, oxychlorination, oxidation, ethylene, hydrogen chloride, 1,2-dichloroethane, vinylchloride

### INTRODUCTION

It has been recognized that fly ash is a potent catalyst for the formation of hazardous compounds from residual organic matter in the flue gas of a municipal waste incinerator. Experimentally it has been demonstrated that a variety of organic compounds can act as precursors for the formation of polychlorinated dibenzofurans (PCDFs) and dibenzo-*p*-dioxins (PCDDs). Laboratory studies revealed that, under appropriate reaction conditions, aromatic structures like toluene (De Leer *et al.*, 1989) and phenol (Born *et al.*, 1990) can lead to considerable amounts of PCDDs.

Our studies (Born *et al.*, 1989, 1990) on the behavior of fly ash have shown that (substituted) phenol - in the presence of this catalyst, hydrogen chloride and air - can be oxidized almost completely within a few seconds at 350 °C. However, besides phenol oxidation, chlorination was observed as well. Already at 150 °C, this reaction primarily leads to *o*- and *p*-chlorophenol. By consecutive chlorination higher chlorinated phenols were formed with increasing temperatures. Under comparable conditions cyclohexene (Valk and Mulder, 1990) yielded an array of reaction products. Chlorination, dehydrogenation, aromatization and combustion of this substrate produced *inter alia* tetra- and pentachlorobenzene.

In order to disentangle this complex reaction pattern, a more systematic investigation of the conversion of nonaromatic model compounds is necessary. In the present paper the behavior of ethylene is dealt with. Industrially (Weissermel and Arpe, 1988) ethylene is converted into the bulk chemical 1,2 dichloroethylene (EDC) both by direct chlorination with Cl<sub>2</sub>, and by oxychlorination, using hydrogen chloride and oxygen by means of a Cu(II)-containing catalyst. Since copper is one of the reactive components in fly ash we have investigated the oxychlorination of ethylene using fly ash as the catalyst in the presence of hydrogen chloride, oxygen and water over a temperature range of 250-500 °C.

### EXPERIMENTAL SECTION

The title reaction was studied in a flow system. The experimental setup has been described in detail elsewhere (Born *et al.*, 1989). Reactions were conducted in a tubular quartz reactor (length 20 cm, internal diameter 8 mm) packed with fly ash obtained from a Dutch municipal solid waste incinerator. A fixed bed of fly ash (length 9 cm) was placed in the center of the reactor. The reactor was mounted horizontally in an electrically heated tubular oven.

Once installed, the fly ash bed (weight 2.5 g) was pretreated at 550 °C in a stream of air for 24 hours to

remove all organic compounds and particulate organic carbon initially present. Residence times of the reactants under the reaction conditions varied between 1.4 and 0.9 seconds based on the remaining free reactor space.

Ethylene (99.9% purity) and air (technical grade) were used as such. Flows were regulated and metered utilizing mass flow controllers. Using a plastic 50 ml syringe driven by a motorized syringe pump, concentrated hydrogen chloride was introduced via a gas-tight rubber septum in the ethylene-air gas flow and vaporized before entering the reactor. The effluent flow was maintained at 150°C by heating tape to prevent the condensation of less volatile products.

Analysis of reaction gas mixtures was performed by collection of 0.50 ml samples of exit gas - gathered frequently five times) following wet HCl scrubbing - via a gas tight syringe. Ethylene, CO and CO<sub>2</sub> were analyzed by GC using a Carboplot (10 m x 0.53 mm ID) wide bore column equipped with a methanizer and a flame ionization detector. Absolute amounts were based on peak surface areas relative to those given by injection of calibration gas mixtures. Chlorinated compounds were analyzed using GC-FID with a CP-Sil-5-CB (50 m) capillary column (temp. program: 40 °C (5 min), 8 °C/min 80 °C, 20 °C/min 250 °C (3.5 min)). Absolute amounts were based on peak surface areas relative to that of ethylene. Finally, oxygen consumption was measured by GC-TCD with a packed Molsieve 5 Å (2 m x 1/8") column, using nitrogen as an internal standard.

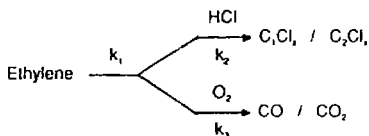
Employing a mass selective detector products were positively identified. In addition, less volatile products, if any, were either collected in tubes filled with Thermotrap, and consequently analyzed in a Chrompack purge and trap injector, or trapped in an ice/salt-cooled two layer system, consisting of aqueous alkali (in order to neutralize HCl, and eventually free chlorine) and pentane (to dissolve possible products). The obtained pentane solution was analyzed by GC-MSD.

## RESULTS AND DISCUSSION

The reactivity of fly ash towards ethylene was followed over a temperature range of 250-500°C. According to common practice in heterogeneous catalysis both the degree of conversion and the product selectivities were determined in two series of experiments. Employing one sample of fly ash the temperature range was scanned from 250 to 500 °C and back again to 250 °C in order to verify if any activity loss of the catalyst had occurred: this was not the case. The results are presented in table 1.

As expected, in the low temperature range 1,2 dichloroethylene (EDC) is the main, if not exclusive, product. With increasing temperature several changes occur. Approaching 350 °C, oxidation sets in; at 500 °C already ca. 70 % of the carbon in decomposed ethylene is converted into CO and CO<sub>2</sub>. Moreover, the production of vinylchloride (VC), together with C<sub>1</sub> and C<sub>2</sub> chlorinated compounds, increases substantially with simultaneous decrease in EDC formation. Typically, CH<sub>2</sub>Cl<sub>2</sub> > CHCl<sub>3</sub> > CCl<sub>4</sub> > CH<sub>3</sub>Cl. In a separate blank experiment, without fly ash, even at 500 °C no oxidation/chlorination products could be detected.

The results in table 1 allow a kinetic analysis of the major reaction routes. At first approximation the conversion of ethylene can be modeled by two distinct pathways: ethylene is either converted into chlorinated products or completely oxidized (Gelperin *et al.*, 1979).

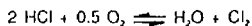


With an excess of hydrogen chloride and oxygen the two processes can be assumed to be first order in ethylene. Using the tubular flow kinetic equations the individual rate constants ( $k_1$  = overall conversion,  $k_2$  = chlorination,  $k_3$  = oxidation) can be derived. In an Arrhenius plot the calculated values show excellent linear correlation with  $1/T$  ( $r^2 > 0.99$ ), leading to the following Arrhenius parameters:  $k_1 = 1.54 \times 10^7 \exp(-12.9/T)$ ,  $k_2 = 5.74 \times 10^6 \exp(9.6/T)$  and  $k_3 = 3.16 \times 10^{11} \exp(-20.6/T) \text{ s}^{-1}$  (note that the catalyst function is incorporated in the calculated pre-exponential factors). We also found that, under our experimental conditions, rates were proportional to the initial ethylene concentration and the amount of fly ash.

A large difference is noticed when ethylene is replaced by phenol; at 350 °C ca. 99% of the latter compound is subject to deep oxidation. This process is about 3000 times faster than ethylene oxidation, suggesting that a phenolic OH group has a much higher affinity towards the fly ash surface. Under comparable conditions benzene is almost completely inert.

With all details on the mechanisms of formation of C<sub>1</sub> and C<sub>2</sub> chlorinated compounds, general trends can be deduced from table 1. The initial product from ethylene is EDC. Thermal unimolecular decomposition

yielding VC under homogenous gas phase conditions is only to be expected above 550 °C (Benson and O'Neil, 1970). However, gas phase pyrolysis of EDC to VC at 450 °C normally proceeds via a radical chain process with chlorine atoms as the chain carrier. This may be valid, but actual rates strongly suggest that a contribution from some surface-catalyzed HCl elimination is important. In oxychlorination of olefins with copper(II)chloride up to 300 °C free molecular chlorine is not involved (Magistro and Cowler, 1986). Above ca 300 °C the production of free molecular chlorine becomes important (according to the Deacon process), as has been experimentally verified.



The theoretical chlorine equilibrium concentration can be derived using thermodynamic values (Stull and Prophet, 1971) and, accepting that  $[\text{H}_2\text{O}]$  and  $[\text{O}_2]$  remain constant, - typically, at  $5 \times 10^{-3} \text{M}$  and  $2.6 \times 10^{-3} \text{M}$  respectively - at 600 K for example with an initial amount of  $1.4 \times 10^{-3} \text{M}$  HCl,  $[\text{HCl}]_{\text{eq}}$  and  $[\text{Cl}_2]_{\text{eq}}$  will be  $4 \times 10^{-4} \text{M}$  and  $5 \times 10^{-4} \text{M}$  respectively. In separate experiments without ethylene we observed a decrease in chlorine concentration with temperature. However, the absolute amounts (at 350 °C  $7.6 \times 10^{-4} \text{M}$ ) were lower than the calculated equilibrium concentrations. Presumably the copper content of the fly ash is not high enough to ensure rapid equilibration (Valk and Mulder, 1990).

Over the temperature range employed, even above 300 °C, it seems unlikely, for kinetic and thermodynamic reasons, that EDC is produced by homogenous radical addition of  $\text{Cl}^\cdot$  to the double bond. The only alternative homogenous route available will be direct formation of VC from ethylene - via H-abstraction by  $\text{Cl}^\cdot$  from ethylene followed by chlorine transfer from  $\text{Cl}_2$ . Therefore we suggest that EDC production will be largely fly ash catalyzed. From table 1 can be inferred that EDC formation decreases above 430 °C because free chlorine atoms will induce HCl elimination from EDC to give VC. Analogously, VC can yield 1,1,2-trichloroethane which, in turn, can lose HCl.

At low degrees of ethylene conversion, besides EDC only  $\text{CH}_2\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  are formed, which can serve to rationalize the  $\text{C}_1$  formation.

Presumably, these products stem from a common intermediate, such as a  $\text{ClCH}_2\text{CH}_2$ , (metal)-Cl entity. EDC will result from reductive elimination, whereas isomerization to a  $\text{ClCH}_2$ , (metal)(Cl)( $\text{CH}_2$ ) configuration can give way to formation of the  $\text{C}_1$ -chlorides. Analogous processes involving higher chlorinated  $\text{C}_2$ -derivatives can lead to  $\text{CHCl}_2$  and  $\text{CCl}_4$  as well. Furthermore, gas phase free radical chlorination is also likely to occur.

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Table 1. Oxychlorination and oxidation of ethylene: conditions and product pattern.

Temp. (°C)	252	276	302	327	352	375	402	427	452	477	502
P (atm)	1.036	1.038	1.042	1.051	1.048	1.049	1.054	1.056	1.059	1.063	1.066
Res. time (s) <sup>a</sup>	1.36	1.30	1.24	1.18	1.14	1.10	1.05	1.01	0.98	0.95	0.92
Inflows (mmol/h) <sup>b</sup>											
C <sub>2</sub> H <sub>4</sub>	3.61	4.10	3.71	4.52	4.05	4.00	4.89	5.04	4.16	3.73	4.36
Total	205.03	205.53	205.14	205.98	205.49	205.42	206.32	206.47	205.56	205.16	205.79
Outflows (mmol/h)											
O <sub>2</sub>	26.08	26.08	26.08	26.05	25.98	25.97	25.68	25.39	24.80	23.91	22.36
C <sub>2</sub> H <sub>4</sub>	3.57	3.87	3.68	4.36	3.79	3.11	4.23	4.36	3.59	2.25	1.82
Outflows (μmol/h) <sup>c</sup>											
CO	ND	ND	ND	ND	5.0	22.7	213.9	498.7	1131.8	2098.5	3909.3
CO <sub>2</sub>	ND	ND	ND	ND	8.4	3.4	48.6	89.6	114.2	119.2	166.5
CH <sub>4</sub>	ND	ND	ND	ND	ND	ND	0.2	2.3	4.7	8.3	8.3
C <sub>2</sub> H <sub>2</sub>	ND	ND	ND	ND	ND	ND	ND	ND	0.9	1.7	5.1
CH <sub>2</sub> Cl <sub>2</sub>	ND	ND	ND	ND	2.7	4.9	5.3	17.3	22.5	16.4	20.0
CHCl <sub>3</sub>	ND	ND	0.9	3.1	6.2	9.7	20.9	28.8	39.8	40.3	64.7
CCl <sub>4</sub>	ND	ND	ND	ND	ND	ND	2.8	8.7	24.1	38.3	104.8
C <sub>1</sub> H <sub>2</sub> Cl-CH <sub>2</sub> (VC)	ND	ND	ND	ND	ND	ND	ND	5.1	15.1	23.5	68.1
C <sub>1</sub> HCl-CH <sub>2</sub> (VC)	ND	ND	ND	ND	ND	ND	4.8	27.7	94.3	244.9	493.1
C <sub>1</sub> H <sub>2</sub> C=CH <sub>2</sub>	ND	ND	ND	ND	ND	ND	ND	1.3	1.9	5.7	20.6
C <sub>1</sub> HCl-CHCl(cis)	ND	ND	ND	ND	ND	ND	ND	0.9	2.4	4.3	10.7
C <sub>1</sub> HCl-CHCl(trans)	ND	ND	ND	ND	ND	ND	ND	0.6	1.7	3.2	8.3
C <sub>1</sub> H <sub>2</sub> C=CHCl	ND	ND	ND	ND	ND	ND	ND	ND	0.8	1.3	4.4
C <sub>1</sub> H <sub>2</sub> C=CCL <sub>2</sub>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.5
C <sub>1</sub> HCl-CH <sub>2</sub> Cl	ND	ND	ND	ND	ND	ND	ND	0.7	1.5	2.0	3.4
C <sub>1</sub> H <sub>2</sub> C-CH <sub>2</sub> Cl(EDC)	3.5	7.7	15.0	36.0	54.0	70.6	134.8	170.3	135.6	57.3	38.3
C <sub>1</sub> HCl-CH <sub>2</sub> Cl	ND	ND	ND	ND	ND	ND	1.3	3.3	8.0	8.0	11.8
C <sub>1</sub> H <sub>2</sub> C-CHOH <sub>2</sub>	ND	ND	ND	ND	1.4	1.1	1.6	1.6	2.7	1.4	1.6
(2.50 min) <sup>d</sup>	ND	ND	1.0	3.6	2.7	0.7	4.3	ND	ND	ND	ND
(2.69 min) <sup>d</sup>	ND	ND	0.5	0.7	1.3	2.0	4.5	5.7	5.8	3.9	3.2
(2.85 min) <sup>d</sup>	ND	4.4	3.4	ND	ND	ND	ND	ND	ND	ND	ND

<sup>a</sup> : Residence time.<sup>b</sup> : Other inflows: O<sub>2</sub> (26.10); N<sub>2</sub> (110.73); HCl (14.24); H<sub>2</sub>O (50.20).<sup>c</sup> : Qualitatively C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>, C<sub>2</sub>Cl<sub>4</sub>, C<sub>4</sub>HCl<sub>5</sub>, C<sub>4</sub>Cl<sub>6</sub> and C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> are identified (GC-MSD).<sup>d</sup> : Retention time of unidentified compound (ethylene at 2.36 min and EDC at 4.52 min): quantified assuming C<sub>2</sub> compound.

ND: Not detected (detection limit: 1-Methanizer-FID ca. 0.1 μmol/h); GC-FID ca. 0.25 μmol/h).