FLY ASH CATALYZED
OXIDATION AND OXYCHLORINATION OF PHENOL

J.G.P. Born, R. Louw and P. Mulder

Center for Chemistry and the Environment, Gorlaeus Laboratories,
Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

ABSTRACT

Fly ash catalyzed oxidation of phenol in the presence of hydrochloric acid at 150 - 450 °C resulted in the formation of chlorinated phenols. Above 350 °C (chlorinated) phenol(s) were converted, mainly into CO, but chlorinated benzenes, monobenzofurans and dibenzo-p-dioxins were also formed. In contrast, under similar conditions, (chlorinated) benzenes are inert with respect to both oxidation and oxychlorination.

KEYWORDS

Phenol, hydrochloric acid, fly ash catalysis, oxychlorination, oxidation, polychlorobenzenes, PCDDs.

INTRODUCTION

In recent years evidence has been gathered that fly ash promotes the formation of PCDDs/PCDFs in the effluent stack gas of Municipal Waste Incinerators (Goldfarb, 1989). Not only has been proven that fly ash can act as a potent oxychlorination catalyst (Eiceman and Rghei, 1982; Rghei and Eiceman, 1984, 1985), MWI fly ash can also engender PCDD formation de novo (Stieglitz et al., 1989; De Leer et al., 1989), or from (polychloro)phenol (Dickson and Karasek, 1987; Karasek and Dickson, 1987; Born et al., 1989), (de)chlorination reactions (Stieglitz and Vogg, 1987; Hagenmaier et al., 1987a, 1987b; Vogg and Stieglitz, 1986) are readily accelerated as well.

In a previous paper (Born et al., 1989) we reported on the fly ash catalyzed combustion of o-chlorophenol. It was shown that at relatively low temperatures of around 350 °C a large part of o-chlorophenol is transformed into typical combustion products like CO_2. This process also results in the formation of polychlorinated products, showing that the liberated chlorine (whether Cl_2 or HCl) was used in a simultaneous (oxy)chlorination of remaining aromatic structures.

In order to gain more insight in the competition between oxidation and oxychlorination, we embarked on a study of the reaction system phenol - O_2 (- HCl) - fly ash.

EXPERIMENTAL SECTION

The oxidation and oxychlorination of phenol was conducted using a computer-controlled microreactor flow system, schematically shown in Fig. 1.

Utilizing mass flow controllers (Brooks 5850 TR Series) a constant nitrogen (Hoekloos: S-80-V) inflow was achieved, resulting in accurately known residence times. Gaseous phenol was introduced in the reactor by purging a metered nitrogen flow through a stainless steel impinger filled with liquid phenol. Employing a temperature controlled oil bath (Tamson TC 9/250) at 74.3 °C, evaporation of phenol was maintained at a well defined rate. HCl was made in situ by combustion of gaseous 1,4-dichlorobutane (evaporated in analogy with phenol, using a water bath) in an oxygen-nitrogen atmosphere at 720 °C.

A two-way switching valve, triggered by a pressurized air driven valve actuator (Whitey Model 151 DA), directed the obtained gas mixture either directly, or via the reactor, towards the on-line gas chromatograph (Howlett Packard 5890A), which subsequently analyzed the initial reactant concentration, or the product distribution upon reaction.

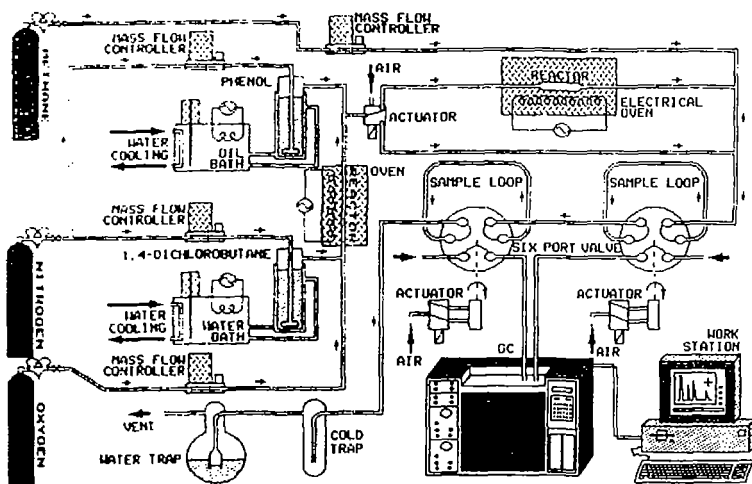Organohalogen Compounds 3   31

Fig. 1 Schematic representation of the experimental set-up.

A quartz microreactor (I.D. 4 mm, length 48 mm, effective volume 0.6 ml), filled with 0.40 g of MWI fly ash was mounted horizontally in an electrically heated tubular oven (Heraeus Model VP), provided with a RKC Rex F-100 programmable temperature regulator. Temperature was measured by chromel-alumel thermo-couples inserted in the oven, and displayed on a digital thermometer (Therma 1, type ST-861-107), equipped with ambient temperature compensation. Both ends of the oven were insulated by quartz wool.
All tubing consisted of glass-lined 1/4" stainless steel or 1/16" pure nickel, maintained at approximately 200 °C by heating tape to prevent condensation of less volatile reactants and products.
Prior to quantitative analysis the product gas mixture was blended with a calibrated amount of CH_4, to serve as an internal standard. Alternatively two pneumatic six-port sampling valves (Valco DC6WT-H1), equipped with 1 ml sample-loops, injected the effluent flow for either packed, or capillary, gas chromatographic analysis. Permanent C_1-C_2-gases were quantified on a packed carbowax (1/8" x 2m) column connected to a flame ionization detector by means of a Chrompack methanizer. Absolute amounts were based on peak surface areas relative to that of the internal standard. Analysis of the aromatic compounds and permanent gases such as oxygen and nitrogen was performed simultaneously. Hereto both a CP-Sil-5-CB (25 m) capillary column and a 25 m capillary molsieve (5 Å) were inserted in the injection port. Analysis was accomplished by a flame ionization and a thermal conductivity detector respectively. In the latter case oxygen quantification was based on its peak surface area relative to that of nitrogen.

RESULTS

Figure 2 represents the difference in stability between chlorobenzene and phenol with respect to fly ash catalyzed oxidation. The experimental conditions are: N_2 90.6 vol%, O_2 9.1 vol%, chlorobenzene 0.13 vol% (43 µmol/h), and phenol 0.17 vol% (55 µmol/h), the residence time ranged from 0.83 s (at 260 °C) to 0.53 s (at 450 °C). Above 350 °C phenol is fully converted, into mainly CO_2, clearly by catalytic combustion (In contrast, the principal product in homogeneous phenol oxidation is CO, which is stable under the present conditions). Chlorobenzene, however, passes the fly ash bed unaffected.
In order to uncover the oxidation turn-over capacity of fly ash for phenol oxidation under the conditions used, the initial phenol concentration was varied (Fig. 3). Experimental conditions: N_2 87.5 vol%, O_2 12.1 vol%, and phenol 0.26-0.52 vol% or 60-180 µmol/h; Temperature 395 °C, residence time 0.58 seconds.
Again phenol is converted neatly into mainly CO_2 (and H_2O) with only minor CO-production, without detectable intermediate products. Fly ash catalyzed combustion appears to be zero order in phenol. With the amount of fly ash employed, only a maximum of about 110 µmol/h phenol per hour can be converted.

Therefore at 395 °C 27 mg phenol per hour per gram of fly ash will be turned over.

In a third series of experiments HCl has been added. The conditions were: N_2 83.7 vol%, O_2 16.3 vol%, and phenol 0.22-0.33 vol% (111-137 μmol/h); Temperature 150 - 470 °C, residence time 1.1 - 0.72 sec.

Even at 150 °C noticeable amounts of o- and p-chlorophenol are produced. The degree of chlorination increases progressively with temperature. However, the stabilities of the chlorinated phenols formed (2-, 4-, 2,4-di-, 2,6-di- and 2,4,6-trichlorophenol) do not differ prominently from that of phenol itself (above 350 °C they are oxidized as well).

At these temperatures the product pattern shifts from chlorinated phenols towards apparently more stable compounds such as chlorinated benzenes, monobenzofurans and dibenzo-p-dioxins.

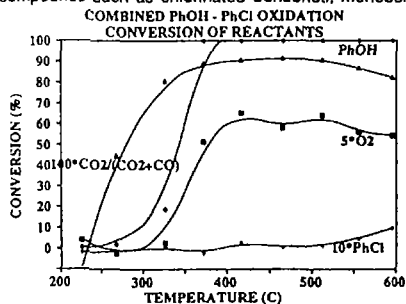Fig. 2

Fig. 3

In total 3.75 μmol/h of chlorinated phenols are observed at 150 °C, (1.08 μmol/h 2-; 2.28 μmol/h 4-; 0.196 μmol/h 2,4-di-; 0.0711 μmol/h 2,6-di- and 0.125 μmol/h 2,4,6-trichlorophenol) comprising a selectivity of the phenol converted of at least 97 %. Interestingly, this result entails that 11 % of the monochlorophenols produced are further chlorinated, whereas only ca. 3 % of the original phenol is converted. As a result of consecutive chlorination, at higher temperatures more heavily chlorinated phenols emerge. For example at 470 °C the sum of chlorophenols measures 2.56 μmol/h (now meaning 1 8 % selectivity only) consisting of 2- (0.0084), 4- (0.292), 2,4-di- (0.0287), 2,6-di- (0.620), 2,4,6-tri- (0.807), 2,3,4,6-tetra- (0.331) and pentachlorophenol (0.470 μmol/h). Apart from CO_2, other important products now emerging are: PCDDs (4.4), chlorobenzenes (3.7) and chlorinated monobenzofurans (0.43 μmol/h). Interestingly the T,CDDs are dominated by the 1,3,6,8- and the 1,3,7,9-substituted isomers (1:1), indicating that the TCDD isomer distribution is kinetically governed by condensation of two 2,4,6-trichlorophenolic entities.
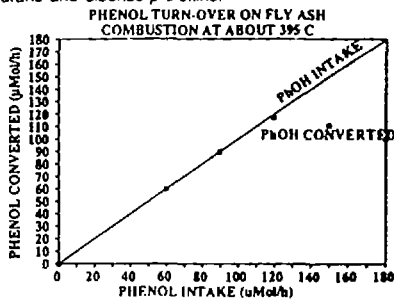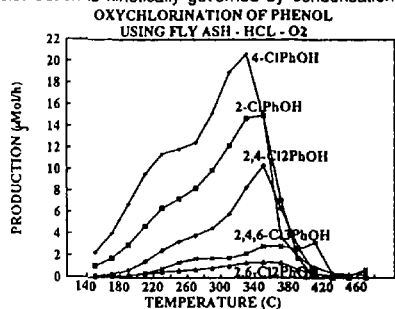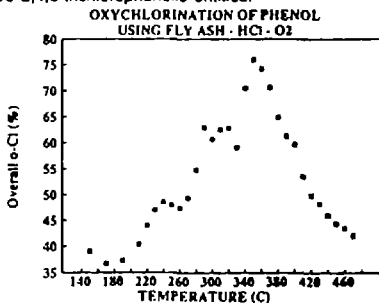
Fig. 4

Fig. 5

This oxychlorination behaviour could be imitated by using a standard commercial oxychlorination catalyst (basically 5% $CuCl_2$ on γ-Alumina), diluted 300 fold (w/w) by purified sea sand. Inter alia, reaction of ethylene (Ahonkhai et al., 1990) rather than phenol revealed 1,2-dichloroethane (and chloroethylene) as the major products, again substantiating the typical oxychlorination behaviour of fly ash (or its $CuCl_2$ contents).

Our observed ratio of o/p monochlorophenol is 39/61 at 150 °C; this ratio is unaffected when counting all o- and p-chlorine substituents in the product mixture above. This result is surprisingly close to that reported for

liquid phase electrophilic chlorination of phenol, using t-butylhypochlorite at pH = 4, viz. 39/61 (Ogata et al., 1984). Passing chlorine gas through liquid phenol at 50 °C gave essentially the same result (40/60). (Harvey and Norman, 1961) With increasing temperature the (overall) o-Cl content varies as shown in Fig. 5. "Full" chlorination, of course, will yield o/p = 2. The maximum ratio - ca. 75/25 at 350 °C - is higher than that; the increase in the 150 - 350 °C range may be kinetically significant and therefore suggest a change in mechanism. Whether (chloro)phenoxyls as radicals and/or anionic ligands play a part is as yet unknown. Note that t-butylhypochlorite and phenoxyl anions (at pH = 4) yield o/p chlorophenol = 81/19 (Ogata et al., 1984). The decrease in o-Cl content observed above 350 °C points at relatively larger rates of decomposition for o-chlorinated phenols. Under these rather drastic conditions, polychlorobenzenes are also formed, presumably by chloro-dehydroxylation, together with condensation products like PCDDs. Mechanistic insight is equally poor as that for chlorination

The deep oxidation of (chloro)phenol - to give CO_2, H_2O (and HCl) - contrasts with the stability of this compound under comparable homogeneous reaction conditions. For comparison, the homogeneous autoxidation of phenol sets in above 550 °C. Due to its radical chain (self)inhibition properties, the thermal stability of phenol is even higher than that of chlorobenzene.

The, already reported (Born et al., 1989), remarkable difference in stability between chlorobenzenes and chlorophenols is confirmed in this study. As (chloro)benzene is far less susceptible to oxychlorination on fly ash too, we believe that the hydroxy group is a prerequisite for both activation of the aromatic ring and adsorption at the fly ash surface, to enable oxychlorination and oxidation.

As (chloro)benzene itself is inert with respect to fly ash mediated oxychlorination (see also De Leer et al., 1989), chlorobenzenes formed upon phenol oxychlorination result from ipso-substitution of chlorophenols rather than chlorination of (chlorinated) benzene(s). .

REFERENCES

Ahonkhai, S.I., H.J.P. de Lijser, J.G.P. Born, R. Louw and P. Mulder (1990). To be published.
Born, J.G.P., R. Louw and P. Mulder (1989). Formation of dibenzodioxins and chlorobenzenes in fly ash catalyzed reactions of monochlorophenols. Chemosphere, 19, 1629-1633.
Dickson, L.C. and F.W. Karasek (1987). Mechanism of formation of polychlorinated dibenzo-p-dioxins produced on municipal incinerator flyash from reactions of chlorinated phenols. J. Chromatogr., 389, 127-137.
Eiceman, G.A. and H.O. Rghei (1982). Chlorination reactions of 1,2,3,4-tetrachlorodibenzo-p-dioxin on fly ash with HCl in air. Chemosphere. 11, 833-839.
Goldfarb, Th.D. (1989). Evidence for post-furnace formation of PCDDs and PCDFs--Implications for control. Chemosphere, 18, 1051-1055.
Hagenmaier, H., M. Kraft, H. Brunner and R. Haag (1987a). Catalytic effects of fly ash from waste incineration facilities on the formation and decomposition of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Environ. Sci. Technol., 21, 1080-1084.
Hagenmaier, H., H. Brunner, R. Haag and M. Kraft (1987b). Copper-catalyzed dechlorination/hydrogenation of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and other chlorinated aromatic compounds. Environ. Sci. Technol., 21, 1085-1088.
Harvey, D.R. and R.O.C. Norman (1961). The ortho:para-ratio in aromatic substitution. Part II. Chlorination with t-butyl hypochlorite. J. Chem. Soc., 3604-3610.
Karasek, F.W. and L.C. Dickson (1987). Model studies of polychlorinated dibenzo-p-dioxin formation during municipal refuse incineration. Science, 237, 754-756.
De Leer, E.W.B., R.J. Lexmond and M.A. de Zeeuw (1989). "De novo"-synthesis of chlorinated biphenyls, dibenzofurans and dibenzo-p-dioxins in the fly ash catalyzed reaction of toluene with hydrochloric acid. Chemosphere, 19, 1141-1152.
Ogata, Y., M. Kimura, Y. Kondo, H. Katoh and F.-C.Chen (1984). Orientation in the chlorination of phenol and of anisole with sodium and t-butyl hypochlorites in various solvents. J. Chem. Soc. Perkin Trans. II, 451-453.
Rghei, H.O. and G.A. Eiceman (1984). Adsorption and chlorination of dibenzo-p-dioxin and 1-chlorodibenzo-p-dioxin on fly ash from municipal incinerators. Chemosphere, 13, 421-426.
Rghei, H.O. and G.A. Eiceman (1985). Effect of matrix on heterogeneous phase chlorine substitution reactions for dibenzo-p-dioxin and HCl in air. Chemosphere, 14, 167-171.
Stieglitz, L. and H. Vogg (1987). On formation conditions of PCDD/PCDF in fly ash from municipal waste incinerators. Chemosphere, 16, 1917-1922.
Stieglitz, L., G. Zwick, J. Beck, W. Roth and H. Vogg (1989). On the de-novo synthesis of PCDD/PCDF on fly ash of municipal waste incinerators. Chemosphere, 18, 1219-1226.
Vogg, H. and L. Stieglitz (1986). Thermal behavior of PCDD/PCDF in fly ash from municipal incinerators. Chemosphere, 15, 1373-1378.