Reduced Combustion Efficiency of Chlorinated Compounds, Resulting in Higher Yields of Carbon Monoxide

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INTRODUCTION

The fire-retardant effect of halogenated compounds, especially the brominated compounds, is well known. The halogen atoms enter the combustion process by reacting with the free radicals necessary to sustain the combustion process. In this way combustion is delayed by temporary or permanent deactivation of the free radicals (e.g. 'OH or O). This free radical trap mechanism, results in a less efficient combustion and hence in an altered composition of the fire effluent, possibly increasing its toxic potency.

In a thermokinetic study of dichloromethane, Ho et al. found evidence of chlorine radicals inhibiting the conversion of CO to CO₂ in H₂/O₂ gas mixtures. Dichloromethane was decomposed at temperatures between 610°C and 820°C during passage through a heated quartz tube with an internal diameter between 0.4 and 1.6 cm. The residence time varied between 0.1 and 2.0 s. The reaction between the combustion products HCl and hydroxyl radicals (1) results in a reduced 'OH concentration, shifting the reaction in (2) to the left inhibiting the conversion of CO to CO₂. This may result in an increased toxic potency of the fire effluent because CO has a much higher toxic potency than CO₂. However, the presence of water for example shifts reaction (1) to the left and increases the CO conversion to CO₂ in reaction (2) through an enhanced 'OH concentration:

\[ \text{HCl} + \text{'OH} \rightleftharpoons \text{H}_2\text{O} + \text{Cl}^- \]  
(1)

\[ \text{CO} + \text{'OH} \rightleftharpoons \text{CO}_2 + \text{H}^+ \]  
(2)

The correlation between the chlorine content of a compound and its suppressing effect on the combustion process (a concentration-effect correlation) is not described in the literature.

Past research concerning fire retardants has generally concentrated on compounds used as additives and not on inherently fire-retarded compounds. For example, Purser found that a polyurethane foam which was fire retarded with bromine- and antimony-compounds gave higher yields of toxic products (particularly CO) than did a non-fire-retarded polyurethane foam. Also, in a polyurethane foam fire retarded with chlorinated phosphates, Braun et al. found that CO₂/CO ratio was reduced by a factor of two, compared with a non-fire-retarded foam. The CO₂/CO ratio in the fire effluent can be used to describe the efficiency of the combustion, a low ratio indicating a poor combustion efficiency.

For materials that are not inherently fire retarded, the CO₂/CO ratio is related to the air/fuel ratio (or oxygen concentration) in the fire. Purser et al. suggest that for inherently fire-retarded compounds low CO₂/CO ratios are obtained due to inefficient combustion even under well-ventilated flaming conditions, reporting much lower CO₂/CO ratios from PVC than from non-halogenated materials used in electric cables, decomposed under well-ventilated flaming conditions.

Halogenated compounds are widely used in industry and large amounts are stored and could be exposed to fire. In this investigation chlorinated compounds were subjected to combustion using the DIN 53 436 furnace at a fixed temperature and air flow, chosen to represent the post-flashover well-ventilated fire. In the compounds investigated only carbon, hydrogen, oxygen and chlorine atoms are present, and the following chemical groups are represented: aliphatic, cyclic and aromatic compounds, carboxylic acids, methoxy-compounds and polymers. Six chlorinated compounds were investigated (four pesticides, a solvent and a plastic) and pine wood was used as reference.

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MATERIALS

The compounds investigated were chlorobenzene 99% (intermediate in industrial production), Merck 801791; Dicamba (3,6-dichloro-2-methoxybenzoic acid) 99.89% (herbicide), supplied by Sun Chemical KVK, Denmark; 1,3-dichloropropene (a mixture of cis- and trans-isomers) > 95% (soil fumigant), supplied by Shell Research Limited, UK; Lindane (hexachlorocyclohexane, γ-isomer) approx. 99% (insecticide), Sigma H-4500; MCPA (4-chloro-2-methylphenoxy) acetic acid) 99.5% (herbicide), supplied by MTM Agrochemicals Ltd, UK; PVC, pipe grade, Neste OY Chemicals, Finland and pine wood.

METHODS

The combustion experiments were carried out in a furnace constructed according to the German DIN 53 436 at 850°C or 860°C with a flow of 1.7 l min⁻¹ of atmospheric air. Some of the experiments have been referred to in an earlier publication by Smith-Hansen and Jørgensen. Approximately 1 g compound was combusted in each experiment (mass load 15 mg l⁻¹), except for wood, where 7 g were used.

At least ten times the amount of oxygen necessary for complete combustion was available in the experiments with chlorinated compounds. There was approximately three times the amount of oxygen necessary for complete combustion in the experiment with wood. Huggett has stated that at least three times the amount of oxygen necessary for complete combustion, in a stoichiometric ratio, has to be available to sustain flaming combustion.

Except for PVC and wood, test specimens were placed in 24 separate quartz vessels in the sample holder to avoid displacement of the compound when melting. This segmentation was essential because the combustion and production of fire effluent will not be uniform if the specimen is displaced. PVC and wood were placed directly in the sample holder.

The fire effluent was analysed on-line every 20 s for oxygen using a Servomex oxygen analyser 570A, and for CO₂ and CO using the Beckman infra-red analysers model 864 and 865, respectively.

RESULTS

The DIN furnace is producing a fire effluent of nearly uniform composition for at least 30 min after reaching 'steady-state' conditions. Runs for Lindane and PVC are shown in Fig. 1 representing runs with and without segmentation, respectively.

Averages of O₂, CO₂ and CO concentrations measured during the 'steady-state' period are given in Table 1. The CO₂/CO ratios, averages of the CO₂/CO ratios from each data sampling during the 30 min of 'steady state', are also given in Table 1. No or only minimal soot residues were remaining in the sample holder after combustion.

![Figure 1. Gas concentrations during combustion of Lindane (a) and PVC (b) in the DIN furnace at 860°C and 850°C, respectively, with a flow of 1.7 min⁻¹. Lindane and PVC represent experiments with and without segmentation, respectively. O₂ (■), CO₂ (□), and CO (▲).](image)

Table 1. Gas concentrations and CO₂/CO ratios from the combustion of chlorinated compounds and wood at 860°C or 850°C in the DIN furnace with a flow of 1.7 min⁻¹

<table>
<thead>
<tr>
<th>Substance</th>
<th>Amount combusted (g)</th>
<th>O₂ (%)</th>
<th>CO₂ (%)</th>
<th>CO (%)</th>
<th>CO₂/CO a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>1.261</td>
<td>18.00</td>
<td>2.86</td>
<td>2796</td>
<td>12.9</td>
</tr>
<tr>
<td>Dicamba</td>
<td>0.991</td>
<td>19.54</td>
<td>1.41</td>
<td>2490</td>
<td>5.85</td>
</tr>
<tr>
<td>1,3-dichloropropene</td>
<td>1.219</td>
<td>19.59</td>
<td>1.09</td>
<td>6245</td>
<td>1.78</td>
</tr>
<tr>
<td>Lindane</td>
<td>0.878</td>
<td>20.54</td>
<td>0.16</td>
<td>5249</td>
<td>0.42</td>
</tr>
<tr>
<td>MCPA</td>
<td>1.038</td>
<td>19.30</td>
<td>1.95</td>
<td>724</td>
<td>32.4</td>
</tr>
<tr>
<td>PVC (850°C)</td>
<td>1.087</td>
<td>19.56</td>
<td>1.05</td>
<td>5064</td>
<td>2.16</td>
</tr>
<tr>
<td>Wood (850°C)</td>
<td>6.701</td>
<td>8.84</td>
<td>12.15</td>
<td>386</td>
<td>608</td>
</tr>
</tbody>
</table>

aSee text for method of calculation.
The CO$_2$/CO ratios from the experiments in the present study are given in Fig. 2 together with data derived from published work. The CO$_2$/CO ratio (conc. in %) is shown as a function of the chlorine content of the compound expressed as the Cl/C ratio (numbers of atoms in molecule). It is assumed that all chlorine in the compound is converted to HCl at the furnace temperature used. Due to deposition of HCl prior to the sampling point the recoveries of HCl from the wash bottles were too low ranging from 42% to 73%. Recent experiments with an improved sampling system showed recoveries of HCl at approximately 75%. Also, decay of HCl during transfer from furnace to sampling point could explain the lower recoveries. Gas chromatography/mass spectrometry analyses of the fire effluent did not indicate the presence, in significant amounts, of the original compound or any other large molecules containing chlorine. During the experiments with the chlorinated compounds the measured oxygen concentration did not fall below 15.8%. In the fire effluent from wood, lower oxygen concentrations were observed at times, but only minute amounts of CO was produced.

If the chlorine content increases the CO$_2$/CO ratio decreases. When the square root of the CO$_2$/CO ratio is compared with the reciprocal Cl/C ratio, linearity is obvious (Fig. 3). The correlation can be empirically expressed as $\sqrt{\text{CO}_2/\text{CO}} = 0.61 \times (\text{Cl/C})^{-1} + 0.13$ (data for wood not included).

**DISCUSSION**

Other authors have observed a reduction of the CO$_2$/CO ratio when decomposing materials fire retarded with halogenated compounds. Purser et al. investigated the combustion of thermoplastic polyurethane with and without added decabromodiphenyloxide and antimony trioxide. He found that the CO$_2$/CO ratio dropped from 37 to 1.4 for the polyurethane without and with fire retardant, respectively. The experiments were performed using a DIN furnace at 600°C under flaming combustion conditions with a mass load at 8.0 mg l$^{-1}$. Purser et al. have also reported recently that under well-ventilated flaming conditions in a modified DIN furnace the CO$_2$/CO ratio for PVC (13) was much lower than from other non-halogenated cable making materials as low-density polyethylene (357) and low smoke and fume cable compound (211). The CO$_2$/CO ratio for PVC is shown in Fig. 2 together with the experimental data from the present study. The exact composition of the commercial PVC is not reported in the paper, and the actual Cl/C ratio will be somewhat lower than for PVC without additives, because the PVC at least also contains calcium.

Braun et al. found a decrease in the CO$_2$/CO ratio from 43 to 20 when testing a flexible polyurethane foam without and with a fire retardant, respectively. The fire retardant was a chlorinated phosphate but was not further specified. The materials were decomposed under flaming conditions, using the NBS(NIST) cup furnace at 450°C. In the same work different types of tests were compared: the NBS cup furnace mentioned above, a Cone calorimeter, a furniture calorimeter, and a room/corridor test. The CO$_2$/CO ratio was reduced by a factor of two in all tests, except with the cone calorimeter where it was reduced by a factor of eight.

The effect of halogen atoms as fire retardants is well known, and the experiments referred to above have shown that the addition of halogenated fire retardants to a material reduces the CO$_2$/CO ratio in the fire effluent. The present investigation concerning inherently fire-retarded compounds shows a correlation between the relative number of chlorine atoms and CO$_2$/CO ratio, implying a less efficient combustion when the compound has a high number of chlorine atoms per carbon atom. The low CO$_2$/CO ratios observed in the present study were not caused by shortage of oxygen during combustion. The oxygen concentrations measured during the experiments with the chlorinated compounds did not fall below 15.8%.

Low CO$_2$/CO ratios during combustion of inherently fire-retarded materials was also seen in experiments carried out by Beitel et al. and by Babrauskas et al. The former investigated the combustion of a PVC coated wire by electrical overload in small and large (room) scale experiments. They found that the CO$_2$/CO ratio in the large-scale experiment was 5.8 (average of measurements from two sampling points near the origin of the fire). The Cl/C ratio for the PVC-insulated electrical wire was 0.24
from elemental analysis of the wire. The small-scale results obtained in the NBS chamber cannot readily be used in this context because the CO₂ and CO concentrations presented are maxima, with a time difference of approximately two min between them. Ignoring this time difference the CO₂/CO ratio is 13.5 (average of four experiments). The two values are shown in Fig. 2 together with the experimental data from the present study.

Babrauskas et al.⁶ report CO₂ and CO yields for commercial PVC. The data are obtained by three different test methods: NBS, SwRI/NIST, and a Cone calorimeter operated at three irradiance levels (the data from the real scale experiments are not considered applicable for use in this paper, because the gas analyses are made quite a distance from the origin of the fire). The reported yields have been converted to mole basis and the results obtained in the NBS chamber cannot readily be used in this context because the CO₂ and CO concentrations presented are maxima, with a time difference of approximately two min between them. Ignoring this time difference the CO₂/CO ratio is 13.5 (average of four experiments). The two values are shown in Fig. 2 together with the experimental data from the present study.

Some abnormalities are seen in the data presented in Fig. 2, but this is to be expected when different test methods (e.g. different temperatures) are used. The correlation observed in our investigation associates with an equilibrium constant, but no chemical equilibrium is obvious.

The effect of chlorine reducing the combustion efficiency may increase the toxic hazard in fires involving chlorinated materials. Both the release of HCl and the increased yield of CO will contribute to an increased toxic potency of the fire effluent. Furthermore, chlorine may interfere with the oxidation of carbon from other materials involved in the fire, thereby increasing the yield of CO.

On the other hand, the (inherently) fire-retarded materials tend to have an improved fire performance regarding ignitability and rate of fire growth. This reduces the risk of fires occurring and the hazard during the early stages of a fire. For the fire scenario of concern, a post-flashover fire involving chlorinated industrial products (e.g. a storage facility), this might not have the same significance because the fire could begin in other non-fire-retarded materials.

**CONCLUSION**

This study shows that combustion of chlorinated compounds produces fire effluents with a significant lower CO₂/CO ratio compared to wood. For an equivalent mass loss, this therefore results in an increased CO concentration and hence an increased toxic potency. In fires involving decomposition of chlorinated materials there may be an increased toxic hazard due to the increased yields of CO, and to the release of HCl. However, the risk of ignition of chlorinated compounds and their contribution to fire growth may be less than that from equivalent non-halogenated compounds. This is of less relevance, though, if the fire begins in other non-fire-retarded materials. Large amounts of chlorinated compounds are stored and used in the industry so the result of this study should be considered in risk analyses of storage facilities and industrial plants.

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**REFERENCES**