Mathematical simulation of gas phase reactions—Combustion of carbon disulphide

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Combustion of fossil fuels generate large amounts of toxic gases such as CO, SO₂ and SO₃. A study of combustion of carbon disulphide may be useful in understanding the nature of products formed and their residence time under defined conditions. The present investigation shows the formation of different transient species and their fate as a function of oxygen concentration. The results show that one of the toxic products, CO, is rapidly oxidised to CO₂ and there exists an equilibrium between SO₂ and SO₃, the ratio of the two oxides being 1:1.107 at equilibrium.

Kinetics of the gas phase reactions of different sulphur and nitrogen compounds with various reactive species have been extensively studied. One of the important reactions is combustion i.e. reaction with oxygen. It is a well established fact that even the simplest combustion reaction such as combustion of molecular hydrogen leading to formation of water proceeds through a set of atomic reactions. A detailed knowledge of the elementary steps taking place and their combined effect on generation of the reaction products are essential in order to obtain maximum yield (in terms of energy) and also to suppress the formation of toxic reactive species. Since combustion of fossil fuel generates large amounts of SO₂ and SO₃ (74% of the total man made contribution) the kinetics and mechanisms of combustion of sulphur compounds need to be studied in detail. There are several experimental investigations on combustion of simple sulphur compounds, however, the major difficulty in such investigations is to follow the concentration profiles of the unstable species. Here, we report a modelling of the combustion of carbon disulphide under isothermal conditions.

Experimental
The experimental kinetics data used in this work were obtained from standard literature. Modelling of the reaction mechanism described below was carried out using ‘REACT for windows’ software developed by Alchemy Software Company (USA). This software integrates the complex, coupled differential equations associated with a chemical reaction mechanism. The calculations were performed on a standard desktop PC equipped with M-III processor and 64 MB of RAM under Version Windows 98 operating system. The initial concentrations of the primary reactants were set empirically. Concentration of CS₂ was fixed at 0.002% and oxygen concentration was varied between 0.020% to 0.010%. The reaction conditions were defined similar to those in experimental conditions. The temperature and pressure during the reactions were left unaltered at lower values (T = 298 K; P = 1 atm) so that all the reactions took place well below 1st explosion limit and the reactions were smooth. Effect of three body collisions (reactants and the container walls) were not included while performing the simulations.

Results and discussion
The present investigation involves simulation of combustion of carbon disulphide at ambient temperature. Like most other combustion reactions, this reaction too proceeds through a set of atomic reactions. Though the primary reactants are molecular oxygen and carbon disulphide, the former dissociates into atomic oxygen before it reacts further. In this modelling work atomic singlet oxygen has therefore, been considered as a primary reactant. The products of the primary reaction further react with oxygen and the reactions proceed as shown in the Scheme 1. The individual chemical reactions along with the respective rate constants are listed in Table 1.

While doing the modelling, the reactant concentrations were kept low enough so that the reactions proceed smooth without any explosion. However, the oxygen concentration was kept high compared to that of carbon disulphide so as to allow all possible secondary oxidation reactions. However, care has been taken to adjust the concentration in such a way that the reactions follow second order kinetics; first order each in atomic oxygen and the other reactant. It is evident from Scheme 1 that there are...
### Table 1—Rate constants of the reactions

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>log ( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O + CS₂</td>
<td>CS + SO</td>
<td>12.3</td>
</tr>
<tr>
<td>O + CS₂</td>
<td>COS + S</td>
<td>8.0</td>
</tr>
<tr>
<td>O + CS</td>
<td>CO + S</td>
<td>13.0</td>
</tr>
<tr>
<td>O + COS</td>
<td>CO + SO</td>
<td>9.8</td>
</tr>
<tr>
<td>O + COS</td>
<td>CO₂ + S</td>
<td>7.0</td>
</tr>
<tr>
<td>O + CO</td>
<td>CO₂</td>
<td>12.6</td>
</tr>
<tr>
<td>O + SO</td>
<td>SO₂</td>
<td>7.2</td>
</tr>
<tr>
<td>O + S</td>
<td>SO</td>
<td>4.2</td>
</tr>
<tr>
<td>O + SO₂</td>
<td>SO₃</td>
<td>15.0</td>
</tr>
<tr>
<td>O + SO₃</td>
<td>SO₂ + O₂</td>
<td>5.6</td>
</tr>
</tbody>
</table>

### Scheme 1—Combustion of carbon disulphide

### Fig. 1—CO residence time

### Fig. 2—Formation of CO₂
mainly three toxic products namely, carbon monoxide, sulphur dioxide and sulphur trioxide. The CO produced is a short lived species and it further reacts to form non-toxic CO\textsubscript{2}. Figure 1 shows the variation of CO residence time as a function of oxygen concentration. With higher oxygen concentrations the conversion to CO\textsubscript{2} as expected is rapid. The formation of CO\textsubscript{2} (Fig 2) also follows the same pattern, however, one must be careful while comparing the results (of Figs 1 and 2) that CO\textsubscript{2} is being produced from COS besides the oxidation of CO.

On the other hand, elemental sulphur and unstable sulphur monoxide are oxidized to SO\textsubscript{2} and the latter is then converted to SO\textsubscript{3}. Interestingly, sulphur trioxide also reacts with O to give SO\textsubscript{2} and O\textsubscript{2}. Figures 3 and 4 depict the formation of SO\textsubscript{2} and SO\textsubscript{3} with time at different oxygen concentrations. In Fig. 5 the ratio between SO\textsubscript{2} and SO\textsubscript{3} and their equilibrium is shown.
From these figures it is evident that formation of SO$_3$ is faster at higher O concentrations, however, a change in oxygen concentration does not alter the equilibrium concentrations of SO$_2$ and SO$_3$ to any appreciable extent. Figure 6 shows the concentration profile of some of the other species formed during the reaction. All these are short lived and react further with oxygen (Scheme 1). Figure 7 shows the concentration profile of products, O$_2$, CO$_2$, SO$_2$ and SO$_3$ when the reactions are carried out with 0.010% oxygen concentration.

To conclude, combustion of carbon disulphide leads to the formation of CO but this is rapidly converted to CO$_2$. The rate of conversion from CO to CO$_2$ and thus residence time of CO can easily be varied by changing oxygen concentration. The main
pollution is due to the formation of sulphur dioxide, which can be converted to a certain extent into SO₃. Amount of oxygen affects the residence time of SO₂ and the conversion to SO₃ is faster with higher oxygen concentrations. Since SO₃ too reacts with oxygen to form SO₂ and O₂ the SO₂—SO₃ equilibrium is not much affected by small changes in oxygen concentration. The concentration of SO₃ becomes 1.107 times of that of SO₂ at equilibrium.

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References