## COMPUTER MODELLING STUDIES OF THE DISTRIBUTION OF PHOTOCHEMICAL OZONE PRODUCTION BETWEEN DIFFERENT HYDROCARBONS

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Abstract—The formation of  $O_3$  and other photochemically generated compounds has been modelled for the region downwind of London, during the slow easterly airflow and other conditions associated with a midsummer anticyclone. The model contains a comprehensive chemical mechanism, including the emissions of 37 hydrocarbons (HCs) and treats HC degradation explicitly in over 300 reactions. As a result it has been possible to disaggregate the production of  $O_3$  amongst the various HCs present in the model, and the percentage of the  $O_3$  production which can be attributed to each HC is therefore known. These results have been used, in conjunction with the emissions inventory, to attribute the  $O_3$  production to the various sources of HCs. By further study the number of molecules of  $O_3$  which are produced by each HC molecule have also been elucidated. The significance of the results both to control strategies for  $O_3$  formation and to the representation of photochemical  $O_3$  production in computational models is discussed.

Key word index: Atmospheric hydrocarbon chemistry, computer modelling, ozone, photochemical oxidants, photochemical reaction mechanisms.

#### 1. INTRODUCTION

Photochemical oxidants are formed in the lower troposphere by the solar irradiation of mixtures of hydrocarbons and nitrogen oxides and the subsequent reactions with the short-lived radical species which are produced. The general principles involved in the formation of these photochemical oxidants [such as O<sub>3</sub> and peroxyacylnitrates (PANs)] are well known (see for instance Logan, 1985; Derwent, 1986) and have been examined extensively in a wide range of computer modelling studies (e.g. Balko and Peters, 1983; Liu et al., 1984; Leone and Seinfeld, 1985; Derwent and Hov, 1979; Hough, 1986). These studies have been applied in particular to considerations of how to reduce the concentrations of such pollutants by emission control strategies (e.g. Hough and Derwent, 1986). However, detailed considerations of this photochemical activity and of the effects of the various policies on emission controls are complicated by the wide range of HCs which are emitted into the atmosphere and subsequently involved in the formation of photochemical air pollution.

The above complication occurs because of the wide range of reactivities and reaction mechanisms which are demonstrated by the HC molecules. In the atmosphere, the rates of their initial reactions with OH radicals vary by factors of > 10,000, and their different structures mean that they possess intrinsically different potentials for the formation of photochemical species such as  $O_3$ . The chemical balance of the other compounds which are present also has an important effect. Dodge (1984) has studied the formation of  $O_3$ from 12 different HCs, and found that the results depend critically on the HC/NO<sub>x</sub> concentration ratio. When this ratio is low, the  $O_3$  forming potential is governed by the reaction rate and structure of the HC. However, when the ratio is high, the low concentrations of NO and NO<sub>2</sub> are the limiting factor, so that the differences between the HCs are much less marked.

It is not only the policies for emission controls which are affected by these differences between HCs. Computational models (upon which such policies may be based) can only include a limited number of HCs (or a parameterization which effectively represents a limited number) and the choice of which compounds to include can have a strong influence on the results obtained in such a study. It is therefore important to understand the chemical differences between the various HCs when constructing the chemical mechanism in any model.

The present study addresses the above problems by using a detailed computational model to study the  $O_3$ formation which is associated with 37 different HCs, CO and SO<sub>2</sub> during a summer photochemical episode over the S United Kingdom. The study indicates the number of molecules of  $O_3$  produced per molecule of HC, together with the contribution which each HC makes to the total amount of  $O_3$  produced. The effects which such results can have on our understanding of how to represent HCs in a computational model of the chemistry of the lower atmosphere are also examined.

### 2. METHODOLOGY

Within the U.K., the largest source of the primary pollutants which give rise to photochemical oxidant formation is the area of Greater London. It was therefore decided to examine the formation of photochemical oxidants in an airmass which included these emissions. So as to maximize the occurrence of photochemical activity, mid-summer clear sky anticyclonic conditions were chosen, with a slow moving E airflow over the S U.K. The path of the airmass considered in the study is shown in Fig. 1.

#### 2.1. Model description

The model used in the study has its origins in the plume model of Derwent and Hov (1979), but incorporates revisions to the content and representation of many of the processes involved. The present form of the model has been presented and discussed in detail elsewhere, together with results obtained for emission control strategies to reduce the concentrations of photochemical oxidants in the area downwind of London (Hough, 1986; Hough and Derwent, 1986).

The model consists of a moving box of lateral dimensions 40 km  $\times$  40 km with a variable height to simulate the diurnal variations in the depth of the boundary layer as described by Smith and Hunt (1978) (see also Derwent, 1981). The choice of a night-time mixing height of  $\sim$  300 m for London in midsummer has been discussed by Derwent (1981). The box moves at a rate governed by the average diurnal variation in the wind speed as measured at the London weather centre during summer anticyclonic conditions when O<sub>3</sub> concentrations exceeded 60 ppb (Derwent, 1981; Hough, 1986).

The chemical mechanism is a revised version of that used by Derwent and Hov (1979), and includes 169 reactive chemical species and 320 chemical reactions. Thirty-seven HCs which are emitted directly as pollutants are included, together with a detailed explicit reaction mechanism for their degradation. Emissions for the same HCs,  $SO_2$ , CO and  $NO_x$  are represented. The photolysis of 27 compounds is included explicitly, as is dry deposition to the earth's surface for  $SO_2$ , O<sub>3</sub>, NO<sub>2</sub>, HNO<sub>3</sub> and peroxyacetylnitrate (PAN) and the scavenging of certain species to form aerosol particles.

The rate constants for the gas phase reactions are taken from recent comprehensive reviews (Baulch et al., 1984; Atkinson and Lloyd, 1984). The photolysis rates are based on the work of Demerjian et al. (1980), Bass et al. (1980) and Horowitz and Calvert (1982). Those for the higher aldehydes are based on the values for the earlier members of the series to which they belong. All photolysis rates are parameterized using the method described by Derwent and Hov (1979). The dry deposition velocities are values recommended by Garland (1983, private communication). The scavenging coefficients for aerosol formation depend critically on the values which are adopted for the accommodation coefficients. If these are unity, then values around  $7 \times 10^{-4}$  s<sup>-1</sup> are obtained (Peters and Carmichael, 1983). However, the values of these coefficients are likely to be several orders of magnitude smaller, and in this study the rate has been set at  $3 \times 10^{-5}$  s<sup>-1</sup> as suggested by Derwent and Hov (1979).

The choice of initial concentrations for the model is important, since these may influence the initial behaviour of the chemistry and have an unspecified influence throughout the whole of the chemical development. Ideally, a complete description of the average chemical composition of each of the starting air masses should be available. Realistically, an alternative approach has to be adopted.

To ensure that there is no conflict between assumed initial concentrations and the emissions inventory, all initial concentrations were derived from tropospheric background concentrations of  $NO_x$ ,  $H_2$ ,  $CH_4$ , CO and HCHO, and from U.K. background emissions. In a separate model experiment (Derwent and Hov, 1982), the initial concentrations adopted for the present study were obtained by using the population to a 400 km by 200 km rectangle, and integrating the model for 2 days. These initial concentrations against air quality data, because the model experiments used to obtain them are illustrative rather than predictive. However, the concentrations are in broad agreement with typical sum-



Fig. 1. The region studied in the moving box models. (a) The geographical area. (b) The position of the 'coastal plume' throughout the day. (c) The position of the 'London plume' throughout the day. (d) The population, in thousands, for 10 km × 10 km Ordnance Survey grid squares.

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