

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

ADRIAN M. HOUGH and RICHARD G. DERWENT

Modelling and Assessments Group, Environmental and Medical Sciences Division, Harwell Laboratory,
Didcot, Oxfordshire, U.K.

(First received 15 June 1986 and received for publication 24 February 1987)

Abstract—The formation of O₃ 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 O₃ amongst the various HCs present in the model, and the percentage of the O₃ 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 O₃ production to the various sources of HCs. By further study the number of molecules of O₃ which are produced by each HC molecule have also been elucidated. The significance of the results both to control strategies for O₃ formation and to the representation of photochemical O₃ 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 O₃ and peroxyacetyl nitrates (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 O₃. The chemical balance of the other

compounds which are present also has an important effect. Dodge (1984) has studied the formation of O₃ from 12 different HCs, and found that the results depend critically on the HC/NO_x concentration ratio. When this ratio is low, the O₃ 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 NO₂ 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 O₃ formation which is associated with 37 different HCs, CO and SO₂ during a summer photochemical episode over the S United Kingdom. The study indicates the number of molecules of O₃ produced per molecule of HC, together with the contribution which each HC makes to the total amount of O₃ 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.

Download English Version:

<https://daneshyari.com/en/article/4474669>

Download Persian Version:

<https://daneshyari.com/article/4474669>

[Daneshyari.com](https://daneshyari.com)