

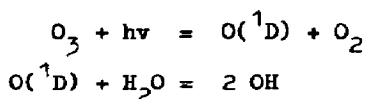
TRACE GAS PHOTOCHEMISTRY IN THE TROPOSPHERE

R. A. Cox

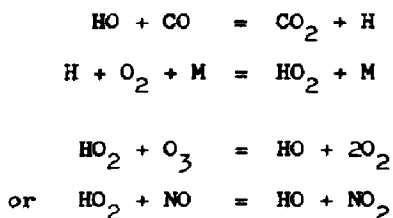
Environmental & Medical Sciences Division, Atomic Energy Research Establishment,
Harwell, Oxon. (Gt. Britain)

Most trace gases emitted to the atmosphere from both natural and man-made sources are removed by scavenging processes operating in the troposphere. The importance of the hydrological cycle for removing trace atmospheric substances has been known for some time, but the role of photochemistry and free radical reactions in global tropospheric chemistry has been recognised only more recently.

Of central importance in tropospheric chemistry is the hydroxyl free-radical HO, which is reactive towards many organic and inorganic gases and vapours. Levy⁽¹⁾ first suggested that relatively high steady-state concentrations of HO may be present in the natural troposphere, resulting from its production in the reaction of excited atomic oxygen O(¹D) with water vapour. O(¹D) is produced throughout the atmosphere by photolysis of ozone by solar UV of wavelength ≤ 310 nm.



The steady state of HO is maintained by a simple chain-reaction scheme involving its dominant atmospheric reaction partner, carbon monoxide, and also nitric oxide



Chains are terminated by simple recombination reactions of HO, HO₂ and NO₂. HO also reacts with atmospheric CH₄ and the resulting CH₃ radical is oxidised to formaldehyde, HCHO. This may then degrade to CO and H₂, which are in turn oxidised by HO to H₂O and CO₂. Analogous oxidation pathways operate for other volatile organic substances.

A simple chemical model of this type with the appropriate kinetic and photochemical parameters may be used to predict HO concentrations in the troposphere, and consequently to estimate the sink strength for trace gaseous components which react with HO.

More elaborate calculations involving atmospheric motions in 2 dimensions as well as chemistry, allow the global budgets of CO, CH₄, O₃ in the troposphere to be determined.

These models have been used to assess the perturbations produced by pollutants in the troposphere. It appears that emissions of CO, NO and hydrocarbons may be now influencing trace gas chemistry on a global scale as well as on the more familiar local scale which manifests itself as photochemical smog. The models have also been useful in assessing the lifetime in the troposphere of certain halocarbons, eg. CH₂CCl₃ which could have an impact on stratospheric ozone.

Although the determination of global trace-gas budgets requires careful attention to the problem of averaging the chemical sink over time and space, the simple model gives us a method of making a preliminary assessment of the scavenging capacity of the atmosphere for a given gaseous pollutant. It also provides a basis for definition of the kind of physico-chemical data that are needed to understand the pathways for removal of pollutants from the atmosphere.

Reference

- (1) H. Levy II, 'Normal Atmosphere - Large Radical and Formaldehyde concentrations predicted', *Science* 173 141-143 (1971)

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