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MEASUREMENT OF ATMOSPHERIC HO BY A CHEMICAL METHOD

R. Subramonia Iyer and F. Sherwood Rowland
University of California
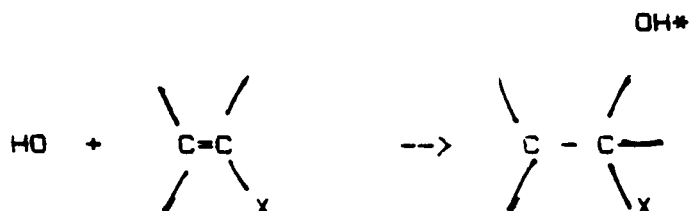Irvine, California

The development of a sensitive chemical technique for the measurement of atmospheric hydroxyl radical concentrations is highly desirable in view of the lack of significant success with current spectroscopic methods. The parameters for a chemical technique can be outlined from the following set of desirable goals: (1) sufficient conversion of tracer species A to product B that B can be measured quantitatively in the presence of A and a great excess of air; (2) specificity of reaction such that A is converted to B only by reaction with HO; and (3) sufficient sensitivity for detection that the ambient concentration of HO is not seriously perturbed by the presence of A and B. The chemical method previously attempted has involved the use of ^{14}CO as a tracer and radiochemical measurement of the $^{14}CO_2$ formed by its oxidation by atmospheric HO.[1] The rate constant for this reaction at 298 K and one atmosphere pressure is about 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}. With HO concentrations in the range 10^4 to 10^7 cm^{-3}, this rate constant is too small to allow formation of sufficient quantities of the $^{14}CO_2$ product in a time period short enough to avoid containment problems for the air mass under test (conversion of 10^{-7} to 10^{-4} per second). This technique was not ready for field application and failed in the NASA-CITE comparison test.

The problems encountered with the HO + ^{14}CO system can be minimized if a reaction of HO forming a specific product can be found with a rate constant up to 100 times faster than with CO. The HO concentration in

remote atmospheres is believed to be controlled chiefly by reaction with CO, whose concentration lies in the 50-150 ppbv range. The limitation on concentration of tracer A is actually an upper limit on total reactivity with removal of HO by reaction with A no more than 10% as large as removal by reaction with CO. With this 10% upper limit on total reactivity as a criterion, a 100-fold increase in HO reactivity of A relative to CO would limit the concentration of A to 10^{-3} x [CO], i.e. to 50-150 pptv. If the tracer species A reacted with HO only 10 times as rapidly as with CO, then the atmospheric concentration limitation would be relaxed to 10^{-2} x [CO] for the tracer reactivity criterion. In addition to a rapid rate constant with HO and specificity of the reaction product, a useful monitor reaction must also satisfy other requirements, such as (a) the background levels of A and B in the atmosphere should be negligible; (b) other removal processes in the atmosphere should be negligible for both the A and B; and (c) A and B must be separable from the air mass and from one another for quantitative assay.

The addition reactions of HO with various alkenes and alkynes are known to occur with rate constants in the range of 10^{-12} to 10^{-11} cm^3 molecule^{-1} sec^{-1},[2] forming a vibrationally excited adduct radical:

$$\text{HO} \; + \quad \overset{\displaystyle \diagdown \quad \diagup}{\underset{\displaystyle \diagup \quad \diagdown_{\text{X}}}{\text{C=C}}} \qquad \longrightarrow \qquad \overset{\overset{\displaystyle \text{OH}*}{}}{\underset{\displaystyle \diagup \quad \diagdown_{\text{X}}}{\overset{\displaystyle \diagdown \quad \diagup}{\text{C}-\text{C}}}}$$

Such excited radicals usually can then undergo either collisional stabilization or unimolecular decomposition. With olefins containing

weakly bonded substituents, the possibility exists that a fast decomposition channel for the adduct radical could be found leading to a specific product (e.g. loss of X in the example above.)

The substituents R can be constructed to have electronegative components such as chlorine atoms which will facilitate highly sensitive product measurement by gas chromatography-electron capture techniques. The use of symmetric substituent molecules such as $X-C=C-X$ might be

$$\begin{array}{cc} | & | \\ R & R \end{array}$$

expected to enhance the product yield. Analogous reactions are known to occur with atomic fluorine or chlorine atoms and various haloalkenes, as in $F + CH_2=CHBr \longrightarrow CH_2=CHF + Br$, and $F + CH_2=CH-CH_2Cl \longrightarrow CH_2F-CH=CH_2 + Cl$. In the latter case, the decomposition of an adduct radical by loss of the Cl atom occurs so rapidly that more than 99% of these radicals decompose at one atmosphere pressure to give the $CH_2FCH=CH_2$ product.[3] It is quite possible that similar reaction channels can be found following HO attack on suitably substituted olefins. Laboratory measurements of product yields and rate constants for their formation are required to determine whether a reactant molecule can be found which has the necessary properties for determination of local HO radical concentrations.

(1)   M. J. Campbell, J. C. Sheppard and B. B. Au, Geophys. Res. Lett., 6, 175 (1979).

(2)   R. Atkinson, K. R. Darnall, A. C. Lloyd, A. M. Winer and J. N. Pitts, Jr., Advances Photochem., 11, 375 (1979).

(3)   R. S. Iyer, L. Vasi and F. S. Rowland, J. Phys. Chem., in press.

Comments

This proposed study involves finding a chemical reaction specific enough for OH, and a measurement of the product formed. What one wants is a rate constant of about 10^{-10} cm^3 s^{-1}, so that 0.1 percent of the OH will be converted in 100 s. Laboratory studies are needed to find a reaction which will fill this bill, yielding a product in quantity sufficient for precise measurement. This is an extremely fast rate constant and the search may be difficult. Again there is a question of perturbing the local environment, while still providing a sensitive measurement. Also the temperature and pressure dependence of the reaction rate is a complicated function for many of these species (that is, one must use an RRKM or Troe-based picture), and must be taken into account.