KINETICS OF THE REACTION OF HO_2 WITH NO

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Abstract: The gas phase reaction of HO_2 radicals with NO was studied using a discharge-flow system and laser-magnetic resonance detection. Concentrations of HO_2 down to 2×10^9 molecules/cm^3 were detectable, thus allowing the reaction to be studied under pseudo-first-order kinetic conditions. The rate constant was measured using three independent kinetic schemes, one of which involved the detection of the reaction products OH and NO_2. The three schemes gave results in excellent agreement. The rate constant, k_1, for the reaction

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (1)$$

is $(8.1 \pm 1.5) \times 10^{-12}$ cm^3/molecule·s at 296K and a pressure of 140-220 Pa (1.1-1.7 torr). The measurements also indicate that the rate constants for two other exothermic channels of the reaction are less than 2% of k_1.

Introduction

Reaction (1) has been identified as one of the most important reactions in atmospheric chemistry because of the uncertainty in the available data and because of its impact on model calculations of photochemical smog chemistry (Dodge and Hecht, 1975) and stratospheric chemistry (Duewer et al., 1977). All of the previous kinetic data on the reaction have been obtained by indirect techniques, i.e., measurements in which the HO_2 reactant was not detected. These measurements were generally based on assumed reaction mechanisms in which Reaction (1) competes with a reference reaction such as

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \qquad (2)$$

The rate constant k_1 is estimated using an equation derived from a kinetic analysis of the reaction mechanism, a literature value for the rate constant of the reference reaction, and laboratory measurements of one or more experimental parameters such as the change in concentration of a stable product. The results of several indirect studies are given later.

Results and Discussion

The experimental methods used in this work were described earlier (Howard and Evenson, 1974). We employed LMR detection of the radicals in a 118.6 μm wavelength water vapor laser spectrometer. Radicals are detectable with LMR when there is a near resonance of a rotational transition in a paramagnetic species with the frequency of the laser. Detection occurs when the molecules are tuned to the fixed frequency of the laser by means of the Zeeman effect and absorb some of the laser radiation. The resultant change in the laser output power is monitored with a sensitive detector and is proportional to the number density of the radicals in the flow tube.

The radicals were generated and the kinetic measurements were made in a 2.54 cm i.d. discharge-flow tube. All kinetic measurements employed a movable reactant gas inlet which was used to add NO reactant gas to the flow tube at distances, z, between about 5 and 50 cm from the detection region. The reaction time was defined by this distance divided by the average flow velocity $\bar{v}$. The HO_2 reactant radicals were formed in the upstream end of the flow tube and traveled a distance of about 35 cm before reaching the nearest point of nitric oxide addition. This distance was equivalent to about 35 ms time and allowed the excited radicals that might be present to be relaxed to the ground state. The far-infrared spectroscopy of HO_2 is well understood (Radford et al., 1974) and (Hougen et al., 1975) and we have not detected excited HO_2 from any of the sources used in this work.

Absolute calibrations were made to determine the response of the apparatus to HO_2, OH, and NO_2 radicals. The purpose of these calibrations was to allow a determination of the ultimate sensitivity of the detection system and to define the concentrations of the radicals in the flow system. Nitrogen dioxide concentrations were the easiest to calibrate. Its flow rate was measured by the rate of change of pressure in a calibrated volume.

The OH response was determined by adding a small flow of NO_2 through the movable inlet to an excess of H atoms which were generated by discharging a mixture of helium and hydrogen. It was assumed that one OH was generated from each NO_2 by the fast reaction

$$H + NO_2 \rightarrow OH + NO \qquad (3)$$

The OH signal was proportional to the NO_2 flow rate over the one decade range of the calibration, $[OH] \simeq 10^{10}$ to 10^{11} molecules/cm^3.

The LMR instrument was calibrated for HO_2 relative to OH. This was accomplished by using reactions that stoichiometrically convert OH to HO_2 or HO_2 to OH. OH was converted to HO_2 by adding H_2O_2:

$$OH + H_2O_2 \rightarrow HO_2 + H_2O, \qquad (4)$$

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and HO_2 was converted to OH by adding NO. At the low radical concentrations used in these calibrations ($< 10^{11}$ molecules/cm^3), there was no significant loss of radicals by reactions such as,

$$HO_2 + OH \rightarrow H_2O + O_2. \quad (5)$$

This was demonstrated by measuring the OH/HO_2 calibration factor ratio over a wide range of radical concentrations.

The measured sensitivities of the spectrometer at 118.6 μm for a signal to noise ratio of 1 and a 1 s time constant are about 7×10^{11} molecules/cm^3 for NO_2, 10^7 molecules/cm^3 for OH, and 2×10^9 molecules/cm^3 for HO_2. These factors are dependent upon experimental conditions such as the gas pressure and the magnetic modulation amplitude.

Reaction (1) has been studied using three different kinetic schemes which are identified as (1) the direct method, (2) the scavenger method, and (3) the product detection method.

The direct measurements used

$$H + O_2 + M \rightarrow HO_2 + M \quad (6)$$

as the source of HO_2. Since k_6 is relatively small, $k_6(M = N_2) = 5.3 \times 10^{-32}$ cm^6/molecule^2·s (Kurylo, 1972), HO_2 was formed in the upstream end of the flow tube by mixing H atoms generated by passing H_2 over a hot tungsten wire with a slow flowing ($\bar{v} \simeq 350$ cm/s) stream of O_2. After traveling about 35 cm, the main helium carrier gas was added. This increased the flow velocity and decreased the O_2 number density by a factor of three to four, effectively terminating Reaction (6), which has gone more than 99% to completion.

A second reaction takes place in the upstream source region

$$H + HO_2 \rightarrow 2OH. \quad (7)$$

This reaction did not interfere with the kinetic measurements but was important because it limited the amount of HO_2 that was formed and also produced a background OH concentration that obscured the OH product from Reaction (1).

A sample of typical data for the direct measurement method is shown in Fig. 1. The initial $[HO_2]$ was less than 2×10^{10} molecules/cm^3 and the [NO] was more than 100 times larger, therefore, the assumption of pseudo-first-order kinetics was valid. The measured change in $[HO_2]$ was in the range of a factor of 2 to 4 for the direct measurements.

The second measurement scheme employed a different source of HO_2 radicals and a scavenger to remove the OH product. HO_2 was generated in the source region by the reaction of F atoms, formed by discharging a mixture of He and a trace of F_2, with H_2O_2.

$$F + H_2O_2 \rightarrow HO_2 + HF. \quad (8)$$

The scavenger, trifluorochloroethylene (C_2F_3Cl), removed OH to prevent HO_2 from being reformed by Reaction (4). C_2F_3Cl reacted with OH with a rate constant of about 6×10^{-12} cm^3/molecule·s (Howard, 1976) while its HO_2 reaction was at least 2000 times slower. Tests were made to demonstrate that the products of the reaction of OH with the scavenger did not interfere with the HO_2 rate constant measurement. One of these tests was to add some C_2F_3Cl to a mixture of OH and HO_2 to confirm that the OH + C_2F_3Cl reaction products did not remove HO_2. The scavenger experiments covered changes in HO_2 concentration by a factor between 2 and 10.

The third measurement scheme, the product detection method, takes advantage of the versatility of the LMR technique to detect both the OH and NO_2 products as well as the HO_2 reactant in Reaction (1). In this study HO_2 was initially formed by Reaction (8). When NO was added through the movable injector in the absence of scavenger, HO_2 was regenerated via Reaction (4). Thus, in the presence of a large excess of both NO and H_2O_2, there was a steady-state chain reaction which quickly established a constant HO_2 to OH concentration ratio which was determined by the ratio $k_4[H_2O_2]/k_1[NO]$. Under typical conditions the first-order rate constants for Reactions (1) and (4) were 300 to 1000 s^{-1}. The rate equation for the formation of the NO_2 product in this reaction system is

$$\frac{d[NO_2]}{dt} = k_1[HO_2][NO]. \quad (9)$$

This can be rearranged to yield

$$k_1 = \frac{\frac{d[NO_2]}{dz}\bar{v}}{[HO_2][NO]}, \quad (10)$$

where $d[NO_2]/dz$ was the slope of a plot of the measured $[NO_2]$ vs z. The NO concentration was calculated from the measured NO flow rate and ranged from (6.6 to 13) $\times 10^{13}$ molecules/cm^3. The HO_2 concentration was determined from the LMR signal and the calibration factor. $\bar{v}$ was varied from 700 to 1300 cm/s. This measurement method was the only one that required absolute radical concentration calibrations.

Typical data for the product measurement method are shown in Fig. 2. Here the LMR measured concentrations of the HO_2, OH, and NO_2 are shown as a function of z. The $[HO_2]$ to [OH] ratio is constant indicating that they are indeed in steady state. The rate of formation of NO_2, $d[NO_2]/dt$, is the slope of the line in the NO_2 plot multiplied by $\bar{v}$. The average $[HO_2]$ was used to calculate k_1.

The results from the three measurement schemes are summarized in Table I, where the number of measurements, the average, and the average deviation are given for each method. There is excellent agreement in the results for all three methods. The error limit on the average includes the estimated systematic errors.

There are two possible mechanisms for the reaction of HO_2 with NO in addition to Reaction (1). These are:

$$HO_2 + NO \rightarrow HNO + O_2 \quad (11)$$

and

$$HO_2 + NO + M \rightarrow HOONO + M \quad (12)$$

Since both reactions are radical chain terminating steps, it is possible to set an upper limit on k_{11} and k_{12} with the steady-state chain data. If the

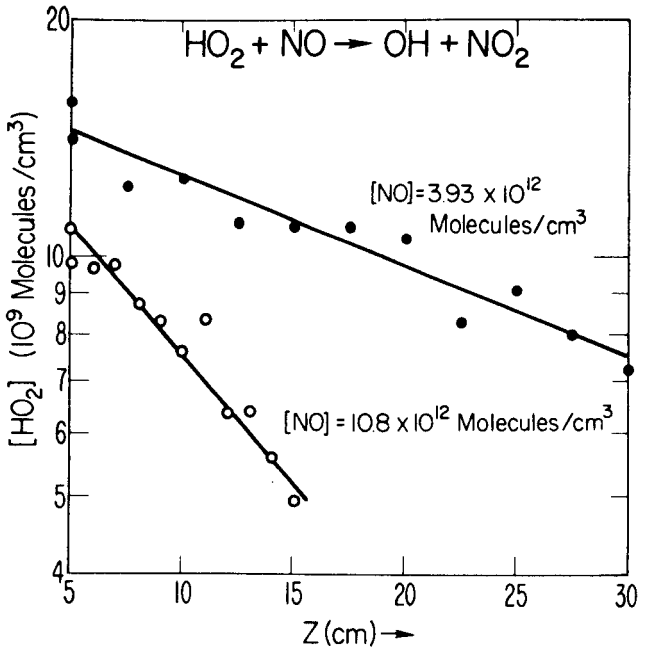

Fig. 1. Example of data for direct measurement. [He] = 3.73 x 10^{16} molecules/cm^3, [O_2] = 1.59 x 10^{16} molecules/cm^3, and $\bar{v}$ = 1290 cm/s. The slopes of the lines multiplied by $\bar{v}$ are the first-order rate constants and the first-order rate constants divided by [NO] equal k_1.

small (10-25%) loss of HO_2 and OH radicals that is measured (for example, see Fig. 2) is attributed to (11) or (12), the following upper limits are established: $k_{11} < 1.6 \times 10^{-13}$ cm^3/molecule·s and $k_{12} < 4.5 \times 10^{-30}$ cm^6/molecule^2·s. We feel these are very conservative upper limits because some of the loss of radicals is probably due to the OH + HO_2 reaction or wall reaction.

The result reported here for k_1 is much larger than all previous measurements. Previous values from indirect measurements range from around 1 x 10^{-12} cm^3/molecule·s by Cox and Derwent (1975) and Simonaitis and Heicklen (1976) to about 3 x 10^{-13} cm^3/molecule·s by Payne et al. (1973) and Hack et al. (1975). Because of this large discrepancy and the importance of k_1 in atmospheric chemistry, the validity of the present result is reasonably questioned. The two major areas of concern deal with errors due to the presence of excited molecules and wall reactions.

One of the strengths of spectroscopic detection in kinetic studies is that one knows the state and therefore the internal energy of the detected molecules. The rotational spectrum of HO_2 is very well understood. From the work of Radford et al. (1974) and Hougen et al. (1975), there is no doubt that the 118.6 μm transitions used to detect HO_2 in this work are ground state $^2A''$ HO_2 transitions and are not due to vibrationally or electronically excited HO_2. In the direct and scavenger methods we measure the disappearance of ground state HO_2 from two different kinetic sources. Also the data for the product detection method strongly contradict the suggestion that a significant number of excited HO_2 molecules are present in the system. In that study, we measure the concentration of HO_2 in the flow tube before NO is added. Upon addition of NO, a fraction of the HO_2 is converted to OH. Since the number of ground state OH radicals formed is equal to the number of ground state HO_2 removed, it is not possible that there is a significant fraction of the HO_2 in any state other than the ground state. We conclude that although it is possible that some of the HO_2 produced by our kinetic sources may be initially in an excited state, they must be very efficiently quenched by gas or wall collisions as, for example, the vibrationally excited OH formed in the reaction of H with NO_2 is efficiently quenched (Howard, 1976).

The possibility of interference by a wall reaction is a little more difficult to discount than the reactions of excited states. The ideal way to measure the contribution from wall reactions is to change the surface to volume ratio of the reactor. Unfortunately, this is not easily accomplished with a flow tube reactor because one is usually limited to a relatively small range of tube sizes. It is possible to make an equivalent change in the destruction rate of radicals at the

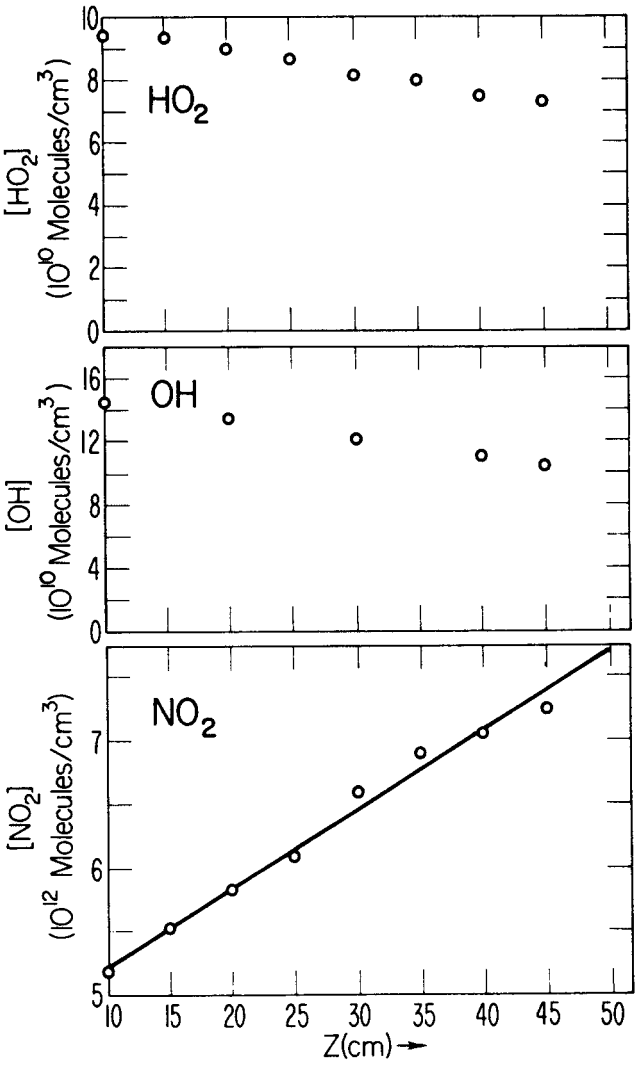

Fig. 2. Example of data for product detection measurement. [He] = 3.73 x 10^{16} molecules/cm^3, [NO] = 1.06 x 10^{14} molecules/cm^3, $\bar{v}$ = 1240 cm/s, and average [HO_2] = 8.4 x 10^{10} molecules/cm^3.

TABLE 1. Summary of measurements of k_1.

Measurement method	No. of measurements	Avg.(average deviation) (cm^3/molecule·s)
direct	5	$7.7(0.8) \times 10^{-12}$
scavenger	6	8.3(0.3)
product detn.	5	8.4(0.5)
AVERAGE ± ESTIMATED ERROR		$(8.1 \pm 1.5) \times 10^{-12}$

wall, k_w, by altering the condition of the surface of the reactor. This method works particularly well with acid coated reactors and has always been an effective way of detecting interference from wall reactions. Changing k_w by a factor of 2 had no effect on our measurement of k_1.

A second reason for believing that our measurement of k_1 is not affected by wall reactions is the measured quantitative conversion of HO_2 and NO to NO_2 and OH. If the surface were an important agent in catalyzing the reaction of HO_2 with NO, it seems reasonable that a significant fraction of the HOONO intermediates would be stabilized and that HOONO would be an important product. However, this was not the case and over 98% of the reactive events produced gaseous OH and NO_2 products.

If the reaction between HO_2 and NO were taking place on the tube wall, one might expect a brief induction period after NO was first added to the tube for the surface to become activated or conditioned. However, this was not the case and the gaseous radicals responded instantaneously when the NO reactant was turned on or off.

With the three different rate measurement schemes we covered a range of first-order rate constants from about 20 to 1000 s^{-1}. It is also unlikely that a wall reaction would remain constant over such a wide range of conditions.

Finally, we point out that the value of k_1 that we report is about the same magnitude as the rate constants for the analogous reactions of ClO and NO_3 radicals with NO.

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