isolated molecule spin-orbit coupling. The data are also shown to be qualitatively consistent, in many respects, with quantum-mechanical formulations of radiationless-transition theory.

A quantum-mechanical rationale is also presented for the phenomenon of saturation, interpreting it as a transformation from the collision-sensitive small or intermediate case to the collision-insensitive statistical limit. This transformation occurs as a result of an increase in the number of coupled levels N. Calculations support Freed's conjecture that this increase occurs on account of lifetime broadening. When the collision interval is sufficiently short, the destination states broaden to the point of overlap and thus create the quasi-continuum of the statistical limit.

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Laser Magnetic Resonance, Resonance Fluorescence, and Resonance Absorption Studies of the Reaction Kinetics of O + OH \rightarrow H + O₂, O + HO₂ \rightarrow OH + O₂, N + OH \rightarrow H + NO, and N + HO₂ \rightarrow Products at 300 K between 1 and 5 torr

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A new tandem axis, laser magnetic resonance-resonance fluorescence-resonance absorption, fast flow system is used to examine the kinetics of four reactions in the oxygen-nitrogen-hydrogen free radical system. The experimental approach emphasizes simultaneous detection of reactants and products, cross calibration of detection axes, multiple sources for free-radical-formation steps, and computer simulation of the time dependence of reactants and products through the course of each reaction. Rate constants are reported as follows: OH + $O \rightarrow H + O_2$, $(3.1 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $HO_2 + O \rightarrow OH + O_2$, $(5.2 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} ; OH + N \rightarrow H + NO, (4.2 ± 0.8) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹; HO₂ + N \rightarrow products, (2.2 ± 0.5) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Cited uncertainties are 95% confidence limits and include consideration of possible systematic errors. All experiments were done in helium or argon at 300 K and pressures between 1 and 5 torr.

Introduction

Hydrogen-containing radicals catalyze the recombination of oxygen atoms and ozone to molecular oxygen in numerous gas-phase reaction systems, including laboratory discharges, combustion and flame processes, chemical lasers, and the upper atmospheres of Earth and Mars. Two such reaction couplets are

$$0 + OH \rightarrow H + O_{2}$$
(1)

$$\frac{H + O_{3} \rightarrow OH + O_{2}}{O + O_{3} \rightarrow 2O_{2}}$$
(1)

$$OH + O_{3} \rightarrow HO_{2} + O_{2}$$
(2)

$$\frac{HO_{2} + O \rightarrow OH + O_{2}}{O + O_{3} \rightarrow 2O_{2}}$$
(2)

in which reactions 1 and 2 are often rate limiting. A particularly important example is the upper stratosphere and mesosphere of Earth (40-90-km altitude) where the reactive hydrogen partitioning into the hydroxyl and hydroperoxyl radicals depends crucially on the ratio of the rate constants for reactions 1 and 2, k_1 and k_2 .¹ Although these two reactions have received considerable attention

in laboratory studies over the past decade,² recent measurements of k_1 by Lewis and Watson³ and Howard and Smith⁴ and of k_2 by Keyser⁵ and Sridharan et al.⁶ have revised accepted room-temperature values of the ratio k_2/k_1 by a factor of 2 from 0.9 to 1.8. For temperatures appropriate for the upper stratosphere and lower mesosphere, ~ 200 K, low-temperature studies³⁻⁶ suggest a value for the ratio k_1/k_2 near 2. These results have altered significantly the predicted concentrations of OH, HO₂, O₃, and ClO in the upper stratosphere and lower mesosphere, and thus changed predictions of chlorine-induced ozone depletion in the upper atmosphere resulting from the ground-level release of fluorocarbon compounds.⁷

We have combined the detection techniques of laser magnetic resonance (LMR), resonance fluorescence (RF), and resonance absorption (RA) with a discharge flow re-

⁽¹⁾ Allen, M.; Yung, Y. L.; Waters, J. W. J. Geophys. Res. 1981, 86, 3617.

⁽²⁾ Hampson, R. F. "Chemical Kinetic and Photochemical Data Sheets (a) Humpsheric Reactions", Federal Aviation Administration, Washington, DC. Report No. FAA-EE-80-17, 1980.
(3) Lewis, R. S.; Watson, R. T. J. Phys. Chem. 1980, 84, 3495.
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⁽⁷⁾ Ko, M. K. W.; Sze, N. D., Geophys. Res. Lett. 1983, 10, 341.



Figure 1. Schematic of laser magnetic resonance, resonance fluorescence, resonance absorption discharge flow system. A second movable source was added for half of the experiments. The detail insert shows the construction of the double injector with the movable 1/16 in. diameter Tefion line inside the 1/4 in. diameter Pyrex tube.

actor to study reactions 1 and 2 as the first step in an extensive examination of the hydrogen-oxygen, atomsmall radical kinetic system. This combination of detection methods gives us sufficiently low detection limits $(\leq 10^9 \text{ radicals cm}^{-3})$ and dynamic range $(\geq 10^3)$ to monitor the reactants OH, HO₂, H, and O either in excess or in decay for pseudo-first-order conditions with respect to either reactant. We can then test each reaction for hydrogen continuity by comparing observations with computer simulations as well as check each radical production scheme for possible interfering reactants and products.

Two other reactions studied in this work are the reactions of nitrogen atoms with hydroxyl and hydroperoxyl:

$$N + OH \rightarrow H + NO$$

$$\Delta H^{\circ}_{298} = -48.8 \pm 1.0 \text{ kcal/mol}$$
(3)

$$N + HO_2 \rightarrow NH + O_2$$

$$\Delta H^{\circ}_{298} = -34.5 \pm 2.8 \text{ kcal/mol}$$
(4a)

$$\rightarrow$$
 NO + OH $\Delta H^{\circ}_{298} = -84.5 \pm 1.2 \text{ kcal/mol} (4b)$

$$\rightarrow$$
 NHO + O (4c)

$$\rightarrow$$
 H + NO₂ $\Delta H^{\circ}_{298} = -55.5 \pm 1.2 \text{ kcal/mol} (4d)$

For each reaction, all the exothermic product channels have been listed. The interest in these reactions is their analogy with the O atom reactions, although reaction 3 also provides a simple cross-check between our measurements of O and N with OH and those of Howard and Smith.⁴

Experimental Section

The apparatus, shown schematically in Figure 1, contains three major subsystems: the detection axes, including laser magnetic resonance (LMR) detection of OH, HO_2 , and NH, resonance fluorescence (RF) detection of OH, O, and H, and resonance absorption (RA) detection of O; the flow system with interchangeable flow tubes, gas-handling manifolds, and flow and pressure monitors; and the chemical sources for the various radicals. This section contains details about this new system as well as an explanation of experimental procedures.

Radical Detection Systems and Sensitivity. The first detection axis incorporated the laser magnetic resonance (LMR) spectrometer. As applied to these studies,⁸ LMR is the Zeeman tuning of a rotational transition of an absorbing molecule into coincidence with a far-infrared laser line and the monitoring of that absorption, usually with lock-in detection techniques. Our 65 cm long vertical far-infrared laser was optically pumped with radiation from a 1.5 m long CO_2 laser capable of 12–25-W CW. The CO_2 radiation was absorbed in the lasing gas region of the far-IR laser while being multiply reflected inside a copper tube. A polypropylene Brewster angle window separated the lasing gas from the kinetic system, as shown in Figure 1. A small portion of the resulting far-IR radiation was diverted by a $1/_4$ -in., 45° angle copper mirror to a liquidcooled germanium bolometer. The molecular absorption levels were split into the magnetic sublevels by the field from a Harvey Wells magnet controlled by a programmable field sweep generator. A small 500-Hz modulating field (20–40 G_{pp}) from 10 cm radius Helmholtz coils on the pole piece faces enabled the lock-in amplifier to measure the absorption and display its first derivative as the magnetic field was swept. These peak-to-peak signals are repeatably observed to be linear with absorber concentration over the entire range of concentrations used in these kinetics experiments. For these particular experiments, the CH₃OH 163.0- μ m laser line was used for detection of HO₂ and OH at 2.3 and 3.8 kG, respectively. For NH detection, the CH_3NH_2 315-µm laser line was used with a magnetic field of 2.2 kG.

Approximately 20 cm downstream from the LMR axis was a rectangular, stainless steel manifold on which UV resonance lamps and detectors were mounted for resonance fluorescence and absorption measurements (see Figure 1). The three detection axes spaced 6 cm apart were used for O atom resonance absorption, atom (O, H, and N) resonance fluorescence, and OH resonance fluorescence, with the absorption axis closest to the LMR system. A 25-mm Teflon-coated glass tube which connected the manifold to the LMR system and lined the inside of the manifold had, in the first axis, two 10 mm diameter holes drilled opposite each other for O absorption measurements and, in the second and third axes, 2.5 cm long gaps for atoms and OH resonance fluorescence measurements. Cross-sectional views of the atom resonance fluorescence axis and the O atom absorption axis are shown in Figure 2. For resonance fluorescence detection in axes 2 and 3, the overlap between the collimated light beam from the lamp and the field of view of the detector, set at a right angle to the lamp, formed the detection volume in the center of the gas flow. The light traps across the detection volume from both the lamp and the detector were necessary to minimize scattered light. At the end of the lamp light trap was a photodiode which acted as both a flux monitor and a crude resonance absorption diagnostic. The flow tube gaps at the LMR axis and the resonance fluorescence axes were necessary for sensitive detection, but they caused a loss of radicals: OH concentrations dropped by about a factor of 2 in passing through a gap. This radical loss was eliminated by Teflon-coated glass tubes, 30-mm i.d. for the LMR axis, and 22-mm i.d. for the atoms RF axis (axis 2), which could be inserted into the gaps to form a continuous, but not leak-tight, path for the flow to the last (OH-RF) axis.

The radiation for the OH-RF detection axis was produced by a 2.45-GHz, 28-W microwave discharge in a flowing helium and water vapor mixture. The light beam was focused by a small lens through an anodized or Black Velvet coated baffle system and a Corning 9863 filter, through the detection volume, and onto a photodiode at the end of a light trap. Resonance scattered radiation from

⁽⁸⁾ Evenson, K. M.; Saykally, R. J.; Jennings, D. A.; Curl, R. F., Jr.; Brown, J. M. "Chemical and Biochemical Applications of Lasers, V"; Moore, C. B., Ed.; Academic Press: New York, 1980; p 95.



Figure 2. Cross-sectional views of (a) the atoms resonance fluorescence axis (axis 2), and (b) the O atoms resonance absorption axis (axis 1). Dashed lines indicate light paths; small vertical rectangles, MgF_2 windows; the concentric circles in the center, the glass flow tube with gas flowing into the page. For a further description, see text.

 $A^2\Sigma^+-X^2\Pi$ (0–0) transition was detected by a bialkali photomultiplier tube in the pulse counting mode, which had a series of baffles, a lens, and a 309.0-nm (4.0-nm fwhm) band-pass filter in front of it. For detection of HO₂ by chemical conversion to OH with NO, a 1.5 cm diameter Teflon-covered stainless steel loop injector was placed 5 cm upstream of the detection axis.

The arrangement of the second axis for O and H detection was similar to that for OH. The light source was a sealed, low-pressure helium lamp with a MgF₂ window and two source arms; one containing $KMnO_4$ for oxygen, and the other containing partially hydrated powdered uranium for hydrogen. The hydrogen arm also acted as a getter for gas-phase impurities. Heat applied to either arm produced a controllable source for either the oxygen triplet at 130.4 nm or hydrogen Ly- α at 121.6 nm. To ensure that both resonance lines were not present at once, a retractable CaF_2 filter and N_2 purge or a flowing O_2 filter was placed between the lamp and the collimating baffles. For H atom detection, 1000 torr of O₂ was flowed through a 2 mm thick cell to remove 95% of the small residual radiation with wavelengths longer than 130 nm and to absorb less than 40% of the 121.6-nm radiation. For O atom detection, the CaF₂ filter with an N₂ purge was used. The light passing through the detection volume was first collimated by a series of baffles and was monitored by a photodiode at the end of a light trap. A CsI photomultiplier with a baffle-restricted field of view was set at a right angle to the lamp for detection.



Figure 3. Typical oxygen atom calibration curve. Absorption at 130.4 nm converted to an oxygen atom concentration with a computer model is compared to NO concentrations. Closed circles are the calibration before a set of experiments; open circles are the calibration after.

The absorption axis, the first axis on the stainless steel manifold, used a microwave-discharge sealed lamp identical with that for the atoms RF axis. Since this axis was used exclusively for O detection, a CaF₂ filter and N₂ purge were always used. The 25-mm absorption path was defined by a MgF₂ window on the lamp side of the flow tube and, on the opposite side, an evacuated glass tube sealed on each end with 8-mm MgF₂ windows, as in Figure 2. The radiation was detected by a Hamamatsu 1187 photodiode with a CsI photocathode which abutted the end window on the evacuated tube.

The relationship between oxygen atom concentration and the absorption signal was established by adding a known amount of NO to excess N atoms to produce a known O concentration. The absorption curve was determined with [O] from $\sim 5 \times 10^{11}$ to $\sim 8 \times 10^{12}$ cm⁻³ and was constant to <5% over the course of a day. A comparison of the absorption-NO concentration curves with a computer Doppler–Doppler overlap absorption model, which included the measured emission ratios of the triplet lines from the lamp and a resonance scattering correction,⁹ showed that the "best-fit" lamp temperature was ~ 1000 \pm 200 K and that variations from this fit for [O] $\lesssim 8 \times 10^{12}$ cm^{-3} were less than $\pm 20\%$ on a day-to-day basis. A typical calibration of [O] is shown in Figure 3. Deviations from the 1000 K model were caused by small residual emissions in the wavelength range 130-160 nm, change in the lamp cooling conditions, and, for $[O] \gtrsim 10^{13} \text{ cm}^{-3}$, breakdown in the Doppler-Doppler model. The advantage of this O detection technique for $[O] \gtrsim 5 \times 10^{11} \text{ cm}^{-3}$ is clear: once calibrated, it is stable, requires only measurements with and without O present, and acts as a continual monitor of [O]. Further, the uncertainty in the calibration is only slightly higher $(\pm 10\%)$ than the NO concentration uncertainty.

In most experiments, O (or N) was run in excess. However, it was necessary to calibrate absolutely the OH, HO₂, and H sensitivities, both LMR and RF, in order to compare experiment to computer simulation predictions. The rapid H + NO₂ \rightarrow OH + NO reaction was used to calibrate the OH-RF axis. Hydrogen atoms were kept in excess (5 × 10¹² \leq [H] \leq 1 × 10¹³ cm⁻³) and NO₂ concentrations added through a movable injector were varied over at least a factor of 5. The sensitivity was typically 2 × 10⁻⁸ (counts s⁻¹)/(molecule cm⁻³) with a scattered light signal of ~100 count s⁻¹, giving an OH detection limit of \leq 5 × 10⁸ cm⁻³ for integration times exceeding 10 s. This sensitivity was quite stable, varying less than 10% over a day.

⁽⁹⁾ Schwab, J. J.; Anderson, J. G. J. Quant. Spectrosc. Radiat. Transfer 1982, 27, 445.

TABLE I: Summary of Calibration Methods

		axis	
species	RF	LMR	RA
ОН	$H + NO_2 \rightarrow OH + NO;$ excess H, measured flow of NO ₂ ; 10 ¹⁰ < [OH] < 5 × 10 ¹² cm ⁻³	same method as for RF axis; movable probe used to cross calibrate LMR and RF axes	
HO2	OH calibration established; excess NO added to convert HO ₂ to OH via HO ₂ + NO \rightarrow OH + NO ₂ ; $10^{10} < [HO_2] < 5 \times 10^{12} \text{ cm}^{-3}$	same method as for RF axis; movable probe also used to cross calibrate LMR and RF axes; conversion efficiency of HO, to OH is 0.97 ± 0.02	
Н	H + NO ₂ → OH + NO: (a) excess NO ₂ , cross calibrated with OH; (b) excess H, Δ [H] equated to added [NO ₂]; 10 ¹⁰ < [H] < 10 ¹² cm ⁻³		same method as for RF axis
0	N + NO \rightarrow N ₂ + O; excess N, measured flow of NO; $10^{10} < [O] < 10^{12} \text{ cm}^{-3}$		same method as for RF axis; compared to computer model for OI 130.4 triplet absorption to establish Doppler width of lamp emission line; $3 \times 10^{11} <$ [O] $< 1 \times 10^{13}$ cm ⁻³
N	N + NO → N ₂ + O; excess NO; cross calibrated against O ab- sorption axis		O absorption calibration estab- lished; excess NO added to convert N to O by N + NO \rightarrow O + N ₂ ; conversion of N to O is ≥ 0.99 ; $3 \times 10^{11} < [N] <$ 1×10^{13} cm ⁻³
NH		$CF_4 \xrightarrow{\text{microwave}}_{\text{discharge}} F; F + NH_3 \rightarrow$ HF + NH ₂ , F + NH ₂ \rightarrow NH + HF; F measured by adding H ₂ O and observing OH with calibrated RF axis; assumed [NH] = 2[F] for minimum	

sensitivity

The HO₂ radical concentrations were calibrated by adding $(1-2) \times 10^{14}$ cm⁻³ of NO approximately 5 cm upstream of the axis. Corrections for HO₂ wall loss, OH wall loss, and OH recombination were not necessary because the calibrations and measurements were made at the same injector position with respect to the NO injection loop. Corrections for OH loss, both heterogeneous and homogeneous, when NO was added were $3 \pm 2\%$ and were made. These necessary corrections have been discussed extensively by Keyser.¹⁰

The laser magnetic resonance spectrometer was calibrated for OH by producing OH in the movable injector, measuring the resonance fluorescence OH signal with the injector at the calibration position for that axis, moving the injector to a position a few centimeters in front of the LMR axis, and measuring the LMR signal. The HO₂ signal was calibrated by adding NO upstream of first the LMR axis and then RF–OH axis, and noting the change in HO₂ and OH signals. Sensitivity varied over the course of these experiments, but generally OH was detectable at ~10⁸ cm⁻³ (S/N ~ 1), and HO₂ at ~6 × 10⁸ cm⁻³.

The detection sensitivity for hydrogen on axis 2 was measured two ways. First, just after a calibration of the OH axis, a small amount of hydrogen ($\lesssim 3 \times 10^{11}$ cm⁻³) was added to the flow and the hydrogen signal was noted. Then, excess NO₂ ($\sim 10^{13}$ cm⁻³) was added through the injector at the position used to calibrate OH, the gap for axis 2 was closed by the sliding glass tube, and the OH signal was recorded. This procedure was repeated for different H concentrations and lamp intensities so that the calibration would not be lost with the gradual decay of the lamp or optics during the course of the experiments. The second method was to add a small amount of NO₂ to hy-

(10) Keyser, L. F. J. Phys. Chem. 1981, 85, 3667.

drogen ($\sim 7 \times 10^{11}$ cm⁻³) and to measure the change in the hydrogen signal. Even though this method has some possible problems, namely, OH wall loss due to the longer time required for the reaction to go to completion, and incomplete relaxation of the OH produced in vibrationally excited states, it gave results comparable to the first. Sensitivities for H atoms of 3×10^{-9} (counts s⁻¹)/(molecule cm⁻³) with a scattered light signal of ≤ 10 count s⁻¹ were typical, giving detection limits of $[H] < 10^9 \text{ cm}^{-3}$ for 10 s or greater integration periods. The atomic oxygen resonance fluorescence detection system was calibrated by adding a known concentration of NO $(10^{10}-5 \times 10^{11} \text{ cm}^{-3})$ to excess N atoms ($\sim 1 \times 10^{13}$ cm⁻³). Sensitivities of $1 \times$ 10^{-8} (counts s⁻¹/(molecules cm⁻³) with a scattered-light count rate of 40 counts s^{-1} were generally used. A summary of all the calibration methods used in these experiments is given in Table I.

Flow Reactor. The flow system had a 70 cm long, 25 mm i.d. jacketed Pyrex reactor tube between the LMR axis and two discharge side arms (see Figure 1), a 60 cm long, 25 mm diameter "dead zone" upstream of the discharge inlet arms, and a 20 cm long, 25 mm diameter Pyrex tube connecting the LMR axis to the RF axes. For some experiments on each of the four reactions, the 70 cm long, 25 mm diameter reactor tube was replaced by a 47-mm tube to test for surface effects on the rate constants. The discharge side arms were used for production of radicals for calibration and for some experiments. Most glass surfaces were coated with Teflon (Du Pont FEP8600) to inhibit radical wall loss. These surfaces were stable, reproducible, and effective in inhibiting wall recombination, with wall recombination coefficients, γ , of $\lesssim 1 \times 10^{-5}$, $3 \times$ 10^{-5} , and 7×10^{-5} for atoms, HO₂, and OH, respectively. Only during the reaction of N with HO₂ did this surface show any degradation.

The movable radical injector was a glass tube, 6 mm in diameter and 180 cm long, which passed through an O ring at the back end of the dead zone. This tube was connected to a small glass T and a discharge tube mounted on a carriage that moved on polished steel rods. Depending on the radical being produced, either the T was closed off, or a 1/16 in. diameter, 180 cm long Teflon line was inserted through a vacuum seal and passed down the 180 cm long glass tube to form a double injector, as illustrated in the detail insert in Figure 1. The reaction time inside the movable radical source was adjusted by sliding the Teflon line until the optimum radical production conditions were obtained. A small Teflon cap drilled radially was fitted to the end of the probe to ensure adequate and rapid mixing in the reactor tube. For most of the experiments, two such movable sources with 180 cm long injectors mounted side-by-side and passing through separate O rings in the back were used. The advantages of being able to move both radical sources are as follows: major radicals produced in each source can be examined before they have had substantial time to react; the wall losses of both radicals can be measured at any time without altering the chemistry; and, for our system, the effects of the detection axis gaps and the gap closures can be determined exactly.

The entire flow system was evacuated by a Welch 1397 mechanical pump which produced bulk flows of 15 STD cm³ s⁻¹, corresponding to a flow velocity of 11.8–14.7 m s⁻¹ for a 25 mm diameter flow tube. Gas flows were measured by either electronic flowmeters (Matheson 8143) calibrated against a Brooks Vol-u-Meter (Model 1057) or a measured rate of pressure change in a known volume. The pressure in these manifolds was measured by either a MKS Baratron differential capacitance manometer or a Validyne reluctance manometer calibrated against an oil manometer. The average pressure in the flow tube was measured in the middle of the reaction zone with a MKS Baratron capacitance manometer. The absolute concentration for H_2O_2 used in the HO_2 source, discussed in the next section, was monitored by bubbling a known flow of He through vacuum-distilled 90% H_2O_2 (FMC Corp.) and measuring the absorption of 214-nm radiation (for $\lambda = 213.9$ nm, $\sigma = 3.22$ $\times 10^{-19}$ cm²) from a Zn lamp over a 10-cm path. Detection with an Ebert-Fastie monochromator (RSI, Model 12-150) and a CsTe photomultiplier tube reduced the contribution from other lamp emissions to less than 1% of the total signal. All lines and valves between the absorption cell and the reaction zone were either Teflon or glass, although some loss of H_2O_2 did occur when it was passed through the long 1/16-in. Teflon line in the movable source injector.

Laboratory gases for these experiments were supplied by Matheson, with the following designations and stated purities: He (HP 99.995%) for the bulk flow gas, He (UHP 99.999%) for flow through the discharges, CF_4 (99.7%), NO₂ (99.5%), NO (CP 99.0%), N₂ (UHP 99.999%), O₂ (UHP 99.99%), Ar (Prepurified 99.998%), NH₃ (anhydrous, 99.99%), and H₂ (Prepurified 99.95%). Passing the helium through heated copper turnings and a molecular sieve trap at LN₂ temperature reduced atom production in the sources by a factor of 2-3 but had no effect on the experiments so that helium was generally used without further purification. The NO was always passed at atmospheric pressure through an Ascarite trap and over potassium hydroxide before use. For the N + NO source of O atoms, which will be discussed below, the NO was purified so that the NO₂ impurity was ≤ 100 ppm by cooling the potassium hydroxide trap to ~ -70 °C in a dry ice-ethanol bath. All other gases were used without further purification, although research-grade H_2 and O_2 were substituted in some initial experiments. Water was distilled and degassed prior to use.

Radical Sources. All radical sources were initiated by discharging trace concentrations of CF_4 , N_2 , or O_2 in helium in a 2.4-GHz, 30–70-W $^1\!/_4$ wave microwave cavity. A $^1\!/_2$ in. diameter alumina tube was used for CF4; uncoated quartz was used for N₂ and O₂. Small flows of CF₄ ($\sim 10^{-2}-10^{-1}$ STD cm³ s⁻¹), O₂ ($\sim 10^{-4}-10^{-2}$ STD cm³ s⁻¹), or N₂ ($\sim 10^{-2}-10^{-1}$ STD cm³ s⁻¹) diluted in helium (0.3-2) STD cm³ s⁻¹) were discharged to produce F, O, and N atoms, respectively. For the OH or HO₂ sources, fluorine atoms were reacted with either H_2O or H_2O_2 added through the 1/16-in. Teflon line inside the injector. The increased concentration inside the injector over the concentrations in the flow reactor (a factor of 26) enabled the HO, forming reactions to have $kt \gtrsim 8$ ($t \sim 10$ ms) before the reactants entered the main flow. Both sources were tested for residual F atoms by setting the injector tip 5-10 ms away from the atoms axis, and adding $(1-3) \times 10^{14}$ cm⁻³ of H₂ to scavenge any unreacted F atoms, converting the H₂ to H atoms. No change in the H signal was observed.

Carbon tetrafluoride discharged with helium in a microwave cavity was the preferred source of F atoms for this work because H, O, and F_2 impurities are nearly absent. and because it is safe and easy to use. The byproduct CF and CF_3 radicals could, in theory, interfere with the kinetics (CF_2 is quite stable), but the following tests demonstrate that CF_n radicals do not affect our studies. First, changes in excess O or N atom concentrations measured with and without the HO_x (that is, HO_2 and OH) source discharge on were consistent with losses due to reaction with HO_x alone. Second, the change in the HO_x concentrations when the sliding injector position was varied was consistent with the small wall loss and was independent of HO_x concentrations from 5×10^{10} to 3×10^{11} cm⁻³, and thus of the CF_4 concentration. Third, the rate constants for the $O + HO_2$ and N + OH reactions are independent of whether the HO_x was added to the flow through the sliding injector or the upstream side arm. This invariability shows that the self-reaction of CF_n radicals was not important, since the CF_n concentrations and reaction times were significantly larger for HO_x made in the sliding injector than in the upstream side arm. Finally, the rate constant for the $O + HO_2$ reaction is independent of excess reactant, either O or HO_2 , implying that different initial CF₄ concentrations, $2 \times 10^{12} - 10^{14}$ cm⁻³, had no effect on the results.

Details of the radical sources are shown in Table II. The discharged gas and reaction used to make the radical are listed along with the appropriate rate constant for the formation reaction. Those species subscripted with i's were determined by timed pressure drop in a known volume (CF₄, NO), or by a pressure increase in the reactor tube (H₂O, N₂, and O₂), or as previously described (H₂O₂).

The H₂O₂ concentration for the HO₂ source had to be kept small for reaction 2 with O atoms in excess in order to prevent the reforming of HO₂ due to the reaction of the primary product OH and the remaining H₂O₂. In order to get sufficient H₂O₂ to drive the F + H₂O₂ \rightarrow HO₂ + HF reaction to completion, a helium flow of ~0.6-1.0 STD cm³ s⁻¹ bubbled through the H₂O₂ was necessary. At slower flow rates, loss of H₂O₂ by decomposition on the 1/16-in. Teflon line walls was evident by the increase in the ratio [OH]/[HO₂] without a significant change in the total [OH] + [HO₂] levels. In order to keep OH and O concentrations from the HO₂ source small ([OH] ≤ 0.05 [HO₂] and [O] <1 $\times 10^{10}$ cm⁻³), the minimum H₂O₂ concentration that could be used was 1.2 $\times 10^{12}$ cm⁻³, measured before the H₂O₂

TABLE II: Radical Sources

radical	ОН	HO ₂	<u></u>	0	Ν
forming reactions	$CF_{4} \xrightarrow{\text{microwave}} F$ $F + H_{1}O \rightarrow OH + HF$	$CF_{4} \xrightarrow{\text{microwave}} F$ discharge $F + H_{2}O_{4} \rightarrow HO_{4} + HF$	$O_2 \xrightarrow{\text{microwave}}{\text{discharge}} 20$	$\frac{N_2 \xrightarrow{\text{microwave}} 2N}{\text{discharge}} 2N$ $N + NO \rightarrow O + N_2$	$N_2 \xrightarrow{microwave}{discharge} 2N$
k^{Π} , $a = \text{cm}^3$ molecule ⁻¹ s ⁻¹	1.0×10^{-11}	2.5×10^{-11}		3.4×10^{-11}	
radical concn, cm ⁻³	$(0.8-3.5) \times 10^{11}$	$(0.6-2.5) \times 10^{11}$	$(0.5-8.0) \times 10^{12}$	$(0.5-8.0) \times 10^{12}$	$(0.5-7.4) \times 10^{12}$
other products:					
[CF ₄] _i [OH]	$<1 \times 10^{12}$	$<1 \times 10^{12}$ (0.05-0.10) × [HO ₂]			
ID.H	$(3.0-10) \times 10^{13}$	(· · · · · / · · · · · · · · · · · · ·			
ÌH.O.Ì.		$< 2 \times 10^{12}$			
ioi '''	$<1 \times 10^{10}$	<2 × 10°			$<1 \times 10^{10}$
[H] [NO] _i	<1 × 10 ¹⁰	<2× 10°	$<1 \times 10^{10}$	$<1 \times 10^{10}$ (0.7-10) × 10 ¹²	$<1 \times 10^{10}$
$[NO_2]_i$				≲10-4 × [NO]	
$\begin{bmatrix} O_2 \end{bmatrix}_i \\ \begin{bmatrix} N_2 \end{bmatrix}_i$			<1 × 10 ¹⁴	<1 × 10 ¹⁵	$<1 \times 10^{15}$

^a Reaction rate.

entered the 1/16-in. Teflon line. The efficiency of conversion of the initial fluorine, which was measured at the OH-RF axis by addition of H_2O ($\sim 10^{14}$ cm⁻³) in the reactor, to HO₂, measured by conversion with NO to OH, was consistently 50-70%.

The other chemical source requiring additional comment is the N + NO source for O atoms. A flow of nitrogen atoms was established, and three monitors were watched as the NO was added: the atomic oxygen absorption, the N₂* LBH chemiluminescence observed by the CsI detector on axis 2, and the NO (0,7) β band emission observed by the OH detector on axis 3. With N₂ discharged in an upstream discharge side arm, NO was added through a line in that side arm, and, when O absorption was maximized the LBH and NO β band chemiluminescence were minimized, the NO concentration was increased an additional 20-30% to ensure that the reaction had gone to completion upstream of the reaction zone, but that minimum NO₂ has been formed by NO + O $\underline{\mathbb{M}}$ NO₂ recombination.

Experimental Procedure. All experiments were run under pseudo-first-order conditions with the excess reactant between 4 and 75 times that of the decaying reactant, and 90% of the experiments had a stoichiometric ratio of at least 10. Oxygen atom absorption was calibrated at the beginning and end of each set of runs (3-10 experiments), with occasional other calibrations in between, and all calibrations for a set agreed to within $\pm 3\%$. Calibrations of OH resonance fluorescence sensitivity were made with the same frequency and demonstrated the same stability. The hydrogen and oxygen resonance fluorescence detection system showed substantial long-term changes due to degradation of the optics but had repeatable calibrations over a few days of use. In general, only the two reactants of interest were monitored, but for $\sim 10-20\%$ of each reaction's runs, several primary and secondary products were monitored. Wall loss of radicals on the Teflon walls changed little but was measured at least twice a day.

Excess reactant concentrations were measured at the beginning and end of each experiment and were found to be constant to less than $\pm 6\%$, with an average drift of $\pm 2\%$ for each reaction. Excess reactants were measured at the beginning and end of the reaction time for which the decay was observed and the concentrations were averaged.

Decays of OH, HO_2 , or O were measured over at least a factor of 3 and, for a set of experiments having all conditions the same except excess reactant concentration, the fastest decay was followed over at least a factor of 8-20. Least-squares fits to the plot of the logarithm of the radical signal vs. distance, $k^{\rm I}_{\rm decay}$, were converted to first-order decay rates, $k^{\rm I}_{\rm obsd}$ by¹¹

$$k_{\text{obsd}}^{I} = k_{\text{decay}}^{I} [1 + (k_{\text{decay}}^{I} + 2k_{\text{wall}})D/\bar{v}^{2}](+k_{\text{probe}}) \text{ or } (-k_{\text{wall}}) (5)$$

where D is the diffusion coefficient, \bar{v} is the mean bulk flow, k_{probe} is the first-order effective gain if the decaying radical is added through a back port, and k_{wall} is the wall loss which is subtracted if it is added through a moving probe. The diffusion coefficients used for HO₂, OH, O, and N in He were 0.72, 0.79, 0.92, and 0.92 atm cm² s⁻¹, respectively, and for OH in Ar was 0.20 atm cm² s⁻¹. Corrections for axial diffusion, in the brackets in eq 5, were in general <2% but, for experiments at pressures less than 2 torr, could be as large as 5%.

Results and Discussion

 $O + OH \rightarrow H + O_2$. This reaction was studied by simultaneously following the decay of OH and the production of H in the presence of excess O atoms. The hydroxyl source was CF₄ discharged in helium and added to water; the O source was either O₂ discharged in helium or N₂ discharged in helium and added to a slight excess of NO. With O added through the movable probe and OH formed in the upstream side arm or through the second movable injector, the OH decays displayed curvature at long reaction times for both O sources. It appears that OH was being regenerated by reactions of H atoms with either ozone or nitrogen dioxide produced in the movable injector, where the molecular densities are over 20 times greater than in the flow tube, by the three-body reactions:

$$O_2 + O + M \rightarrow O_3 + M \tag{6}$$

$$NO + O + M \rightarrow NO_2 + M \tag{7}$$

When O atoms were formed in an upstream 1/2 in. diameter side arm and OH was added through the movable injector, these interfering reactions were eliminated and curvature in the decay plots was minimized. For this reason, reaction 1 was studied with the excess reactant, O, added upstream and the OH added through the movable injector, thus making the observed first-order decay dependent on both O and OH wall loss. The wall loss of

⁽¹¹⁾ Howard, C. J. J. Phys. Chem. 1979, 83, 3.

Oxygen-Nitrogen-Hydrogen Free Radical Kinetics

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	TABLE III: $O + OH \rightarrow$	$H + O_2$ Summary ^a
no. of experiments35press. range1.0-3.0 torr at $T = 300$ Kflow velocity range12.5-14.4 m s ⁻¹ carrier gas(es)He, Arspecies detectedOH (LMR, RF), O (RF, RA), H (RF)reactant in excessO atomsO concn $(0.85-7.80) \times 10^{12}$ cm ⁻³ OH concn $(1-3) \times 10^{11}$ cm ⁻³ , initial $[O]/[OH]_i^c$ $4-75$ wall coatingTeflonfirst-order wall removalOH, $k_w^{OH} \leq 5 s^{-1}$; O, H, $k_w^{atoms} \leq 1 s^{-1}$ corrections to observed1. axial diffusion (0-3%)first-order rate $(0.5 \pm 0.02) \times [O]_{measured}$ constantsOH wall loss, $k_w \leq 5 s^{-1}$ 4. residual OH signal with only O atoms in the flow, $[OH] \sim (0.5-3.0) \times 10^9$ cm ⁻³ rate constants reported by others1. $(3.1 \pm 0.8) \times 10^{-11}$ cm ³	k_1^{b}	$(3.1 \pm 0.5) \times 10^{-11} \text{ cm}^3$ molecule ⁻¹ s ⁻¹
$\begin{array}{llllllllllllllllllllllllllllllllllll$	no. of experiments	35
flow velocity range carrier gas(es) flow velocity ra	press. range	1.0-3.0 torr at $T = 300$ K
$\begin{array}{lll} \mbox{carrier gas(es)} & \mbox{He, Ar} \\ \mbox{species detected} & \mbox{OH (LMR, RF), O (RF, RA), H (RF)} \\ \mbox{carrier gas(es)} & \mbox{OH (concn} & \mbox{OH concn} & \mbox{(0.85-7.80)} \times 10^{12} \mbox{ cm}^{-3} \\ \mbox{OH concn} & \mbox{(1-3)} \times 10^{11} \mbox{ cm}^{-3}, \mbox{initial} \\ \mbox{[O]/[OH]}_1^C & \mbox{4-75} \\ \mbox{wall coating} & \mbox{Teflon} \\ \mbox{first-order wall removal} & \mbox{OH, } k_w^{\mbox{OH}} \lesssim 5 \mbox{ s}^{-1}; \mbox{O, H}, \\ \mbox{wall oss, for sector s to observed} \\ \mbox{first-order rate} & \mbox{constants} & \mbox{OH wall loss, } [O] = \\ \mbox{(1.05 \pm 0.02)} \times \mbox{[O]}_{\mbox{measured}} \\ \mbox{a. OH wall loss, } k_w \lesssim 5 \mbox{ s}^{-1} \\ \mbox{4. residual OH signal with} \\ \mbox{only O atoms in the flow,} \\ \mbox{[OH]} \sim (0.5 - 3.0) \times 10^9 \mbox{ cm}^{-3} \\ \mbox{1. (3.1 \pm 0.8)} \times 10^{-11} \mbox{ cm}^{-3} \\ \mbox{a. (3.5 \pm 0.4)} \times 10^{-11} \mbox{ cm}^{3} \end{array}$	flow velocity range	12.5–14.4 m s ⁻¹
$\begin{array}{llllllllllllllllllllllllllllllllllll$	carrier gas(es)	He, Ar
reactant in excess O concnO atomsO concn (OH concn [O]/[OH]_1^c 	species detected	OH (LMR, RF), O (RF, RA), H (RF)
$ \begin{array}{lll} & (0.85-7.80)\times 10^{12}\ {\rm cm}^{-3} \\ & (1-3)\times 10^{11}\ {\rm cm}^{-3}, \mbox{ initial} \\ & [O]/[OH]_{\rm i}{}^{\rm c} \\ & wall coating \\ & first-order wall removal \\ & rate \\ & corrections to observed \\ & first-order rate \\ & constants \\ & \mbox{ constants } \\ & rate \mbox{ constants } \\ & rate \mbox{ constants } \\ & rate \mbox{ constants reported } \\ & by \mbox{ others } \\ & by \mbox{ others } \\ & \mbox{ constant } \\ & const$	reactant in excess	O atoms
$ \begin{array}{lll} & (1-3)\times 10^{i1}\ {\rm cm}^{-3}, \mbox{ initial} \\ & [O]/[OH]_{i}{}^{c} & 4-75 \\ & \mbox{wall coating} & \mbox{Teflon} \\ & \mbox{first-order wall removal} & \mbox{OH} \lesssim 5\ {\rm s}^{-1}; \mbox{O}, \mbox{H}, \\ & \mbox{tw}^{\rm atoms} \lesssim 1\ {\rm s}^{-1} \\ & \mbox{corrections to observed} \\ & \mbox{first-order rate} \\ & \mbox{constants} & \mbox{constants} \\ & \mbox{constants} & \mbox{OH} \lesssim 5\ {\rm s}^{-1}; \mbox{O}, \mbox{H}, \\ & \mbox{tw}^{\rm atoms} \lesssim 1\ {\rm s}^{-1} \\ & \mbox{1. axial diffusion} (0-3\%) \\ & \mbox{2. O wall loss, } [O] = \\ & \mbox{(1.05 \pm 0.02)} \times [O]_{\rm measured} \\ & \mbox{3. OH wall loss, } k_{\rm w} \lesssim 5\ {\rm s}^{-1} \\ & \mbox{4. residual OH signal with} \\ & \mbox{only O atoms in the flow,} \\ & \mbox{[OH]} \sim (0.5-3.0) \times 10^9\ {\rm cm}^{-3} \\ & \mbox{1. (3.1 \pm 0.8)} \times 10^{-11}\ {\rm cm}^3 \\ & \mbox{2. (3.5 \pm 0.4)} \times 10^{-11}\ {\rm cm}^3 \\ \end{array} $	O concn	$(0.85-7.80) \times 10^{12} \text{ cm}^{-3}$
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	OH concn	$(1-3) \times 10^{11} \text{ cm}^{-3}$, initial
wall coating first-order wall removal rate corrections to observed 	[O]/[OH] _i ^c	4 -75
$ \begin{array}{lll} \mbox{first-order wall removal} & \mbox{OH}, \ k_w^{\rm OH} \lesssim 5 \ {\rm s}^{-1}; \ {\rm O}, \ {\rm H}, \\ \ k_w^{\rm atoms} \lesssim 1 \ {\rm s}^{-1} \\ \ {\rm corrections to observed} \\ \ {\rm first-order rate} \\ \ {\rm constants} & \ {\rm COM} \\ \ {\rm scale observed} \\ \$	wall coating	Teflon
rate $k_w^{atoms} \leq 1 s^{-1}$ corrections to observed1. axial diffusion (0-3%)first-order rate2. O wall loss, $[O] =$ constants $(1.05 \pm 0.02) \times [O]_{measured}$ 3. OH wall loss, $k_w \leq 5 s^{-1}$ 4. residual OH signal withonly O atoms in the flow, $[OH] \sim (0.5-3.0) \times 10^9 \text{ cm}^{-3}$ 1. $(3.1 \pm 0.8) \times 10^{-11} \text{ cm}^3$ 2. $(3.5 \pm 0.4) \times 10^{-11} \text{ cm}^3$	first-order wall removal	OH, $k_w^{OH} \lesssim 5 \text{ s}^{-1}$; O, H,
molecule ⁻¹ s ⁻¹ , ref 4 3. earlier studies discussed in ref 3 and 4	rate corrections to observed first-order rate constants rate constants reported by others	bill, $k_w \gtrsim 5.5 \text{ s}^{-1}$ 1. axial diffusion (0-3%) 2. O wall loss, $[O] =$ (1.05 ± 0.02) × $[O]_{\text{measured}}$ 3. OH wall loss, $k_w \lesssim 5.5^{-1}$ 4. residual OH signal with only O atoms in the flow, $[OH] \sim (0.5-3.0) \times 10^9 \text{ cm}^{-3}$ 1. $(3.1 \pm 0.8) \times 10^{-11} \text{ cm}^3$ molecule ⁻¹ s ⁻¹ , ref 3 2. $(3.5 \pm 0.4) \times 10^{-11} \text{ cm}^3$ molecule ⁻¹ s ⁻¹ , ref 4 3. earlier studies discussed in ref 3 and 4

ref 3 and 4 ^a The bimolecular rate constant is independent of pressure, carrier gas, O source, OH detection method, initial OH and O concentrations, initial stoichiometric ratio, and flow tube diameter to within ±10%. ^b Reported rate con-

stant. ^c Initial reaction stoichiometric ratio.

O atoms $(k^0_{wall} \leq 1 \text{ s}^{-1})$ consistently decreased the O concentrations between the absorption axis and the center of the reaction zone by $5 \pm 2\%$, so that [O] determined by absorption was multiplied by 1.05 ± 0.02 to give [O] in the reaction zone. The OH wall loss was small ($\leq 5 \text{ s}^{-1}$) and invariant for a set of runs and was subtracted from the first-order rate constant as in eq 5. In support of this method of rate constant determination, the bimolecular rate constants obtained for reactions 2 and 3 were the same regardless of whether the excess atoms were added in the upstream side arm or through the movable injector.

With only the O atoms source on, OH signal was still observed in the LMR axis and to a much lesser extent in the RF axis, and was probably caused by OH production from O atom reactions with certain surfaces. The LMR signal was equivalent to an OH concentration of (0.5-3.0) $\times 10^9$ cm⁻³ and could be diminished but not eliminated by adding a buffer gas, either Ar or He, to the laser tube. No residual OH signal was seen when N was substituted for O; no residual HO₂ signal was seen for any reaction. Also, for O added through a movable injector, all positions of the injector produced approximately the same signal, indicating that OH was generated inside the laser tube and to a lesser extent in the RF axis. Oxygen atom reactions on surfaces are believed to be a source of OH because the OH signal was greatly reduced (to the levels listed above) when some polypropylene and Delrin far-IR laser parts were replaced with Teflon ones. Decay plots which showed some curvature in the second decade of decay displayed none when this residual signal was subtracted. In any case, the first-order decay rate was increased by less than \sim 5-10% by the subtraction.

The experimental conditions are shown in Table III, the summary of important parameters for reaction 1. The 35 experiments were performed in either helium or argon at 1.0, 2.0, or 3.0 torr to test for effects of mixing and three-body reactions. Oxygen atom concentrations were



Figure 4. Pseudo-first-order decays of OH for reaction 1. Numbers are oxygen atom concentrations in units of 10^{12} cm⁻³.



Figure 5. Plot of k_{obsd}^{I} against [O] for O + OH reaction. Closed circles are data taken with LMR; open circles are data taken with RF.

varied almost a factor of 10 and the initial stoichiometric ratio was varied almost a factor of 20. Typical decays are shown in Figure 4. Since the OH wall loss contributes to the decay, it was subtracted from the first-order decay rate obtained by a linear least-squares fit to the OH signal.

A plot of the first-order decay rate vs. the oxygen atom concentration is given in Figure 5. Linear least-squares fits to these data were performed by using two weighting functions which represent the extremes in the type of dependence on $k^{\rm I}_{\rm obsd}$ that the uncertainty of a single measurement might have (see, for example, Cvetanović et al.¹²). Some random errors contributing to the uncertainty of a single measurement of $k^{\rm I}_{\rm obsd}$ are independent of $k^{\rm I}_{\rm obsd}$, such as errors in the wall loss. Other random errors contributing to the uncertainty are directly dependent on $k^{\rm I}_{\rm obsd}$, such as errors in the [O] absorption measurement, carrier gas flow rate and pressure, and slope of the decay curve. For the first weighting function, the bimolecular rate constant, k_1 , and intercept are $(3.05 \pm 0.14) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and -0.5 ± 6 s⁻¹, where the uncertainty is at the 95% confidence limits; for the second, they are $(3.03 \pm 0.14) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and -0.6 ± 6 s⁻¹.

⁽¹²⁾ Cvetanović, R. J.; Singleton, D. L.; Paraskevopoulos, G. J. Phys. Chem. 1979, 83, 50.

The small intercept indicates no other interfering reactions. The average value of the first-order rate constants divided by the corresponding oxygen concentrations is $k_1 = (3.03 \pm 0.38) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, where again the uncertainty is at the 95% uncertainty limits. The statistical uncertainty, $\pm 5-13\%$, is comparable to the estimated uncertainty of a single measurement, $\pm 15\%$, which includes errors in carrier gas flow rate ($\pm 2\%$), temperature ($\pm 1\%$), pressure ($\pm 2\%$), slope of the decay plot ($\pm 8\%$), and excess reactant ($\pm 10-14\%$, depending on the excess reactant). Examination of uncertainty in calibration procedures for the flowmeters, pressure transducers, and flow tube diameter gives an additional error of $\pm 5-10\%$. Including systematic and random errors, the bimolecular rate constant for reaction 1 is

 $k_1 = (3.1 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

To within $\pm 10\%$, the rate constant is independent of pressure, carrier gas, O source, OH detection, initial OH and O concentration, initial stoichiometric ratio, and flow tube diameter.

Two other recent direct measurements are in agreement with the result: Lewis and Watson³ obtained (3.1 ± 0.8) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹; and Howard and Smith,⁴ (3.5 \pm 0.4) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Other indirect or earlier measurements presented in the paper by Lewis and Watson are, in general, also consistent with our result. The Lewis and Watson experiment used discharge flow and resonance fluorescence detection of OH, with NO_2 added to a large excess of H as the OH source in the presence of excess O atoms. Our observation of a residual OH concentration might explain the negative intercept in their k vs. [O] plot, where k is determined with a ratio of the fluorescence signal with no O present to that when O is present: OH wall loss does not decrease, but rather, the OH signal is enhanced in the presence of O inside the detection axis. Since it is observed that large O concentrations produce smaller residual signals, the k^{I}_{obed} for lower values of [O] are reduced by the greatest factor, resulting in a slight negative intercept.

Howard and Smith used a slow discharge flow of excess atom radicals in conjunction with flash photolysis of water vapor to study reactions 1 and 3. The decay of the hydroxyl radical was monitored by resonance fluorescence of the $A^2\Sigma^+-X^2\Pi$ (0,0) transition. N and O atom concentrations were determined by titration with a known NO concentration until NO, N₂*, and NO₂ visible chemiluminescent signals were all extinguished, and all N atoms were converted to O. Atom concentrations were usually greater than 10¹³ cm⁻³ and OH concentrations were kept between 1 × 10¹¹ and 3 × 10¹² cm⁻³, ensuring an adequate stoichiometric ratio and minimum interfering reactions.

Concentrations derived from absolutely calibrated signals of OH decay and H production were compared with a computer model for five experiments in order to assess radical hydrogen (HO_x = H + OH) continuity. The computer reaction scheme included 51 reactions listed in Table VII. A typical comparison is shown in Figure 6, where the circles are OH data, triangles H, and the solid lines are the results of computer simulations. The absolute time scale for the reaction was determined by measuring the change in OH with the O source on and off at the shortest reaction time when the data were taken and then using the measured first-order decay rate to give the effective time of reaction to that point. By monitoring the decay of the appropriate radicals, we measured the absolute time scales for each axis. The upper and lower hydrogen production curves are the results of simulations in which the rate constant for reaction 1 has been changed to 4.5×10^{-11} and



Figure 6. Comparison between observations and computer simulations for O + OH. Conditions: $[O] = 1.8 \times 10^{12} \text{ cm}^{-3}$, $[OH] = 1.2 \times 10^{11} \text{ cm}^{-3}$. Computer-generated H production curves show effect of different rate constants for the O + OH reaction.

 2.0×10^{-11} cm³ molecule⁻¹ s⁻¹, respectively. They are provided only as a guide for the differences in curvature which would result from a slower or faster rate constant. For five experiments, the data and simulated results are in reasonable agreement, although the observed hydrogen concentrations for all reaction times greater than ~10-20 ms were in general 5-30% higher than predicted by simulation. This effect was consistently evident when O atoms were in excess over H, OH, or HO₂, and for both sources of O atoms. One possible explanation, that O atoms react with surfaces to form OH, and then react with the OH to form H, is consistent with the observed formation of OH in the presence of large O atom concentrations mentioned previously.

 $O + HO_2 \rightarrow OH + O_2$. This reaction of oxygen atoms and the hydroperoxyl radical was studied primarily with O atoms in excess, because of the greater range of O atom concentrations easily available and the small oxygen heterogeneous and disproportionation losses. For 20 experiments, HO₂ was in excess and the O atom decay was monitored with resonance fluorescence. The O source was O₂ discharged in helium. The ranges of parameters are summarized in Table IV. It is important to note the limitations on the hydrogen peroxide concentration, since the reaction

$$H_2O_2 + OH \rightarrow HO_2 + H_2O$$

 $k_8 = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
(8)

is the predominant pathway for regeneration of HO₂ radicals. Computer simulations show that H₂O₂ concentrations as little as 5×10^{12} cm⁻³ can have a large (>20%) effect on the inferred rate constant measured with oxygen atom concentrations $\sim (2-5) \times 10^{12}$ cm⁻³. However, for [H₂O₂] $\leq 2 \times 10^{12}$ cm⁻³, the inferred rate constant is decreased less than a few percent for all oxygen atom concentrations. For the range of initial HO₂ concentrations, this decrease in the rate constant is offset by the slight increase due to the reactions

k

$$OH + HO_2 \rightarrow H_2O + O_2$$

$$v_9 \sim 7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(9)

$$H + HO_2 \rightarrow \text{products}$$

$$k_{10} \sim 7.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(10)

TABLE IV: $O + HO_2 \rightarrow$	$OH + O_2$ Summary ^a
$\overline{k_2^{b}}$	$(5.2 \pm 0.8) \times 10^{-11} \text{ cm}^3$ molecule ⁻¹ s ⁻¹
no, of experiments	51
press, range	1.0-4.0 torr at $T = 300$ K
flow velocity range	$11.8-14.6 \text{ m s}^{-1}$
carrier gas(es)	He
species detected	HO, (LMR, chemical
•	conversion to OH, RF),
	OH (LMR, RF), Ó (RÉ,
	RA), $H(RF)$
reactant in excess	O atoms (31 experiments),
	HO, (20 experiments)
O concn	$(0.49-4.40) \times 10^{12} \text{ cm}^{-3}$
	in excess; $(0.6-1.0) \times$
	10 ¹¹ cm ⁻³ initial, in decay
HO, concn	$(0.62-3.50) \times 10^{12} \text{ cm}^{-3}$
*	in excess; $(0.5-1.6) \times$
	10 ¹¹ cm ⁻³ initial, in decay
[O]/[HO₂]i ^c	4-40
[HO ₂]/[O] ^c	5-40
wall coating	Teflon
first-order wall removal	$HO_2, k_w HO_2 \lesssim 4 s^{-1}; OH,$
rate	$k_{\rm w}^{-\rm OH} \lesssim 5 {\rm s}^{-1}$; H, O,
	$k_{}^{atoms} \lesssim 1 \text{ s}^{-1}$
corrections to observed	1. $axial diffusion (0-3\%)$
first-order rates	2. HO, probe or wall loss,
	$k \lesssim 4 \mathrm{s}^{-1}$
	3. O atom wall loss, $[O] =$
	$(1.05 \pm 0.02) \times [O]_{measured}$
	(for 17 experiments with O
	added in a back port)
rate constants reported	1. $(6.1 \pm 0.4) \times 10^{-11} \text{ cm}^3$
by others	molecule ⁻¹ s ⁻¹ , ref 5
	2. $(5.4 \pm 0.9) \times 10^{-11} \text{ cm}^3$
	$molecule^{-1} s^{-1}$, ref 6
	3. other results reported in
	ref 5 and 6

^a The bimolecular rate constant is independent of pressure, reactant in excess, whether excess O is added in the upstream side arm or movable injector, initial O and HO₂ concentrations, initial stoichiometric ratio, and flow tube diameter to within $\pm 10\%$. The rate constant measured with HO₂ in excess is 2% lower than that measured with O in excess. ^b Reported rate constant. ^c Initial reaction stoichiometric ratio.

It should be stressed that these effects on the measured rate constant are at most a few percent. The measured bimolecular rate constant showed no systematic change when the initial HO₂ concentration was varied from $0.5 \times$ 10^{11} to 1.6×10^{11} cm⁻³ or H₂O₂ concentration was varied from 1×10^{12} to 2×10^{12} cm⁻³.

The conditions for reactions with HO_2 in excess are as follows: pressure = 2.0 torr; flow velocity = 15 m s^{-1} ; [O] = $6 \times 10^{10} \text{ cm}^{-3}$; [HO₂]₀ = (0.62-3.50) × 10^{12} cm^{-3} ; [H₂O] $= \sim 10^{13} \text{ cm}^{-3}$; $[OH]_0 = (0.5-2) \times 10^{10} \text{ cm}^{-3}$. The HO₂ concentration was calibrated by conversion to OH with $\sim 10^{14}$ cm⁻³ of NO, as described previously in the experiment detection section. The HO_2 concentration was measured at the extremes of the O decays and averaged, with the change in $[HO_2]$ being ~15-30%. The faster decays were followed over a factor of 10, with the slowest followed over a factor of 3.

The observed first order rates are plotted against excess reactant concentration in Figure 7. The bimolecular rate constant and the intercept derived from a least-squares fit with the weight of uncertainty independent of k_{obsd}^{I} , with 95% confidence limits, are $(5.20 \pm 0.13) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and -0.6 ± 2.6 s⁻¹ and, for the fit with weights of uncertainty directly dependent on $k_{\text{obsd}}^{\text{I}}$, are (5.06 ± $(0.13) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } 0.9 \pm 2.6 \text{ s}^{-1}$. The average value of k_{obsd}^{I} /[excess reactant] is $(5.18 \pm 0.31) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The 31 experiments with O in



Figure 7. Plot of k^{I}_{obed} against [O] or [HO₂] for the O + HO₂ reaction. Closed circles are data taken with O in excess; open circles are data taken with HO₂ in excess.



Figure 8. Comparison between observations and computer simulations for O + HO₂. Conditions: $[O] = 1.45 \times 10^{12} \text{ cm}^{-3}$, $[HO_2]_i = 1.2 \times 10^{11} \text{ cm}^{-3}$, $[OH]_i = 6 \times 10^{10} \text{ cm}^{-3}$; $[H_2O_2] \lesssim 1.5 \times 10^{12} \text{ cm}^{-3}$. Closed circles are HO₂ data; open circles, OH data taken with LMR; crosses, OH data taken with RF; triangles, H data.

excess give the same results as all 51 experiments to within $\pm 1\%$, and the 20 experiments with HO₂ in excess give rate constants slower by 1-4%. The rate constants derived from individual sets of data show that, to within $\pm 10\%$, the results are independent of carrier gas pressure, reactant in excess, whether excess O was added through the upstream side arm or the movable injector, initial HO_2 and O concentrations, initial stoichiometric ratio, and flow tube diameter. With the same possible systematic errors as for reaction 1, the rate constant and uncertainty at the 95% confidence limits is

$$k_2 = (5.2 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This number is lower than, but in agreement with, the recently published values of Sridharan et al.⁶ ($k_2 = (5.4 \pm$ $(0.9) \times 10^{-11} \text{ cm}^3$ and Keyser⁵ $(k_2 = (6.1 \pm 0.4) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹). Both of these followed, with resonance fluorescence, the decay of O atoms in excess HO₂. Other measurements discussed in these two papers either were indirect or relied on other rate constants and will not be recited here.

TABLE V: $N + OH \rightarrow H + NO$ Summary^a

$\overline{k_3}^b$	$(4.2 \pm 0.8) \times 10^{-11} \text{ cm}^3$
	molecule 's '
no. of experiments	32
press. range	1.0-5.0 torr at T = 300 K
flow velocity range	$12.4-14.7 \text{ m s}^{-1}$
carrier gas(es)	Не
species detected	OH(LMR, RF), O(RF),
	N (chemical conversiion
	to O, RA), H (RF)
reactant in excess	N atoms
N concn	$(0.50-5.52) \times 10^{12} \text{ cm}^{-3}$
OH concn	$(1.0-2.7) \times 10^{11} \text{ cm}^{-3}$, initial
$[N]/[OH]_c$	5-30
wall coating	Teflon
first-order wall removal	OH, $k_w^{OH} \lesssim 7 \text{ s}^{-1}$; N, O, H,
rate	$k_{\rm w}^{\rm atoms} \lesssim 7 { m s}^{-1}$
corrections to observed	1. $axial diffusion (0-5\%)$
first-order rates	2. OH probe or wall loss,
	$k \lesssim 7 \mathrm{s}^{-1}$
rate constants reported	$(4.7 \pm 0.44) \times 10^{-11} \text{ cm}^3$
by others	$molecule^{-1} s^{-1}$, ref 4

^a The bimolecular rate constant is independent of pressure, OH detection method, initial N and OH concentration, initial stoichiometric ratio, and flow tube diameter to within $\pm 10\%$. The ratio of the reported rate constants for reactions 1 and 3 k_3/k_1 , is 1.4 ± 0.2 , in agreement with 1.4 ± 0.1^{13} and 1.4 ± 0.3 .⁴ ^b Reported rate constant. ^c Initial reaction stoichiometric ratio.

An example of the comparison between experimental data and computer simulations is given in Figure 8. The $[HO_2]$ was followed with LMR, [OH] with both LMR and RF, and [H] with RF. Agreement for HO₂, OH, and H are reasonable, but observed [H] was again 5–30% higher than computer predictions for the seven experiments in which excess O, HO₂, OH, and H were measured. The possible role of the large amount of O atoms reacting with surfaces or excited species to form H atoms cannot, unfortunately, be tested by experiments with excess HO₂ because the H atoms formed in the reaction rapidly react with the HO₂ and are removed.

 $N + OH \rightarrow H + NO$. For this reaction, the pseudofirst-order decay of OH was followed in the presence of excess nitrogen atoms produced in a microwave discharge. Nitrogen atom concentrations were calibrated by converting N to O atoms with excess NO ($\sim 1 \times 10^{14}$ cm⁻³) 4–6 ms before the O absorption axis which had been previously calibrated. Computer simulations and tests involving nitrogen atom resonance fluorescence and oxygen atom absorption show that the N-to-O conversion efficiency is 0.99 ± 0.01 and that no corrections are needed. Experimental conditions for the 32 experiments are given in Table V. The hydroxyl signal was observed over at least a factor of 10 for the faster decays in a set of experiments. First-order rate constants were taken as the linear leastsquares fit to these data, corrected for axial diffusion $(\leq 5\%)$ and for OH wall or probe loss.

A linear least-squares fit to the plot of the observed first-order rate, k_{obed}^{I} , against the nitrogen concentration shown in Figure 9 gives a bimolecular rate constant, k_3 , of $(3.96 \pm 0.22) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and an intercept of 4.4 ± 5.6 s⁻¹ for data weighted with uncertainty independent of k_{obed}^{I} . For data weighted with the uncertainty of each point proportional to k_{obed}^{I} , k_3 and the slope and intercept are $(4.15 \pm 0.22) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and -0.2 ± 5.6 s⁻¹, respectively. The average value of k_{obed}^{I} [N] is $(4.22 \pm 0.78) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ where all uncertainties are at the 95% confidence level. The bimolecular rate constant is independent to within $\pm 10\%$ of pressure, initial OH and N concentrations, detection with either LMR or RF, initial stoichiometric ratio, and flow



Figure 9. Plot of k^{I}_{obsd} against [N] for the N + OH reaction. Closed circles are data taken with LMR; open circles are data taken with RF.

tube diameter. Our data represent a bimolecular rate constant of

 $k_3 = (4.2 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Howard and Smith⁴ made the only other direct measurement of this rate constant by following the decay of OH, produced by flash photolysis of water vapor in the presence of a large excess of N, as described for reaction 1. Their room-temperature rate constant is (4.74 ± 0.44) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ where the error is statistical uncertainty at the 95% confidence limit. The only other study, a relative rate measurement by Campbell and Thrush,¹³ yielded a ratio for the rate constants k_3/k_1 of 1.4 ± 0.1 , in agreement with the ratios 1.4 ± 0.3 for Howard and Smith, and 1.4 ± 0.2 from this study. Our results for k_1 and k_3 are in reasonable agreement with those of Howard and Smith, although our lower values for both reactions suggest a small systematic difference between their measurements and ours. In a test for systematic errors in our system, recent measurements of the reaction of O with NO₂ gave a bimolecular rate constant of 9.6 \times 10^{-12} cm³ molecule⁻¹ s⁻¹, in excellent agreement with the currently accepted value, 9.3×10^{-12} cm³ molecule⁻¹ s⁻¹. The agreement between the experimental data for OH and H and the computer simulations for six experiments is within $\pm 10\%$ for OH, H, and total H, and no comparisons are shown.

 $N + HO_2 \rightarrow Products$. Four exothermic reaction channels exist for this reaction. Experiments had N in excess and followed the pseudo-first-order decay of HO_2 with LMR. The source of N was a N₂ and He discharge; the source of HO₂ was CF₄ discharged to produce F atoms which then were reacted with hydrogen peroxide to give HO₂. The conditions for the experiments are shown in Table VI. Decays were followed over at least a factor of 10 for each set of conditions and were treated as described earlier. Figure 10 shows the first-order rate, k^{I}_{obed} , plotted against [N] for the 25 experiments. Again, no trend was discovered in variation of either pressure, initial HO₂ or N concentration, initial stoichiometric ratio, or flow tube diameter.

The slope and the intercept, quoted with 95% uncertainty limits, for weights of uncertainty proportional to k^{I}_{obsd} are $(2.06 \pm 0.13) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and 5.6 ± 5.0 s⁻¹ and for weights of uncertainty independent of k^{I}_{obsd} are $(2.06 \pm 0.13) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and 4.7

⁽¹³⁾ Campbell, I. M.; Thrush, B. A. Trans. Faraday Soc. 1968, 64, 1265.

TABLE VI: $N + HO_2 \rightarrow Products Symmary^a$

-	
k ^b	$(2.2 \pm 0.5) \times 10^{-11} \text{ cm}^3$
	molecule s
no. of experiments	25
press. range	1.0-4.0 torr at $T = 300$ K
flow velocity range	12.4–14.7 m s ⁻¹
carrier gas(es)	He
species detected	HO, (LMR), OH (LMR, RF).
-p	N (chemical conversion to
	O(BA) O(BF) H(BF)
	$\mathbf{N}\mathbf{U}$ (TMP)
	N stand
reactant in excess	IN atoms
N concn	$(0.88-7.66) \times 10^{12} \text{ cm}^{-3}$
HO ₂ concn	$(1.0-2.0) \times 10^{11} \text{ cm}^{-3}$, initial
$[N]/[HO_2]_i^c$	6-65
wall coating	Teflon
first-order wall removal	HO ₁ , $k_{\rm m}$ ^{HO₂} $\lesssim 4 {\rm s}^{-1}$; OH.
rate	k_{0}^{0} OH $\leq 7 \mathrm{s}^{-1}$: O H N
1400	$h_{W} \approx 10^{\circ}$, $0, 10, 10$
	R_{w} atoms $\gtrsim 3 \text{ s}^{-1}$; NH,
	$k_{w}^{NH} \lesssim 3 \text{ s}^{-1}$
corrections to observed	1. axial diffusion (0-3%)
first-order rates	2. HO, probe or wall loss.
	$k \leq 3 \hat{s}^{-1}$
rate constants reported	no other known studies
by others	no outer And wit blutteb

^a The bimolecular rate constant is independent of pressure, initial N and HO₂ concentrations, initial stoichiometric ratio, and flow tube diameter to within $\pm 10\%$. ^b Reported rate constant. ^c Initial reaction stoichiometric ratio.



Figure 10. Plot of k^{I}_{obsd} against [N] for the N + HO₂ reaction.

 \pm 5.0 s⁻¹. These small intercepts show that no important secondary or simultaneous reactions are occurring. The average of $k_{obsd}^{I}/[N]$ is (2.26 \pm 0.50) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, slightly larger than either slope. Including systematic error, our data give

$$k_{\star} = (2.2 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This rate constant has not been measured directly before. The reaction may play a role in high-temperature combustion but, at 300 K, there are few processes which involve free nitrogen atoms. It is, however, another example of atom-HO₂ reactions, of which $O_{,5,6}^{5,6}$ H,⁶ and Cl¹⁴ have also now been directly measured. The question of whether these reactions proceed in part by atom attack on the hydrogen end of the HO₂ molecule or only by rearrangement of a complex with the atom attacking the oxygen end has not been resolved.^{6,14}

TABLE VII: Reactions Used in Computer Simulations

bimolecular reactions	rate constants, ^{<i>a</i>} cm^3 molecule ⁻¹ s ⁻¹
$O + OH \rightarrow H + O$	$3.1 \times 10^{-11} b$
$0 + H0 \rightarrow 0H \pm 0$	5 2 × 10-11 b
$\mathbf{O} + \mathbf{IO}_2 \rightarrow \mathbf{OII} + \mathbf{O}_2$ $\mathbf{N} + \mathbf{OH} \rightarrow \mathbf{H} + \mathbf{NO}$	$4.9 \times 10^{-11} b$
$N + U n \rightarrow n + N U$	4.4 × 10 ····
$N + HO_2 \rightarrow \text{products}$	2.2×10^{-110}
$H + HO_2 \rightarrow OH + OH$	6.4×10^{-11}
$H + HO_2 \rightarrow H_2O + O$	$3.0 \times 10^{-12} c$
$H + HO_2 \rightarrow H_2 + O_2$	$7.0 \times 10^{-12} c$
$OH + HO_2 \rightarrow H_2O + O_3$	7.0×10^{-11}
$OH + OH \rightarrow HO + O$	1.9×10^{-12}
$HO_1 + HO_2 \rightarrow H_1O_2 + O_2$	1.6×10^{-12}
$H + NO \rightarrow OH + NO$	1.3×10^{-10}
$F + H O \rightarrow OH + HF$	1.0×10^{-11}
$F \perp H \perp H \perp UF$	2 8 V 10-11
$F + \Omega H \rightarrow \Omega + \Pi F$	4.0×10 1 0 \vee 1 0-12 d
$\mathbf{F} + \mathbf{U}\mathbf{\Pi} \rightarrow \mathbf{U} + \mathbf{\Pi}\mathbf{F}$	1.0×10^{-10}
$r + n_2 U_2 \rightarrow n U_2 + h r$	2.0 X 10 ***
$\mathbf{F} + \mathbf{HO}_2 \rightarrow \mathbf{HF} + \mathbf{O}_2$	1.0×10^{-11}
$N + NO \rightarrow N_2 + O$	3.4×10^{-11}
$N + NO_2 \rightarrow N_2O + O$	1.4×10^{-12}
$O + NO_2 \rightarrow O_2 + NO$	9.3×10^{-12}
$HO_1 + NO \rightarrow OH + NO_2$	$8.3 imes 10^{-12}$
$H + O_{a} \rightarrow OH + O_{a}$	2.9×10^{-11}
$OH + O_{A} \rightarrow HO_{A} + O_{A}$	6.8×10^{-14}
HO, $+$ O, \rightarrow OH + 2O	2.0×10^{-15}
$OH + H \rightarrow H O + H$	67×10^{-15}
OH + HONO = UO + NO	1.2×10^{-13}
OH + HO + HO + HO = HO + HO = HO = HO =	1.0×10^{-1}
$O_1 + \Pi_2 O_2 \rightarrow \Pi O_2 + \Pi_2 O_2$	1.7 X 10 **
$O + H_2O_2 \rightarrow OH + HO_2$	2.3×10^{-13}
$H + H_2O_2 \rightarrow OH + H_2O$	1.5×10^{-14}
$H + H_2O_2 \rightarrow HO_2 + H_2$	3.0×10^{-14}
$NH + NO \rightarrow N_2 + OH$	4.7×10^{-11}
$N + H_0 \to NH + HO_0$	$2.0 \times 10^{-15} d$
$N + NH \rightarrow NO + H$	$1.7 \times 10^{-11} e$
$O + NH \rightarrow NO + H$	$1.7 \times 10^{-11} e$
$NH + NH \rightarrow NH + N$	$5.7 \times 10^{-13} e$
$NH \perp OH \rightarrow N \perp H O$	5 0 × 10-12 e
	0.0 × 10
	rate constants, ^a
termolecular reactions	cm ⁶ molecule ⁻² s ⁻¹
OH INO IM JONO M	0 6 V 10-30
$OH + NO_2 + M \rightarrow HONO_2 + M$	2.0 X 10 -31
$OH + NO + M \rightarrow HONO + M$	6.7×10^{-31}
$HO_2 + NO_2 + M \rightarrow PNA + M$	2.3×10^{-31}
$H + O_2 + M \rightarrow HO_2 + M$	5.5×10^{-32}
$H + O + M \rightarrow OH + M$	2.0×10^{-31}
$H + OH + M \rightarrow H_2O + M$	1.6×10^{-31}
$O + O_2 + M \rightarrow O_2 + M$	6.0×10^{-34}
$N + O + M \rightarrow NO + M$	1.0×10^{-32}
$O + NO + M \rightarrow NO + M$	1.2×10^{-31}
$H + NO + M \rightarrow NOH + M$	3.0×10^{-32}
	rate con-
surface reactions	stants, s ⁻¹
$OH + wall \rightarrow x$	3-7
$H + wall \rightarrow x$	≲1
$O + wall \rightarrow x$	≲1
HO, $+$ wall $\rightarrow x$	2-5
$N + wall \rightarrow x$	$\leq \tilde{1}$
NH 1 wall -> v	~1_9
ANIE WAIL - A	1-0

^a All rate constants except those noted are taken from ref 2 and 16. ^b Measured in this work. ^c Taken from ref 6. ^d Estimated. ^e Taken from ref 17.

Attempts to determine the branching ratios into the four exothermic channels were frustrated by the rapid or unknown secondary reactions. Channels 4b and 4d yield the same observable intermediate and final products (O, H and OH), as might channel 4c, for which the rates of NHO reactions are not well-known. The first channel, 4a, has a distinct reaction product, NH, which can be monitored with LMR, but simple calibration procedures are unknown. A lower limit to the sensitivity was determined by adding NH₃ (10^{14} - 10^{15} cm⁻³) to a known amount of atomic fluorine ($\sim 10^{10}$ - 10^{12} cm⁻³), observing the NH LMR spectrum, and assuming that a minimum of two fluorine atoms are nec-

⁽¹⁴⁾ Lee, Y. P.; Howard, C. J. J. Chem. Phys. 1982, 77, 756.

essary to produce one NH molecule. The fluorine concentration was measured by turning off the NH₃, introducing water, and monitoring the OH signal. By this process, the largest amount of NH that can go undetected (S/N = 1) is 2×10^9 cm⁻³. No NH was detected in several experiments where $[HO_2]_i = (1-2) \times 10^{11}$ cm⁻³ and [N] = $(1-5) \times 10^{12}$ cm⁻³, but poor knowledge of NH reaction kinetics, and hence the NH removal rate, prevents us from placing a meaningful upper limit on the branching ratio into this channel.

The 4a reaction channel with NH(X³Σ⁻) and O₂(X²Σ_g⁻) products is expected to be negligible by electronic correlation rules if a coplanar collision complex is assumed. Reactants N(⁴S) and HO₂(²A'') adiabatically correlate to only the A'' term of the coplanar collision complex and products NH(X³Σ⁻) and O₂(X³Σ_g⁻) only to the A' term, so that no adiabatic surface exists for the reaction. If the energetically allowed O₂(a¹Δ_g) is a product, however, then an adiabatically correlated pathway exists from reactants to products via the ³A'' term.

A comparison between observations of HO₂, OH, and H and a computer simulation, assuming that the branching ratio for channel 4b is 1.0, shows all hydrogen-containing radicals to be in agreement with the simulation to within $\pm 10\%$. For seven experiments in which O was monitored along with HO₂ and OH, the observed O concentration at reaction times greater than ~ 20 ms was 50–70% of the simulation values. Oxygen atom concentrations measured by RF are subject to considerable uncertainty for this reaction because the N₂* chemiluminescent background signal was larger than the O resonance fluorescence signal. The subtraction of signals with the HO₂ source on and off does not account for possible altered chemical conditions and may not accurately determine the O concentration.

Conclusion

The new rate constants reported here, obtained with different detection and calibration techniques, confirm the results of other recent studied that, at 300 K, reaction 1 proceeds ~25% slower than previously believed, and reaction 2 proceeds ~60% more rapidly. The new ratio of the rate constants, $k_2/k_1 = 1.8$, is confirmed. The implications for atmospheric chemistry center on the upper stratosphere and lower mesosphere (40–90-km altitude) where oxygen atom concentrations are comparable to those of ozone and catalytic cycles involving reactions 1 and 2 are important mechanisms for the destruction of odd oxygen.¹⁵ Atmospheric model calculations of Ko and Sze⁷

and of Prather¹⁸ have shown that the new rate constants have four primary effects on the modeled atmosphere above 40 km: (a) The OH concentration is increased by a factor of 1.3 (and HO₂ is decreased); (b) the CH₄ concentration is decreased by 20% due to CH₄ reactions with increased OH; (c) the Cl and ClO concentrations are increased by a factor of 1.4 due to the reaction of HCl with increased OH; (d) the ozone concentration is decreased about 10% due to enhanced HO₂-catalyzed recombination of odd oxygen. Interestingly, the new model-determined ClO concentration near 40 km now agrees better with observations, both in altitude dependence and in absolute value, while the agreement for ozone is marginally worsened.

We are continuing our study of the hydrogen-oxygen, atom-small radical system with measurements of the rate constant and its temperature dependence for the reaction of OH with HO_2 , which is a major loss mechanism for odd hydrogen radicals throughout much of the stratosphere and mesosphere.

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Appendix

The 51 reactions and rate constants used in the computer simulations are listed in Table VII. Simulations were used to test the radical production sources, the conversion efficiency of calibrating reactions, and the effects of interfering reactions on the observed rate constants. Simulation results of reactions 1–4 were also compared to the observed time-dependent reactant and product concentrations.

Registry No. O, 17778-80-2; OH, 3352-57-6; HO₂, 3170-83-0; N, 17778-88-0.

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