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# Yields of HO<sub>2</sub> in the reaction of hydrogen atoms with ozone

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The reaction of hydrogen atoms with ozone is well known<sup>1</sup> to produce vibrationally excited hydroxyl radicals, OH<sup>†</sup>(X<sup>2</sup>Π<sub>i</sub>)<sub>v≤9</sub>, and O<sub>2</sub>:



Recently the yield of oxygen atoms O(<sup>3</sup>P) in this reaction was measured<sup>2</sup> using resonance fluorescence. In these studies<sup>2</sup> excess hydrogen atoms ( $[\text{H}]_0/[\text{O}_3]_0 \geq 4$ ,  $[\text{H}]_0 = 1 - 3 \times 10^{12}$  molecule cm<sup>-3</sup>)<sup>3</sup> were present in order to deactivate the vibrationally excited OH (OH<sup>†</sup>),<sup>2,4</sup> thus minimizing the possible contribution of its secondary reactions to the O(<sup>3</sup>P) yield. Additional tests for such processes were carried out by adding known quenchers of OH<sup>†</sup>,<sup>4-8</sup> which did not alter the O(<sup>3</sup>P) yield. Yields of ground state OH (OH<sub>0</sub>) were also measured by resonance fluorescence and found to be lower than expected if only Reaction (1a) followed by deactivation of the OH<sup>†</sup> to the ground state occurs. Finally, indirect evidence for HO<sub>2</sub> was obtained by observing an increase in the OH<sub>0</sub> yield upon addition of NO.

These results were most consistent with the existence of a second primary process, (1b),



which is spin-allowed and sufficiently exothermic (-21.6 kcal/mole) to produce HO<sub>2</sub> in either the (<sup>2</sup>A'') ground state or in the (<sup>2</sup>A') first electronically excited state. The O(<sup>3</sup>P) yields were consistent with ~20%-30% of the reaction proceeding via (1b), i.e., the branching ratio  $\alpha = k_{1a}/(k_{1a} + k_{1b}) \approx 0.2 - 0.3$ . Direct measurement of the HO<sub>2</sub> yields was desired, however, to support this interpretation. We report here the results of laser magnetic resonance (LMR) studies of the yields of HO<sub>2</sub> from the H+O<sub>3</sub> reaction at room temperature. These suggest that in contrast to the earlier resonance fluorescence studies, Reaction (1b) accounts for an upper limit of 3% of the net reaction.

Experiments were carried out using a fast-flow discharge system with LMR detection, described in detail elsewhere.<sup>9</sup> The one-inch diameter flow tube was coated with boric acid to deactivate<sup>4,8,10</sup> the OH<sup>†</sup> produced in (1a) as well as to minimize heterogeneous recombination of the ground state radicals and atoms. HO<sub>2</sub> (<sup>2</sup>A'') and OH<sub>0</sub> were directly detected<sup>11</sup> by LMR using the 118.6 μm line from a water vapor discharge laser. The ratio [HO<sub>2</sub>]/[OH] was obtained from the ratio of the peak-to-peak amplitudes of the first derivative spectra<sup>9</sup> assuming that the relative sensitivity for OH and HO<sub>2</sub> is 600:1 as measured earlier.<sup>12</sup>

Hydrogen atoms were produced by passing a very dilute H<sub>2</sub>/He mixture over a hot tungsten wire and further diluting the mixture with He. O<sub>3</sub> in He was obtained by trapping O<sub>3</sub> from an O<sub>3</sub>/O<sub>2</sub> mixture on silica gel, pumping off the O<sub>2</sub> and eluting with He; the O<sub>3</sub> concentration in the mixture was determined by the absorbance at 253.7 nm using an absorption cross section of  $1.15 \times 10^{-17}$  cm<sup>2</sup>.<sup>13</sup> The CO was purified by passing over quartz wool at a temperature of ~800 °C and the NO was purified<sup>14</sup> by passing through silica gel at -77 °C. Except as otherwise noted, the total pressure in the flow tube was 1.7 ± 0.1 Torr.

Three sets of experiments were carried out. In the first LMR was used to search for HO<sub>2</sub> (<sup>2</sup>A'') at an initial hydrogen atom concentration of  $2 \times 10^{11}$  and with initial ozone concentrations of  $(0.9 - 8.7) \times 10^{12}$ . Excess O<sub>3</sub> was used to minimize the removal of HO<sub>2</sub> by its rapid reaction<sup>15,16</sup> with H. Secondary production of HO<sub>2</sub> by the reaction of OH<sup>†</sup> with O<sub>3</sub> is expected to be small since OH<sup>†</sup> should be rapidly deactivated at the boric acid coated walls<sup>4,8,10</sup>; in any case, this would lead to an overestimate of the contribution of (1b). The ratio [HO<sub>2</sub>]/[OH] observed in these experiments at a reaction time  $\tau \sim 6$  ms, was  $\leq 0.02$ . Several runs were also carried out in excess H ( $[\text{H}]_0 = 1.4 \times 10^{12}$ ,  $[\text{O}_3]_0 = 2 \times 10^{11}$ ) with  $\tau \sim 6$  and  $\tau \sim 30$  ms, which gave [HO<sub>2</sub>]/[OH] < 0.06 and < 0.02 respectively. Thus  $\alpha \leq 0.02$  for the production of ground state HO<sub>2</sub>.

In the second set of experiments, carried out at a total pressure of 2.6 Torr, large concentrations ( $3.2 \times 10^{16}$ ) of CO were added to the system ( $[\text{H}]_0 \approx 3 \times 10^{10}$ , and  $[\text{O}_3]_0 = 2.8 - 18 \times 10^{12}$ ) in order to convert OH back into H via Reaction (2):



CO<sub>2</sub> ( $1.3 \times 10^{16}$ ) was also present in the experiments to quench the OH<sup>†</sup>. The sequence of Reactions (1a), (1b), and (2) where the OH reacting in (2) may be vibrationally excited, regenerates (1 - α) hydrogen atoms in each cycle.

Because all H reacting in (1a) is being regenerated, any observed decay of H should be due to Reaction (1b), the three-body reaction with CO or recombination at the walls. While the concentration of hydrogen atoms could not be followed directly, the steady state OH<sub>0</sub> concentration is proportional to that of H. Thus the OH<sub>0</sub> decay was followed as a function of [O<sub>3</sub>]<sub>0</sub> to obtain the rate of decay of H under these conditions. The observed

first order rates of decay of  $\text{OH}_0$  at initial ozone concentrations of 0.28, 0.94, and  $1.82 \times 10^{13}$  were 13.7, 18.1, and  $25.1 \text{ s}^{-1}$  respectively. Thus the observed rate of decay varied linearly with  $[\text{O}_3]_0$  as expected, giving  $k_{1b} \leq 7.5 \times 10^{-13.3}$  from the slope and an intercept of  $11.4 \text{ s}^{-1}$ . Taking  $k_1 = k_{1a} + k_{1b} = 2.4 \times 10^{-11}$ ,<sup>4</sup>  $\alpha \leq 0.03$ . The significant intercept represents an increase in the loss of H in the presence of CO, which may be due to an increased wall loss.

In this analysis possible secondary reactions of  $\text{HO}_2$  to regenerate H [(e.g.,  $\text{HO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{OH}$  followed by Reaction (2)] have been assumed to be negligible. This is supported by the fact that ground state  $\text{HO}_2$  reacts very slowly with CO ( $k < 10^{-19}$ ).<sup>17</sup> The corresponding rate constant for the reaction of electronically excited  $\text{HO}_2$  ( $^2A'$ ) which may be produced in (1b) is however, unknown.

In the third experiment with  $[\text{H}]_0 = 1.9 \times 10^{12}$ ,  $[\text{O}_3]_0 \sim 8 \times 10^{11}$  and  $\tau \sim 6 \text{ ms}$ , NO was added at a concentration of  $9 \times 10^{13}$  to convert any  $\text{HO}_2$  present into  $\text{OH}_0$ , which was monitored. The  $\text{OH}_0$  signal decreased by  $\sim 20\%$  regardless of whether or not  $\text{CO}_2$  ( $1.2 \times 10^{16}$ ) was present as a quencher of  $\text{OH}^\dagger$ . Oxides of nitrogen are known to increase the wall loss of OH in this system and this may be at least partially responsible for the decrease, which, however, is surprisingly large considering the short reaction time.

Thus, the results of these experiments indicate that  $\alpha \leq 0.03$  for the production of  $\text{HO}_2$  ( $^2A''$ ). While  $\text{HO}_2$  ( $^2A'$ ) would not have been detected at the same magnetic field strengths as the ground state, production of  $\text{HO}_2$  ( $^2A'$ ) is compatible with the results of the CO experiments only if it reacts rapidly with CO, ultimately regenerating H. The decrease in OH upon the addition of NO, however, suggests that unless unknown complicating secondary reactions are occurring, the yield of  $\text{HO}_2$  in either electronic state is small.

The results of the present work are consistent with the results of recent studies<sup>18</sup> by Washida *et al.* in which a search for the production of  $\text{O}_2$  ( $a^1\Delta_g$ ) in the H +  $\text{O}_3$  system was carried out. None was observed, from which they conclude that  $\text{O}_2$  ( $a^1\Delta_g$ ) is not produced in the primary process and that the production of  $\text{HO}_2$  via (1b) must account for  $< 6\%$  of the net reaction since H +  $\text{HO}_2$  is known to produce small amounts of  $\text{O}_2$  ( $a^1\Delta_g$ )<sup>19</sup> and/or  $\text{O}_2$  ( $^1\Sigma_g^+$ ).<sup>20</sup>

In summary, using conventional kinetic techniques, high yields of oxygen atoms,  $\text{O}(^3P)$  were observed<sup>2</sup> in the H +  $\text{O}_3$  system and their kinetic behavior appeared to be

most consistent with the second reaction channel (1b). However, it appears from the present work that (1b) accounts for  $\leq 3\%$  of the overall reaction of H with  $\text{O}_3$ . The results of recent studies<sup>5</sup> show that the  $\text{O}(^3P)$  yields fall by a factor of approximately two in a boric acid-coated tube, as compared to a halocarbon wax coated tube. In addition, very small yields of  $\text{O}(^3P)$  are observed in excess  $\text{O}_3$ . Thus, an as yet unknown very fast secondary reaction producing  $\text{O}(^3P)$  must be occurring. Studies are currently under way to elucidate this process.

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<sup>1</sup>See for example, J. C. Polanyi and J. J. Sloan, *Int. J. Chem. Kinet. Symp.* **1**, 51 (1975), and references therein.

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