Abstract for poster presentation for The 17th International Symposium on Gas Kinetics. Essen, Germany. August 24th-29th 2002

$OH + NO_2$: Continued Investigation.

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The reaction of OH radicals with NO_2 is an extremely important reaction in the troposphere, the stratosphere, and in polluted urban environments. However, it has also become a much debated reaction, with the products and mechanism both unsure. The possible channels for the reaction are shown below.

$$OH + NO_2 + M \Rightarrow HNO_3 + M \quad (1a)$$
$$\Rightarrow HOONO + M \quad (1b)$$

In the troposphere reaction 1a, which forms the stable nitric acid molecule, acts as a major sink for OH, while in the urban atmosphere the fact that it also consumes NO_2, a major source of ozone in polluted environments, is more important. Channel 1b which forms the much more weakly bound peroxynitrous acid and therefore will have none of these effects on an atmospheric timescale. Thus in the lower atmosphere the partitioning between these two products will be critical in the modeling of the effect of reaction 1. When kinetic data obtained using instruments designed to operate at lower pressures (in the range from 2 to ~760 torr) is compared with data from those experiments that operate at higher pressures a discontinuity can be seen around 1 atmosphere. The lower pressure results fall significantly below the curve that would be predicted if only the higher pressure results were considered. Golden and Smith recently proposed that this effect was due to channel 1b being observed in the high pressure laser-induced fluorescence (LIF) experiments but not playing an observable part in the lower pressure experiments. Using RRKM modeling they proposed that up to 30% of the reaction would proceed through this channel at atmospheric pressure. Subsequent experiments have both supported and disagreed with this hypothesis. The kinetic investigations of D'Ottone *et al* (pulsed flash photolysis-LIF) and Dransfield, Donahue, and Anderson (high pressure flow reactor) show no evidence of significant HOONO formation. However the subsequent isotopic labeling experiments of Donahue *et al* show some evidence for a weakly bound complex which may be stabilised as HOONO at significantly higher pressures. Finally Nizkorodov and Wennberg have produced indirect spectroscopic evidence that HOONO is indeed formed in the reaction of $OH + NO_2$, albeit at 253K and Bean *et al* have directly detected the OH stretch of HOONO using cavity ringdown spectroscopy.

With these observations in mind the JPL Chemistry and Photochemistry group will apply our newly constructed Laser Photolysis/Laser-Induced Fluorescence (LP/LIF) apparatus to the reaction of $OH + NO_2$. LP/LIF has been used to study the disappearance kinetics of OH radicals for several years but sensitivity limitations have limited the upper pressure of nitrogen, oxygen, or air at which they can operate. These gases rapidly quench the OH excited electronic state, reducing the fluorescence yield. The JPL system differs

significantly from previous LIF experiments that have been used to study the OH/NO2 system in that it has a high repetition (10 kHz) Cu vapour laser pumping the dye laser that is used to probe the OH fluorescence. Other experimenters have used a low repetition laser and thus have to vary the delay between photolysis and probe lasers to generate a kinetic decay; the JPL system will be able to measure a full decay with each photolysis shot. OH decays at higher pressures should be measurable providing some overlap with the higher pressure measurements. Also at these pressures some divergence from pseudo-first order kinetics may become visible as a result of channel 1b. At 1 atmosphere Golden and Smith predict that any HOONO formed with have a lifetime with respect to thermal decay of ~3ms as a result of collisional stabilisation. Some of this HOONO should decompose during the course of the experiment giving a source of OH at late times. D'Ottone et al looked for this effect in their highest pressure point (600 Torr) and did not observe it but this may be a result of there being less HOONO formed than the model of Golden and Smith predicts.

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