Comment on “Atmospheric Hydroxyl Radical Production from Electronically Excited NO2 and H2O”

Scott Carr,1 Dwayne E. Heard,1 Mark A. Blitz1,2*

Li et al. (Reports, 21 March 2008, p. 1657) suggested that the reaction between electronically excited nitrogen dioxide and water vapor is an important atmospheric source of the hydroxyl radical. However, under conditions that better approximate the solar flux, we find no evidence for OH production from this reaction.

The most important radical for driving the chemistry of the atmosphere is the hydroxyl radical, OH, because of its ability to react with almost all the gases emitted into the atmosphere (1). OH is predominately formed when O(1D), produced from ozone photolysis (λ ≤ 340 nm), reacts with water vapor in the atmosphere, and subsequently OH is removed by reaction with, among other compounds, CO, NO2, and hydrocarbons. The rapid rate of formation and removal of OH results in a steady-state daytime concentration that is sensitively controlled by the concentration of OH sources and sinks. There have been a number of newly identified sources and sinks for OH, for example, the regeneration of OH after the oxidation of isoprene (2). Li et al. (3) recently identified a new atmospheric source of OH, in which nitrogen dioxide excited by visible light (denoted NO2*) was found to react with water vapor to generate OH:

NO2 + hv (λ > 420 nm) → NO2* (1)

NO2* + H2O → OH + HONO (2)

NO2* + H2O → NO2 + H2O (3)

Li et al. report that only about one collision in a thousand between NO2* and water vapor gives OH (Eq. 2), with the rest deactivating NO2* (Eq. 3). However, the solar flux in the visible region of the spectrum is so large that despite being inefficient (OH yield ~ 0.001), this reaction still represents a major source of OH—up to 50% of that produced from O(1D)/H2O (3) at high solar zenith angles under polluted conditions.

Verifying the existence of reaction 2 is very demanding because of the low yield of OH. In addition, other molecules present in the experiment may deactivate NO2* (3–5):

NO2* + M → NO2 + M

(where M is NO2, He, O2) (4)

Such a low yield of OH places very stringent demands on its detection, and high initial NO2* concentrations are required to facilitate the experiment, achieved by Li et al. using a combination of a large excitation laser pulse energy and a lens to focus the laser light and generate a large fluence.

We also measured the OH yield from reaction 2 but have failed to observe OH, finding an OH yield of <0.00006. In our experiments, we used a sensitive off-resonance laser induced fluorescence (LIF) scheme to detect OH (6), using a laser fluence for the visible excitation radiation at least an order of magnitude lower than that used by Li et al. The observed OH LIF signal gives only a relative measure of concentration and must be calibrated using a known concentration of OH, which we generated by frequency doubling the laser light (either at 563.5 or 567.5 nm) to the ultraviolet, where acetone is photolysed (7):

(CH3)2CO + hv (λ ~280 nm) → CH3CO + CH3 (5)

In the presence of oxygen, OH is formed with a known yield (8) by

CH3CO + O2 → OH + products (6)

We reduced the laser fluence so that the OH concentration as predicted by Li et al. from reaction 3 should be similar to that generated by our calibration reaction 6. Figure 1 shows the two experimental OH time profiles for the OH calibration reaction and the reaction of NO2* with water vapor, together with a calculated profile for OH from reaction 2 using the reported yield from Li et al. Our results provide no evidence for the occurrence of reaction 2. Using the standard deviation of the noise of our experiment, we estimate an upper limit for the OH yield from reaction 2 to be a factor of 17 lower than that reported by Li et al. (3), at the 2σ level. This result is in agreement with Crowley et al. (9).

The reason for this difference is not clear but both Crowley et al. (9) and our current study used unfocused laser light, whereas Li et al. used a lens to focus the laser light. Multiphoton processes were ruled out by Li et al. because the dependence of the OH signal on laser fluence was observed to be linear, but the plots shown in Li et al. to support this conclusion show negative intercepts, whereas a genuine single-photon process should only produce zero OH signal at zero pulse energy.

Another intriguing result from the work of Li et al. is the observation of vibrationally excited hydroxyl radical, OH(v), even at red wavelengths, where its formation is not thermodynamically possible [566 nm is the limit (10)]. It was suggested that OH(v) results from reaction between NO2* with vibrationally excited water vapor (H2O*), with the latter being formed by rapid collisional energy transfer

NO2* + H2O → NO2 + H2O* (7)

followed by the reaction between H2O* and NO2*:

NO2* + H2O* → OH(v) + HONO (8)

As noted by Li et al., this mechanism requires two NO2* molecules to form OH(v), so the LIF signal from OH(v) should exhibit a squared dependence on the laser fluence used to excite NO2*. It was suggested that this mechanism was minor because of the linear dependence of the OH signal on the NO2 excitation laser energy. However, if the OH signal versus the NO2 excitation laser energy of Li et al. were indeed squared, it could explain both the observed negative intercepts of their linear fits and the absence of any OH signal in our lower fluorescence experiments. Unfortunately, the maximum laser fluence used in our experiments was below the threshold required by Li et al. to generate OH signal, so we were unable to test this hypothesis.

Fig. 1. OH time profiles for the reaction reference 6 (red circles) and the reaction NO2* + H2O vapor, 2 (black squares), together with that predicted from Li et al. (3) for reaction 2 (black line). Reaction 6 data were obtained from laser excitation of NO2* at 567.5 nm, 3.3 μJ/pulse; reaction 2 data were obtained after laser photolysis of acetone at 283.75 nm, 0.11 μJ/pulse.

Downloaded from http://science.sciencemag.org/ on April 14, 2017
In conclusion, we studied the reaction between excited state nitrogen dioxide, NO$_2^*$, and water vapor and, contrary to the study by Li et al. (3), failed to observe the formation of the hydroxyl radical. We assign an upper limit for reaction 2 and suggest that this reaction has little impact on atmospheric chemistry.

References and Notes
6. Materials and methods are available as supporting material on Science Online.
10. www.iupac-kinetic.ch.cam.ac.uk/
Editor's Summary

Comment on "Atmospheric Hydroxyl Radical Production from Electronically Excited NO₂ and H₂O"
Scott Carr, Dwayne E. Heard and Mark A. Blitz (April 17, 2009)
Science 324 (5925), 336. [doi: 10.1126/science.1166669]