

Review of OH + NO₂ ms in ACP

This is a very carefully executed and analyzed kinetic study of a very important reaction in the atmosphere. The literature reports conflicting data, so this new study is welcome. I have only one significant technical issue for the authors to address, plus a number of requests for clarification or corrections of minor points.

Significant technical issue:

From the reported maximum flow rate of 9900 sccm and the 500 cm³ reactor size, the residence time of the gas in the reactor would be as high as 3.6 seconds (at 1.2 bar and 298 K). This is inconsistent with the statement on page 3 (line 24) “A fresh gas sample was thus available for photolysis at each laser pulse (laser frequency = 10 Hz).” Since the authors made an effort to keep the flow rate relatively constant, it would seem that the gas sample would typically have been subjected to at least ~15 laser pulses. Please address this issue, especially in light of the comments, further down, on the large extent of O atom production from NO₂ photolysis.

Related to this, the manuscript states “We additionally carried out some experiments at a lower repetition rate to rule out any influence of product build-up on the measured rate coefficient.” I would like the authors to document these experiments (at least in the Supplementary Information).

Minor points

Section 2.1 Please list

- the energy of the photolysis laser pulse
- the delay time between photolysis and probe pulses, and the gate width, if different than in Wollenhaupt et al., 2000.

Page 3, line 20. 500 cm⁻³ should be 500 cm³.

Section 3.1.1 Please specify the temperature at which these experiments were carried out

Section 3.1.2 The paragraph describing the pressure-dependence of the NO₂ absorption spectrum is confusing. I believe that part of this is because at least one of the citations of Vandaele et al., 2002 should be Vandaele et al., 1998. Possibly, too, contradiction noted between the two papers Vandaele may be resolved by noting that the 1998 paper could only detect a pressure dependence at 500-833 nm, whereas the discussion here is for 400-450 nm.

Also, the manuscript seems to state (page 7, lines 11-15) that applying the broadening factor of Nizkorodov et al. (2004) to the data of Nizkorodov et al. (2004) does not agree with the spectra of Nizkorodov et al. (2004). Are you saying their reported broadening factor is inconsistent with their data? In any case, some clarification would be helpful.

On page 9, lines 23-27, discussing the correction for N₂O₄ formation. I suggest the authors note here that the size of these corrections is listed in Table 1 for each (P,T) set of conditions.

On page 9, line 32, “respectively resulting in a factor ten change in [OH]”.

- There should be a comma after “respectively”
- “[OH]” presumably refers to “[OH]₀”
- the factor of “ten” is only a factor of three at 500 Torr (according to the data in Table 1)

Page 10, lines 5-9. While NO_2 has a very low cross section at 248 nm, the cross-section of HONO_2 is only twice as large. Given that $[\text{NO}_2]$ is typically much larger than $[\text{HONO}_2]$, we may expect $[\text{O}]_0$ to be $2-4 \times [\text{OH}]_0$. I agree with the authors that this would not be a problem if “A fresh gas sample was thus available for photolysis at each laser pulse,” but I am not clear on that point. In any case, I would like to see the manuscript acknowledge that $[\text{O}]_0 \approx 2-4 \times [\text{OH}]_0$.

Is it possible to harmonize the presentation of the IUPAC and JPL versions of the Troe expression? They are different, but the way the equations are formatted here makes it harder to see how they are similar.

Page 11, line 29. “In low-pressure flow-tube studies, correction is rarely made for the surface-reaction induced heterogeneous loss of OH”. It would be good to append “...in reaction with NO_2 ” to this sentence, to clarify that you are not referring to k_w .

According to the JPL recommendations for R5b, dissociation of HOONO will have, at most, a rate constant of 20 sec^{-1} under the conditions of this experiment. This means that HOONO dissociation is unimportant on the time scale of the experiment, so the present work determines the sum of the rate constants for R5a and R5b: formation of HONO_2 and HOONO ; the manuscript should at least note this fact prominently.

But in comparing the experimental data to the JPL and IUPAC recommendations, it appears that comparison is made to the expressions for R5a, alone. While R5b is a modest fraction of the overall reaction, it is not entirely negligible (up to 17% of the reaction, using the JPL recommendation). This should be made explicit. The manuscript could also compare the present data to the sum of the recommendations to R5a and R5b.

Caption to Figure 2: The text describes Figures 2a and 2b, while the caption incorrectly lists Figure 2b as an inset. The caption should specify the temperature of these experiments.

Caption to Figure 4: Please specify the excitation wavelength. Also, the description of the lines is clearer in the text of the manuscript than here. The lines correspond to the values expected after correcting for NO_2 dimerization.

Thoughts on formation of HOONO vs. HONO_2

This work cannot address the competition between formation of HOONO and HONO_2 , and this fact should certainly not hinder publication. I want the authors to be aware of the fact that the difference in the values of β for O_2 and N_2 may not be the same for HOONO and HONO_2 , although discussion of this point may not be necessary here. The most recent paper I am aware of on the issue of bath gas mixtures and multichannel reactions is from M. P. Burke of Columbia (not this reviewer!): <https://pubs.acs.org/doi/pdf/10.1021/acs.jpca.8b10581>.