

Interactive comment on “Absolute rate constant and O(³P) yield for the O(¹D)+N₂O reaction in the temperature range 227 K to 719 K” by S. Vranckx et al.

S. Vranckx et al.

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1. The introduction of the manuscript has been very slightly expanded to include a reference to the findings of Crutzen and Bruhl. (J. Phys. Chem. A 2001, 105, 1579-1582)

Abstract "The rate constant for the reaction that is the major source of stratospheric NO_x (N₂O + O(¹D) = 2NO, and other products) has been determined....."

Introduction "Of the HO_x, ClO_x, and NO_x chain catalytic ozone destruction routes it has been demonstrated by Crutzen and Bruhl (2001) that the NO_x sequence is the main cause of the Spring to Autumn stratospheric ozone decline in the Northern Hemisphere"

2. The method for following the transient signal of O(1D) used in the work reported by Blitz et al. is sound as far as we are aware, though this method has not been used by us. Since we can see no obvious difficulties of either side or secondary reactions for that study we can only propose that the uncertainties quoted by these authors are somewhat under-estimated. The authors reported only two determinations of the rate constant for O(1D) + N₂O and it is therefore not possible to assess to random uncertainty in those determinations. The quality of the plots of k' vs reactant concentration for the chemiluminescence method we use and the reproducibility of the rate constant show it to have a much lower random uncertainty than other methods used determine k for O(1D) reactions. Our rate constant determinations are about 20% greater than those reported by Blitz et al. Side reactions and impurities in our experiments cannot possibly account for this difference. Since the reaction O(1D) + N₂O occurs at nearly every collision one would require a very large impurity (of several percent) in the N₂O mixture that we use in order to account for the difference. C₂H, which also contributes to the chemiluminescence time profile in our experiments, is unreactive toward N₂O. This is supported by both our experimental and computational work, as described in the manuscript.

Any products of the primary reactions cannot influence the kinetics of either C₂H or O(1D) due to their very low relative concentrations. Also there are no reactions in our system besides C₂H + O(1D) and C₂H + O(3P) that can give rise to CH(A) and hence influence our chemiluminescence signal. An extensive search of possible reactions giving rise to CH(A) has already been carried out by this group (Elsamra et al. J. Phys Chem. 109 (2005) 10287)

2. The interested reader is referred to "Unimolecular reactions: a concise introduction", W. Forst, Chapter 7, Cambridge University Press, 2003. This reference has been added to the manuscript.

3. Referring to the 2 microsecond rise time in the profile of figure 6 and the nearly prompt rise seen in Figure 3. The precise shape of the graph in the first couple of

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microsecond is not entirely reliable as the decays are extracted from the subtraction of a baseline signal that contains some laser scattered light in the first few microseconds.

4. The typographical errors have been noted and corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8881, 2008.

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