

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.

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1. All reactions are subject to a variational effect, in that the bottle-neck structure will change slightly as the average collision energy changes. This is hardly noticeable for reactions having a significant barrier since the minimum in the number of available states for random energy distribution is determined mainly by the rapidly varying potential energy defining the barrier. For reactions proceeding without a barrier, such as for several reactions involving O(¹D), a decrease in rate constant with increasing temperature is expected. However, computing the extent, and point of onset, of the downward curvature of the rate constant at higher temperatures is difficult as this requires quite accurate values for the potential energy of interaction at long/medium separations.

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2. We normally use two types of oil to cover the temperature range we require. For the low temperature range, we use SiliOil M90.055.03, and for high temperatures SiliOil M20.235.20, both supplied by Huber. The latter is able to cover the range 253 K to 508 K.

3. As you have pointed out in your paper, there appears to be a good correlation between reaction cross-section of O(1D) reactions with non-polar reactants and ionisation energy of the co-reactant. Whether such a correlation can be used to pick out possibly overlooked systematic uncertainties in previous measurements is not clear in the case of O(1D). It might however be worthwhile to take a closer look at those reactions whose determined rate constants are found to depart significantly from the correlation line. As far as the CH₄ + O(1D) reaction is concerned, our paper on this is in press (Phys. Chem. Chem. Phys.). We determine a rate constant value about 20 % greater than the currently recommended value, so this would indeed bring that data point quite close to the correlation line as plotted in your recent paper. We have also performed extensive rate constant determinations on O(1D) + H₂O and O(1D) + H₂. We find the former to be in line with current recommendations, whilst the latter we find to be greater. This work is about to be submitted. For O(1D) + O₃, we plan to look at this reaction during our ongoing investigation into the photolysis of O₃.

4. Indeed your recent room temperature rate constant determination of $(1.47 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for O(1D) + N₂O was overlooked by us. Our first draft of this manuscript was actually completed before your paper appeared. A reference to that work will now be included in the final manuscript.

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

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