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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Absolute rate constant and O(^{3}P) yield for theO(^{1}D)+N_2O reaction in the temperature range227 K to 719 K" *by* S. Vranckx et al.

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1. Our estimated uncertainty in temperature at the lowest temperatures reported in this work (227 K) is +/- 5 K at ca. 95 % confidence. This uncertainty decreases to ca. +/- 1 K at room temperature and increases again to ca. +/- 4 K at 422 K. If these temperature uncertainties are considered to be random and uncorrelated their contribution to the statistical uncertainty for each point (0.09 cm3 s-1) does not impact on either the rate constant value or the associated uncertainty (1.37 +/- 0.09) to within 3 significant figures. A certain degree of randomness is expected in the temperature measurements due to placement and replacement of the thermocouple. In the most extreme scenario, one could consider only systematic errors and all temperature measurements to be under-estimated at low temperatures and over-estimated at higher temperatures. This

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would mean that the actual rate constants below room temperature would be slightly greater than those we quoted (the maximum change would be at 227 K where the rate constant would be a factor 0.02 greater - 1.38 cm3 s-1 instead of 1.35 cm3 s-1) and those at higher temperature would be slightly less.

If one takes this extreme situation, which is beyond 95 % confidence, and makes a fit to the corrected data, one finds a very slight negative T dependence over the T range 227 K to 446 K. The best straight-line fit to these data passes through 1.39 +/- 0.03 at 220 K, through 1.37 +/- 0.01 at 300 K to 1.35 +/- 0.03, where the uncertainties indicate the extent of the 95 % confidence bands. Thus by far the largest contribution to the uncertainty remains the determination of the fraction of N2O in the gas cyclinder by absorption.

In order to take into account a slight temperature dependence in the rate constant over the range 227 K to 446 K we increase our 95 % confidence limits from +/- 0.09 to +/- 0.11 in this range. A note has been added to the text concerning this point. The uncertainty limits in figure 5 have also been altered accordingly. We do not consider a positive T dependence in the above temperature range as this would be unrealistic given the negative T dependence at higher temperatures.

2. The equation as written in the text is not correct as the referee has pointed out; a parenthesis is in the wrong place. The equation has now been re-written in the correct form. We note that the correct formula was used throughout the investigation.

3. An upper limit to the fraction of O(3P) produced on photolysis can be taken from our data at 245 K. In this case, if one assumes that no quenching occurs for the title reaction then direct production of O(3P) via 193 nm photo-dissociation of N2O accounts for a fraction 0.007. A sentence to this effect has been added in the text. At these low quenching values it is not possible to distinguish between direct production of O(3P) via photodissociation of N2O and production of O(3P) by quenching. In our experiments the sum of both contributions is observed. In case of no direct photolytic O(3P) produc-

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tion, all of our reported quenching fractions would need to be increased by slightly less than 0.005. In such a case our main conclusion about this remains exactly the same; that the quenching channel is entirely negligible for this reaction. We have added a sentence to the manuscript explaining this situation.

Minor corrections : these have been attended to.

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

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