**Atmospheric
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Discussions**

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Comment

Interactive comment on "Rate coefficients for the reaction of $O(^1D)$ with the atmospherically long-lived greenhouse gases NF$_3$, SF$_5$CF$_3$, CHF$_3$, C$_2$F$_6$, c-C$_4$F$_8$, n-C$_5$F$_{12}$, and n-C$_6$F$_{14}$" *by* M. Baasandorj et al.

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This paper presents results from experiments on reactions of O(1D) with some potent greenhouse gases. These reactions are important as they may, if sufficiently rapid, represent a significant removal pathway for otherwise persistent atmospheric pollutants. The experiments appear to have been carefully carried-out, the results are generally presented clearly in the manuscript with suitable conclusions made. I recommend publication of this work in ACP following consideration of a few points detailed below.

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Section 2.1, regarding the use of 248 nm laser photolysis throughout. Do any of the reactant molecules absorb photons at this wavelength?

Section 2.2. On page 24020 the description of k_rise is a little confusing; it reads as if reaction 11 is $O(^1D) + O_3$, and therefore as if reaction with butane is not important. It may be better to state that k_rise is dominated by reaction 11 (with butane), with a small contribution from reaction 12 (with O_3). The importance of the butane reaction is easy to overlook as in Figure 1 the y-axis plots k_rise – k_0. Were the measurements of k_0 consistent with [butane] and literature k-values for $O(^1D)$ + butane?

Section 3.1, results for $O(^1D) + NF_3$. The value obtained is stated in the text & table 2 to be $(2.55 +/- 0.2) \times 10^{-11}$ cm3 molecule-1 s-1, whereas in table 3 this is listed as $(2.55 +/- 0.38) \times 10^{-11}$ cm3 molecule-1 s-1. Does the inclusion of systematic error estimates account for this discrepancy? Please clarify in the text (perhaps in section 3.5). As stated in the text, there is reasonable agreement between the three recent determinations of k_total (2.0, 2.35 & 2.55 $\times 10^{-11}$ cm3 molecule-1 s-1); all are significantly larger than the first determination from Sorokin et al.

The relative rate determinations of k from this work (all around 2.2×10^{-11} cm3 molecule-1 s-1) also fall within this range of recently reported k-values. Since the relative rate results are only sensitive to reactive product channels, it seems to me that the results from this work underpin the conclusions of both Zhao et al. and Dillon et al., who both report a near-unity yield of reactive products. This result is particularly robust since all used very different methods to probe the product distribution.

The final paragraph of section 3.1 is therefore slightly misleading, emphasising differences between the reactive product yield reported here (0.87 +/- 0.13) and that from Zhao (0.99). First, there is no great difference given the reported uncertainties. Second, use of only the k-total value from this work (the largest reported) to calculate product yields may skew the data. Perhaps it would be more sensible to use an average of the three recent k_total values (= 2.3×10^{-11} cm3 molecule-1 s-1) to calculate

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a yield of reactive products from the relative rate data in this work (2.21 / 2.3 = 0.96). The only reason to rely solely upon the k_total from this work would be if systematic errors present in both the absolute and relative-rate determinations were to cancel-out. This does not appear to be the case. The apparent agreement between the product yield calculated in this work, and that of Sorokin offers false reassurance, as it was subsequently demonstrated that the FO monitored by Sorokin is not a primary product of O(1D) + NF3 (see Dillon et al., 2011).

Section 3.6. I strongly suggest you mention the new measurements of IR band strengths for NF3 in the abstract. Otherwise this important result may get lost when future calculations of lifetime, GWP etc. are conducted.

In section 4, conclusions, regarding the O(1D) + perfluorocarbons it is stated that "The improved upper-limit reactive rate coefficients result in longer calculated atmospheric lifetimes and greater global warming potentials for these persistent greenhouse gases (WMO, 2011) than those obtained using the currently recommended rate coefficient data (Sander et al., 2011)." Could you try to quantify this statement? If reaction with O(1D) is the principal loss process for these compounds then any change in k will impact on lifetime calculations. Calculated lifetimes and GWPs for these compounds must surely be more dependent upon VUV photolysis rates than any upper-limits for O(1D) reaction rates.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 24011, 2012.