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Atmospheric
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Discussions

Interactive comment on "Potential impacts of CF_3I on ozone as a replacement for CF_3Br in aircraft applications" *by* Y. Li et al.

Y. Li et al.

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Reply to comment by W. Bloss on "Potential impacts of CF3I on ozone as a replacement for CF3Br in aircraft applications" by Y. Li, K. Patten, D. Youn and D. Wuebbles

"This paper reports a model study of the effect of CF3I emissions upon atmospheric ozone levels. A kinetic and photochemical scheme for iodine chemistry is added to an existing 2-dimensional model, and used to assess the impact of iodine upon atmospheric ozone levels resulting from prescribed emissions of CF3I at different altitudes, and hence obtain ozone depletion potentials for CF3I."

"My comment relates to aspects of the iodine chemistry used in this paper. As the authors note, the kinetics and photochemistry of iodine-related species have been the subject of considerable attention over the past decade, prompted in part by the

Solomon et al. (1994) study, and subsequently by IOx observations in the marine and polar boundary layers. Consequently a revision of calculations of the impact of iodine upon atmospheric ozone is both welcome and timely. However in several respects this paper has not used the most recent (or recently evaluated) data available, which may alter the conclusions reached regarding ozone destruction through the iodine catalytic cycles, and hence the ODP values obtained for CF3I."

Dear Dr. Bloss,

Thank you for your insightful comments. Most of the iodine chemistry used in this study is consistent with the NASA chemistry recommendations assessed in JPL 02-25 (Sander et al., 2003). For the chemical reactions not available in JPL 02-25, we either used prior kinetics assessments (e.g., JPL 00, JPL 97 and IUPAC (Atkinson et al., 1997)) or cited recently published journal articles. We tried to update our model with the best available chemistry, but there might be a few cases where we did not find the newest reported values. This is sometimes due to the time lag between the model runs being made and the analysis of the results being written up and published. It is also possible that we selected a data source that provided not only point values but also comprehensive results because our 2-D model takes large temperature, pressure and light wavelength range into account. For the two examples you raised, we presented below our explanation and more model runs were made according to your suggestion.

"1. IO + BrO reaction The authors refer to the study of Gilles et al. (1997) for the kinetics used in their analysis. Gilles et al. measured the temperature dependence of the non-I atom producing channels of the IO + BrO reaction, obtaining 2.5x10Ĺ-11exp(260/T) for these channels, ca. 50% higher than the value given in this paper (Table 1) of 1.63x10Ĺ- 11exp(260/T) for production of IBr + O2. Gilles et al. also estimated that additional I atom producing channels accounted for 35 % of the total rate constant (at 298 K), indicating an estimated rate for this channel of 1.35x10Ĺ-11exp(260/T) - if the same temperature dependence is assumed - rather than the value of 8.75x10Ĺ-12exp(260/T) used in this work. If the authors prefer the Gilles et al. study for the kinetics of this reaction, they should check the parameters are correctly implemented in their model. In addition to the study of Gilles et al., measurements of the IO + BrO kinetics have been reported by Laszlo et al. (1997), Bedjanian et al. (1998) and Rowley et al. (2001), which have indicated that the total reaction rate constant is indeed ca. 30% higher than the non-I-atom channels measured by Gilles et al. at 298 K, and that the I atom channels are of increasing importance at lower temperatures, pointing to potentially enhanced ozone destruction through this reaction in the upper atmosphere. The studies of Bedjanian et al. and Bloss et al. also found that production of OIO + Br, rather than IBr + O2, dominated the non-I atom channels of the reaction. The most recent evaluation (IUPAC; Atkinson et al., 2006 - these reactions have not been reevaluated in the JPL evaluations of Sander et al., 2000 / 2003) indicates that production of OIO + Br dominates, with a branching ratio of 0.80 (298 K). The impact of the IO + BrO catalytic cycle upon ozone loss may therefore differ from that calculated by Li et al., with increased ozone destruction due to enhanced production of I + Br + O2, especially at lower temperatures. The extent to which this occurs will however depend upon the photolytic fate of OIO:”

For IO + BrO reaction, JPL 02 cited two references, Gilles et al. (1997) and Laszlo et al. (1997). Gilles et al. (1997) provided a temperature dependent expression of 2.5x10-11exp(260/T) for non-iodine atom producing channels and a branching ratio of <0.35 for channels producing I atoms, while Laszlo et al. (1997) provided a constant reaction coefficient mainly for room temperature. Considering the large temperature range presented in our model, especially the coldness in the upper troposphere and lower stratosphere where our study focused on, we decided Gilles et al. (1997) was more appropriate for our study. We did make a mistake in calculating reaction coefficients for the I atom producing channel by assuming it was 35% of the non-iodine atom producing channels. That is how 8.75x10-12exp(260/T), which equals 2.5x10Ĺ-11exp(260/T)*0.35, was obtained instead of 1.35x10-11 exp(260/T). To see the difference this error can make to our results, we updated our model with the most recent evaluation of IO + BrO reaction in IUPAC (Atkinson et al., 2006) and made runs with CF3I emissions at 30-40N latitudes following Rupnik profile. The comparison of this alternative run and the original results has been shown in the figure www.atmos.uiuc.edu/˜yueli2/iobro.jpg. As we can see in the figure, the differenceis at most 1.0%. Therefore, this did not meaningfully impact our results presented in the manuscript.

“2. OIO Photolysis - Cross Sections & Quantum Yield Li et al. refer the OIO photolysis reaction, given as OIO + hv -> O + IO, to the JPL evaluation of DeMore et al. (1997), and comment that the photolytic fate of OIO is uncertain. In practice OIO cross sections (or photolysis products) are not mentioned in the 1997 or 2003 JPL evaluations; however various literature measurements (Bloss et al. (2001), Joseph et al. (2005), Martin et al. (2005), Tucceri et al. (2006)) have been published, with estimates of the absorption cross-sections converging around the (1.3 - 1.5)x10Ĺ-17 cm-2 range. What values were actually used for the OIO absorption cross sections in this paper ? Potential atmospheric photolysis channels for OIO are O + IO or I + O2. Laboratory measurements (Ingham et al., 2000) and theoretical calculations (Misra and Marshall, 1998) indicate that the yield of the O + IO channel is negligible. Recent research (Joseph et al., Tucceri et al.) indicates that production of I + O2 is also low, with most (> 90%) of the OIO which is excited undergoing rapid internal conversion back to the ground state, followed by vibrational relaxation (rapidly on the timescale of atmospheric processes). OIO may therefore be largely photostable in the atmosphere, with a small photolysis yield (< 10%) producing I + O2. As the authors of this paper comment, the photolytic fate of OIO is indeed rather uncertain, however they should consider the impact of the kinetic parameters and OIO photolysis processes described above, which are likely to significantly alter the calculated ozone destruction rates.”

We did have a hard time on deciding on the OIO photolysis cross sections. In the UIUC 2-D CRT model, there are 128 bins for light wavelengths from 175 to 735 nm. The JPL 02 (00 or 97) did not have recommendations on the photochemical cross-sections of OIO, while other reported OIO photolysis cross sections were limited and only avail-

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able for several particular wavelengths in the visible bands. We thought this was also the reason that JPL did not include evaluations on OIO photolysis. To make the parameterization self-consistent in the model, we chose to red shift the OClO spectrum from JPL by 100 nm to obtain the OIO spectrum. The resultant cross sections in the visible bands were peaked at 6.5*10-18 cm-2 around 450nm and spread in the range of 375 to 575 following the pattern of OClO spectrum. Compared to the normalized OIO spectrum in Tucceri et al. (2006), a further 100nm red shift would make the model estimates more comparable with the laboratory experiments. We are sorry that we did not explain this clearly. We have put footnotes in Table 1 explaining the source of OIO cross-sections. To see the difference that using the newest OIO spectrum available in Tucceri et al. (2006) can make, model runs have been made and compared to the original results in the figure at www.atmos.uiuc.edu/˜yueli2/oio.jpg. As shown in the figure, the difference is generally within 1.0% and should not impact our results presented in the manuscript significantly.

“Other Points -Absorption cross sections and kinetics of formation/loss for a number of the inorganic iodine species have been measured subsequent to those referred to (the Atkinson et al., 1997 evaluation) in the paper, e.g. HOI - Bauer et al. (1998), IONO2 - Mössinger et al. (2002), IO - Bloss et al. (2001) / Martin et al. (2005). The authors should consider if the differences between these measurements, and the earlier values (or more likely estimates) from 1997, are likely to be significant in their study.”

Thank you for providing many useful resources for our study. The next phase of our work is to calculate the ODPs of CF3I emissions using our state-of-the-art 3-D MOZART model, for which we will definitely use the most up-to-date iodine chemistry to obtain more accurate results.

“The issue raised here - inclusion of recent laboratory data - raises the more philosophical question of how "up to date" chemical mechanisms used in modelling studies should strive to be. While it is obviously impractical for every such study to be completely up to date with all kinetic data available in the literature, not least due to the

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timescales involved in conducting the work and manuscript preparation, where a study focuses upon a particular aspect (e.g. atmospheric iodine chemistry) use of the more recent evaluations, and reference to subsequent measurements in the literature, will help ensure the relevance of the work. This seems particularly pertinent to this paper, as the use of updated iodine kinetics, measured after the Solomon et al. study of 1994, is mentioned as a motivating factor."

We agree with your philosophical question - it is one we always have to address in a new research study. This study was carried out with the main goal of evaluating the eligibility of CF3I as a fuel-inerting or fire-fighting agent in the aircraft. The previous studies only focused on the surface emissions of CF3I, but the ozone depletion effects of a compound with such short lifetime can differ a lot for different locations (altitudes, latitudes) where the emissions occur. We proved that the CF3I is a proper replacement for CF3Br in the aircraft from the atmospheric chemistry standing point. Chemistry update is a necessity to reflect the current understanding of iodine-related chemical reactions and obtain more accurate results.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5163, 2006.