“Interactive comment on “Potential impacts of CF$_3$I on ozone as a replacement for CF$_3$Br in aircraft applications” by Y. Li et al.

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Received and published: 7 August 2006

This paper reports a model study of the effect of CF$_3$I 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 CF$_3$I at different altitudes, and hence obtain ozone depletion potentials for CF$_3$I.

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 IO$_x$ 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.

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 $2.5 \times 10^{-11} \exp(260/T)$ for these channels, ca. 50% higher than the value given in this paper (Table 1) of $1.63 \times 10^{-11} \exp(260/T)$ 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 $1.35 \times 10^{-11} \exp(260/T)$ - if the same temperature dependence is assumed - rather than the value of $8.75 \times 10^{-12} \exp(260/T)$ 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 re-evaluated 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:

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)x10^-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.

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.

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 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.

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References


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