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Atmospheric Chemistry and Physics 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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Response to comments 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

Below is a detailed point-by-point list of changes to the manuscript, following referees' comments.

Answers to Anonymous Referee #1

"This paper presents calculations using a 2D model to assess the impact of replacing a current bromine-based fuel-inerter and firefighting compound on aircraft with an iodine-based compound. Since the atmospheric chemical lifetime of the replacement compound is much shorter than that of CF3Br it is expected that it would not build up to levels in the atmosphere that could impact stratospheric ozone; however, on a per

molecule basis in the stratosphere is more efficiently destroyed by iodine than other halogens. Also because of its shorter lifetime the stratospheric impact is somewhat sensitive to the location of release, both height and latitude in the troposphere. They used updated rate data for iodine reactions to improve the results from earlier studies and found that in spite of the greater efficiency of the iodine catalytic cycles compared to Bry and Cly cycles based on a per molecule of halogen basis that the replacement, CF3Br could safely be used." "I consider that this is a useful contribution but I would prefer is some of the more qualitative and emotive language was replaced! I have made some suggestions below."

"Page 5169, section 3.2. The assumption is made that rain out of IONO2 , HI and HOI is efficient. But I have not seen any discussion in the literature regarding the possible (probably) evolution of dissolved species such as HI and HBr from rain water in a fashion that occurs in MBL and Arctic/snow chemistry. Is this likely to be a limitation? I mention this because of the uncertainty of the Bry stratospheric budget which is likely subject to similar problems regarding short lived bromine-containing compounds and rainout."

It is possible that model parameterization of the rainout effects would be a limitation in this study if the rainout were not efficient. The previous studies have shown that HI, HOI and IONO2 are soluble and trapped by clouds and aerosols (e.g. Davis et al., 1996). Taking very small concentrations of HI, HOI and IONO2 in the atmosphere into account, they are not likely to turn back into gas phase once captured by rain droplets. Therefore, the assumption of rainout/washout processes is still valid for the iodine species. There are no basis at this time for including reemission from snow, but even if it did, the emitted HI would be so short-lived as to not be important to stratospheric ozone. Short-lived gases are already included in the model for stratospheric bromine, but HBr from snow and the MBL are not an important contributor to explaining the Bry in the lower stratosphere. We have added some discussion to the manuscript.

"Page 5170, line 11. Figure 1. This Figure needs cleaned up. For example, a species

ACPD
6, S3308–S3314, 2006

Interactive Comment

EGU

I2O2 is listed in the topmost box. The HO2 arrow from HOI to IO is the wrong direction. The HOI photolysis to IO is not listed in Table 1. Please check others."

The figure has been modified accordingly. Only primary HOI photolysis (HOI + hv → I + OH) to is considered in this study since secondary channel HOI photolysis to IO is occurring at the lower wavelengths ≤ 296 nm and larger ∆H.

"Page 5172, line 6ff. The discussion here on the temperature dependence of the reactions is a bit misleading and possibly wrong. There is no discussion about the availability of [O] and the fact that the O + O2 +M -> O3 + M reaction is faster at lower temperatures so limiting the availability of [O] for the same amount of ozone. And since the reaction O + IO -> I + O2 is important and also rate limiting this will modify the discussion."

The supply of [O] is governed by the photolysis of ozone in the atmosphere since O + O2 +M  O3 + M is a very rapid reaction in the stratosphere and upper troposphere (e.g., various WMO ozone assessments; Seinfeld and Pandis, 1998). Therefore, the reaction of O + O2 +M  O3 + M is not the determinant factor of the availability of [O] in this case. Atomic oxygen has its maximum concentrations in the tropical middle stratosphere where ultraviolet light and ozone are sufficient. In the catalytic cycle of I+O3 IO + O2 ($k < 2.30*10-11$) and IO + O  I + O2 ($k = 1.20*10-10$), the first reaction is the rate-limiting step. As a result, the discussion in the paper should be valid.

"Page 5176, line 10. See above. I don't think that the rationale for the larger polar ozone loss is correct. (1) as the authors note there is more Iy due to transport, similar to NOy, Cly etc. {A 2D zonal plot of Iy might be appropriate here.} (2) There is also more [O] since there is more O3 in polar regions at lower altitudes."

As discussed above, [O] has its maximum concentration in the tropical middle stratosphere. The largest ozone depletion occurs in the polar region because of the iodine species transported from the lower latitudinal region as well as the favorable condi-

ACPD
6, S3308–S3314, 2006

EGU

tions for the iodine catalytic cycles. A similar pattern has been found by the science community for the ozone depletion by chlorine species (e.g., various WMO ozone assessments).

“Page 5178, line 10. “We find that iodine self-catalytic cycles dominate the ozone depletion mechanisms in the stratosphere” As it stands this is incorrect. I assume that the authors mean to say that the efficiency of the iodine catalalytic cycle on a per unit Xy (total inorganic halogen) basis is the largest.”

We meant “iodine self-catalytic cycles dominate the ozone depletion mechanisms in the stratosphere among the four iodine catalytic cycles”. Changes have been made accordingly.

“Table 1. It would be very useful for the Table to have rates at 300K and perhaps even more importantly if J values were given at 3 heights, say 0, 20 and 50 for overhead Sun.”

Reaction rates at 300K have been added to the Table 1. For J values, since it is dependent on temperature and incoming sun light, each grid box at same level in the model has a different value according to spatial position as well as temporal variation. Averages for a certain height are not representative. However, we have added J values at 30N in June and December for the three heights you mentioned.

“Minor stuff Page 5164, line 26. “that could destruct ozone dramatically” sounds excessively hyperbolic! Better to just remove or replace with something like “with a lifetime of about 65 years (WMO) so that tropospheric release will make its way into the stratosphere.”

We have modified the manuscript accordingly.

“Page 5166, line 1. Perhaps add after “in aircraft uses” “particularly as usage is increasing.”

We have modified the manuscript accordingly.

ACPD

6, S3308–S3314, 2006

“Page 5167, line 24 (see also p5169, line 8). “efficiently” I + ozone is slower than Br + ozone which is slower than Cl + ozone. I would prefer that efficiently is kept until there is some explanation of “rate limiting reactions” and halogen reservoir fraction etc.”

We have deleted “efficiently”.

“Page 5171, line 3-4; “due to the fact that”ˇEEˇ prefer “because the”

We have changed the manuscript.

“Page 5171, lines 15-17. “Catalytic cycles refer to Eˇ ..linked with ozone.” I don’t see (a) the point of and also (b) the necessity for the previous sentence.”

We have deleted the sentence.

“Page 5171, lines 25ff. Loss by catalytic cycles. Evaluation of the cycles is not always straightforward due to possible problems in identifying rate limiting steps and also the possibility of several channels. How were the cycle-strengths evaluated?”

The “cycle-strengths” were evaluated based on their rates of ozone destruction as shown in Figure 3. The rates were decided by the slowest chemical reaction rates within the cycles (i.e. rate-limiting steps). All the channels have been added together according to the group (one of the four iodine catalytic groups mentioned in the paper) they belong to.

“Page 5172, line 23. “Products with iodine will be removed” suggest “Products containing iodine are removed””

We have changed the sentence accordingly.

“Page 5172, line 24. “tiny fraction”. Can this be made a wee bit more quantitative?”

In the case of uniform surface emission in the Northern Hemisphere, about 0.1% CF3I gets to the stratosphere. The fraction values can be quite different for various emission profiles. It is found through our various tests that at most 1% of CF3I can reach the

ACPD
6, S3308–S3314, 2006

EGU

stratosphere finally.

“Page 5172, line 28ff. Exactly how is ODE defined? It is a big vague here.”

The ozone depletion efficiency (ODE) has been defined and explained in section 3.4. To account for all the ozone loss procedures (efficiency) involving a chemical, the formula is total local chemical reaction rates of iodine-related catalytic cycles divided by those of chlorine-related catalytic cycles on the per unit mass basis.

“Page 5173, line 24. “favorable” suggest “useful””

We have changed it.

“Page 5174, line 18. “strongly”. The difference in ozone depletion versus latitude etc is only a factor of two. Strongly seems a bit qualitative.”

“Strongly” has been deleted.

“Page 5174, section 4. Is it worth to briefly describe “fuel-inerting”?”

“Fuel-inerting” refers the safety action to protect fuel tank that contains highly flammable material, by pumping some inert gas or vapor into its air space in order to displace oxygen. This has been added to the manuscript.

“Page 5176, Figure 6. The scale of the figure and the contours are impossible to read (leastwise I had problems).”

This problem seems to happen because of the orientation of the figure. We will let the publisher know about this problem.

“Page 5176, line 10. “Due to the nature that ” try “Because””

We have changed it.

“Page 5177, line 2. “The calculation results” why not simply “The results”?”

We have changed it.

ACPD

6, S3308–S3314, 2006

“Page 5177, line 3. “tropicAL” “resultANT” spelling”

We have changed it.

“Page 5177, line 8. Very qualitative wording used again “deplete ozone severely etc””

“Severely” has been deleted.

“Page 5177, line 17. It is mentioned that OIO photolysis is uncertain - however this should be mentioned in the discussion on rate data at the beginning but detailed in the current section (6).”

Two sentences, “It should be noted that many iodine-related chemical reactions are still highly debatable (e.g. OIO photolysis.) This is discussed in detail later.”, have been added in the previous discussion on rate data with regard to this.

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