Atmospheric Chemistry and Physics Discussions

Interactive comment on "Kinetic isotope effects in the gas phase reactions of OH and Cl with CH$_3$Cl, CD$_3$Cl, and ^{13}CH$_3$Cl" by A. A. Gola et al.

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The following anonymous reviewer comments were recieved after the open discussion was closed.

This paper describes the determination of kinetic isotope effect (KIE) for reactions of Cl and OH with different isotopoanalogues of methyl chloride. The experiments presented in this paper are very important for both atmospheric chemists (methyl chloride budget) and physical chemists (kinetic isotope effect. I recommend this paper for publication in ACP, however I would like authors to address following comments:

1. The uncertainty presented in this paper came only from a statistical analysis. I

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would like authors to discuss and estimate sources of possible systematic errors. The uncertainty associated with these errors should be included in the final values quoted in abstract and table 1.

2. Is it possible that the photolysis of methyl chloride can compete with OH reaction? Did you do the "dark" test? i.e. mean photolysis of methyl chloride and air mixture without adding ozone. It is not mentioned in the text. Your light source most likely emits light at 185 nm, or maybe even at shorter wavelengths. At these wavelengths methyl chloride absorbs light. This could be an additional removal process for CH3Cl. It would not be important when OH concentrations were high. However, using air as a bath gas and reaction O(1D)+H2 as a source of OH radicals you generated high concentration of HO2 radicals, so high that the HO2+OH reaction might become important (HO2+O3 is slow). It would make steady state OH concentration low. What was your estimated OH concentration? With the low OH radicals concentration photolysis could compete in removing of CH3Cl. The low OH concentration will affect the removal process of CD3Cl more then removal of CH3Cl. This will lead to the underestimation of KIE.

3. Using air as a bath gas may possibly complicate the Cl+CH3Cl experiment too. Quite recently Tyndall et al. (Int. J. Chem. Kinet. 29 (1997) 655) and Blitz et al. (Chem. Phys. Lett. 365 (2002) 374) reported that OH can be formed in the reaction of CH3C(O) with O2. Would it be possible that CH2Cl radicals reacting with O2 generate OH? What yield of OH from CH2Cl + O2 reaction would influence your measurement?

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 3873, 2005.

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