

Interactive comment on “Laboratory study on heterogeneous decomposition of methyl chloroform on various standard aluminosilica clay minerals as a potential tropospheric sink” by S. Kutsuna et al.

Anonymous Referee #1

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General comments

This study is an extension of the previous study under the same title by Kutsuna et al. in *J. Geophys. Res.* **105** (2000) 6611-6620 (cited as Kutsuna et al., 2000a). The experimental set-up was not changed or improved. By increasing the number of substrates used from 4 to 23 previous results were confirmed but qualitatively no new results were obtained, and the conclusions are the same as in the previous paper. The analysis of the data was changed, however, since the determined pseudo-first-order rate constant seems to be of restricted reliability, the derived values for uptake coefficients, equilibrium constants, activation energies and adsorption heats should be regarded as

highly uncertain. Two formerly wrong citations were corrected and the new references (Levenspiel, 1999; Mahowald et al., 2002) were added to the list of references.

Specific comments

1. Pressure drop

- (a) The problem of pressure drop due to change in the circulation route was known from the previous study (Kutsuna et al., 2000a). Would it have been possible to insert a dummy volume in the by-pass route in order to reduce the pressure drop after changing the route (p. 1852, l. 17-25) and to increase the precision in the detection of the initial uptake process?
- (b) p. 1848, l. 22-27: What's the gas flow through the system? How long does it take for one round?
- (c) Please, add to Fig. 3 A an example for the signal drop in the absence of dust.
- (d) In Fig. 3 B, how can you be sure that the x-axis intercept ($-\Delta P_{MC}$) means a real loss of CH_3CCl_3 to the substrate (p. 1860, l. 20-22) and is not a consequence of the pressure drop? Please, say a few words about the equilibration of the system after changing the route.

2. Decay of CH_3CCl_3 :

- (a) Does the deviation from first-order-kinetics point to a more complicated uptake / equilibration mechanism or is it a consequence of the pressure drop and subsequent mixing?
- (b) The text says that P_0 is the pressure at $t = 0$ after beginning of contact (p. 1853, l. 20-21), but the red line representing the fit in Fig. 3 A starts at $t = 14$ min after beginning of contact; so P_0 actually is P_{14} , or is P_0 the pressure at $t = 0$ extrapolated from the fit?

- (c) It appears to me to be quite arbitrary to restrict the mono-exponential fit to $t = 14$ to 114 min (p. 1853, l. 18-20) just because it does not match the rest of the data points. If the deviation from first-order kinetics was due to the pressure drop, why does it take ca. 14 min at $T = 313$ K to come to first-order kinetics, but ca. 74 min at $T = 283$ K (Fig. 8 A and B; p. 1858, l. 13-14)?
- (d) I doubt that the application of mono-exponential fits to the data is valid. Please, justify the use of mono-exponential fits instead of more complicated ones, which take into account the competition between surface reaction and system equilibration, and discuss the implications for the error of k_1 (which should be bigger than $\pm\sigma$ of the fit).
3. Photodecomposition of $\text{CH}_2=\text{CCl}_2$ (p. 1853, l. 8-9):
- (a) Did you check the stoichiometry of $\text{CH}_2=\text{CCl}_2$ loss versus HCl production?
- (b) If photodecomposition of $\text{CH}_2=\text{CCl}_2$ took place heterogeneously on the dust surface (p. 1859, l. 2-4), why did you see release of HCl to the gas phase, in contrast to heterogeneous CH_3CCl_3 decomposition where HCl was retained by the dust surface? Or did you actually see gas-phase photolysis of $\text{CH}_2=\text{CCl}_2$?
- (c) What about production of CO and COCl_2 as reported in Kutsuna et al., 2000a?
4. p. 1854, l. 14-16: Is the montmorillonite sample used in the previous study identical to one of the samples used in the present study (all samples are from Iwamoto Mineral Co.; give API numbers for the previous study's samples)? If so, which conclusions can be drawn with respect to the reliability of the errors given in Table 1 (for most substrates just one experiment was performed)?
5. Uptake coefficient (p. 1855, l. 1):

- (a) What is the error of the uptake coefficient?
- (b) How does this value compare to the gammas given in Kutsuna et al., 2000a which are about one order of magnitude higher than the present ones?
- (c) Which lifetimes for CH_3CCl_3 with respect to decomposition on mineral dust do you calculate using this gamma? Please, compare to the results from section 3.4.1 and 3.4.2.
6. p. 1859, l. 2-27: Using a xenon lamp for photoillumination, you heat the sample due to the presence of IR light.
- (a) How much water release did you detect and what was the effect on homogeneous and heterogeneous chemistry in the reaction cell?
- (b) Can you be sure that the CH_3CCl_3 increase is due to CH_3CCl_3 desorption?
7. Fig. 11 and p. 1861-1862: What is the uncertainty in a_{MC} due to the pressure drop/system equilibration?
8. Please, give a more detailed explanation for the origin of the factors $1.71 \times 10^{-17} \text{ m}^2 \text{ Pa}$ (in eq. 13) and $1.17 \times 10^{-22} \text{ mol}$ (in eq. 16). A more detailed derivation of eq. 13 would be helpful, as well.

Technical corrections

- eq.s 14, 17: unit of T (even if it is clear that it must be K)
- Table 1 and Fig.s 5, 6, 8, and 11 are too small to be read.
- p. 1859, l. 13 and 16: "for most of clay minerals", " in most of the reactions" - cancel "of".

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- Please check if "adsorption constant" in your presentation of the Langmuir formalism really means "adsorption constant" and not "equilibrium constant" (e.g. p. 1861, l. 13; p. 1863 l. 23-24).

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