**Atmospheric Chemistry and Physics Discussions**

Interactive Comment

# *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.

**S. Kutsuna et al.**

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Major revised points: We have done the following two major revisions:

M1. The wrong numbers in Eqs.16 and 17 (p.1864, lines 12 and 17) are corrected.

M2. Physical meaning of $k_1$ and how to estimate lifetime using $k_1$ are described.

Details of these two main revisions are as follows.

M1. The wrong numbers in Eqs.16 and 17 are corrected (p.1864, lines 12 and 17):

The wrong factor of 1.17E-22 in Eq. 16 is corrected to 1.66E-24. The number of 4.53E-13 in Eq.17 is corrected to 6.43E-15. Lifetimes derived in the 3.4.1 and 3.4.2
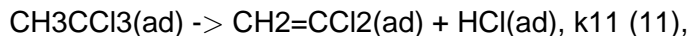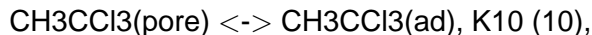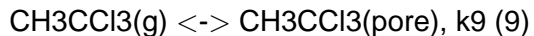
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sections are not changed because these lifetimes had been calculated with the correct equations.

M2. Physical meaning of k1 and how to estimate lifetime using k1 are described:

We assume that all the processes concerned can be approximated by linear processes under the steady state. This assumption seems to apply for illite (API no.35*), judging from the relation between the amount of CH3CCl3 adsorbed and the partial pressure of gaseous CH3CCl3 as shown in the 3.3.1 section.

In the 3.2.2 section, the activity of clay materials is compared via k1 and k1/s. The k1/s value represents a flux of gaseous CH3CCl3 to unit area of the clay surface. To simplify an explanation, only reactions on the surface in pores are considered. This simplification is reasonable because the surface area in pores is much larger than the surface area outside pores of most clay materials examined. The following reaction scheme will be used in the revised manuscript instead of the scheme (9)-(11) (p.1862, lines 9-11).

$CH3CCl3(g) <-> CH3CCl3(pore)$, k9 (9)

$CH3CCl3(pore) <-> CH3CCl3(ad)$, K10 (10),

$CH3CCl3(ad) -> CH2=CCl2(ad) + HCl(ad)$, k11 (11),

where k9 is a constant originating from diffusion of CH3CCl3 in pores; K10 is the adsorption equilibrium coefficient of CH3CCl3 in pores; k11 is the first-order surface reaction rate constant in pores; CH3CCl3(g) and CH3CCl3(pore) are gaseous CH3CCl3 outside and in pores, respectively; CH3CCl3(ad) is CH3CCl3 adsorbed on the surfaces in pores; and CH2=CCl2(ad) and HCl(ad) are CH2=CCl2 and HCl, respectively, adsorbed on the surfaces in pores.

Since the k11 value is much smaller than the adsorption rate and the desorption rate, equilibrium of CH3CCl3 between in air and on the surface can be estimated to be determined by K10. The steady state flux of CH3CCl3 to pores by diffusion (F) is

represented by Eq.(S1).

$F = k_9(PMC(g) - PMC(pore))$ (S1),

where $PMC(g)$ and $PMC(pore)$ are partial pressure of gas-phase $CH_3CCl_3$ (outside clay samples) and equilibrium partial pressure of $CH_3CCl_3$ adsorbed in pores. It is assumed that $CH_3CCl_3$ in pores is removed according to first-order kinetics by reactions on the inner surface of pores of clay minerals by Eq. (S2).

$dPMC(pore)/dt = -k_d PMC(pore)$ (S2),

where $k_d = k_{11} K_{10}$.

Since $F = -dPMC(pore)/dt = -k_1 PMC(g)$ at steady state, Eq.(S3) is obtained.

$1/k_1 = 1/k_9 + 1/k_d$ (S3).

The $k_9$ value is estimated to be $>1E-3$ s-1 at 313 K, because $CH_3CCl_3$ decayed according to first-order kinetics after 14 min-reaction period. In addition, the formation rate of $CH_2=CCl_2$ is measured to be almost same as the decay rate of $CH_3CCl_3$ except for the initial period after changing the gas-circulating route. These facts indicate that $k_1 << k_9$ and that $k_1$ is nearly equal to $k_d$. Physical meaning of $k_1$ is represented by Eq.(S3) on the assumption of the steady state and linear processes.

The lifetime cannot be calculated directly from the $k_1$ value, because the $k_1$ value is nonlinearly dependent on density of clay minerals. The $k_{clay}$ and $fMC'$ are needed to estimate lifetime of $CH_3CCl_3$. The $k_{clay}$ is the overall first-order rate constant of $CH_3CCl_3$ in and on the clay material and it is defined by Eq.(S4).

$d M(clay) /dt = - k_{clay} M(clay)$ (S4),

where $M(clay)$ represents total amount of $CH_3CCl_3$ adsorbed on the surface and in the pores of the clay material. When the $M(clay)$ value is proportional to partial pressure of gaseous $CH_3CCl_3$, the $k_{clay}$ and $fMC'$ value are represented by Eqs. (S5) and (S6) in the steady state.

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kclay = {(1 + fMC) / fMC } k1 (S5),

fMC = fMC' ns (S6),

where fMC is the mole fraction of CH3CCl3 adsorbed on the surface and in the pores of the clay material to CH3CCl3 in air (outside the clay material); and ns in m-1 is the surface area of clay minerals per unit volume of air.

In the 3.2.2 section, the kclay = {(1 + K) / K} k1, which is briefly described (p. 1855, line 6), is obtained by approximating fMC by K. On the other hand, in the 3.3.1 section, fMC' is experimentally determined on the basis of the data shown in Fig. 11, and kclay is calculated from the experimentally determined fMC' and k1. The experimentally determined fMC' and kclay for illite (API no.35*) in the 3.3.1 section are used to estimate lifetime of CH3CCl3 in the 3.4.1 and 3.4.2 sections. In Eq. 16 (p. 1864, line 12) in the 3.4.1 section, fMC' = KAMC R T.

to Specific comments

In Abstract, the physical meaning of n (p. 1844, lines 9-11):

The parameter n reflects the average pore size of clay minerals and small values of n mean that the average pore size is small. This is described in the abstract section of the revised manuscript.

Steps having taken to ensure that the results obtained in this study to real atmospheric conditions are described as follows:

These steps will be described as mentioned above (in the main revision [M2]).

Definition of parameters:

All parameters will be defined when used for the first time.

Physical meaning of the first-order rate constant, k1:

The rate-determining step is judged to be a surface reaction from the following reasons.

1. The decomposition rate of CH3CCl3 on clay minerals is too slow for gas-phase diffusion to be a rate-limiting step.

2. Except for the initial period, the amount of CH2=CCl2 formed was almost same as that of CH3CCl3 decreased.

Physical meaning of k1 will be described as mentioned above (in the main revision [M2]).

Effect of change in diffusion due to humidity:

The adsorption of CH3CCl3 is found to decrease with increasing relative humidity as shown in Fig. 13. The K value (p. 1853, line 24), which reflects the adsorption, decreases with increasing relative humidity. We consider that the inhibitory effect of water vapor is mainly attributed to competitive adsorption on the surface of water and CH3CCl3. This discussion will be added in the revised manuscript. Change in diffusion will also be evaluated by Eq. (S3), which is shown in the main revision [M2].

The results by each experimental set-up:

The second experimental set-up was used only in the experiment mentioned in part of the 3.3.2 section. The first experimental set-up was used for all the other experimental runs. This will be described in the Experimental section of the revised manuscript.

Effect of water diffusing through Teflon tube in the second experimental set-up:

As the referee indicates, water is considered to diffuse through Teflon. The main part of the reactor is about 10 cm long and the water diffusion through this part is insignificant. But the He flow passes through about 2 m long Teflon tube (1/8 inch in outer diameter) in water at 313 K before it is introduced to the reactor. In the previous study, increase of water in air flow at 400 mL min-1 by diffusion through Teflon is about 5 ppmv for 2 m long Teflon tube (4 mm in outer diameter) in water at 308 K. The increase in water pressure in our study is estimated at about 400 ppmv in He flow at flow rate of 5 mL min-1. The 400 ppmv of water vapor corresponds to 0.5 % of relative humidity at 313 K.

The possible relative humidity (about 1 %) will be mentioned in Fig.13D in the revised manuscript.

The number of Figures:

The number of Figures is not changed. The results obtained from Figures will be described more clearly in the revised manuscript.

Table 1:

Uncertainties of K are added. Errors represent +-s for N=1 and the standard deviation of the mean for N>1, where N is the number of the measurement.

Negative value of C:

The physical meaning of the C value is an indication of the magnitude of the adsorbent/adsorbate interactions. Since the C value must be positive, the negative C values obtained from Eq. 1 was the reason of using Eq. 2. This is stated in the 3.1 section but it will be more clearly stated in the revised manuscript.

The order of activity of clays in the reaction of CH3CCl3 is different from that in the reaction of fluorinated ethers (p.1854, line 23):

The order of activity of clays is different between the decomposition of CH3CCl3 and the decomposition of CHF2OCH2CF3 or CHF2OCH2C2F5. Although the k1 value in the reaction of CH3CCl3 is roughly proportional to the surface area, the k1 value in the reaction of these fluorinated ethers is not proportional to the surface area. The kaolinite has the relatively high activity in spite of its relatively small surface area. The reason for this difference is not obtained yet. The decomposition products of CHF2OCH2CF3 and CHF2OCH2C2F5 are HC(O)OCH2CF3 and HC(O)OCH2C2F5, respectively. These decomposition reaction should involve H2O or OH as a reagent, although these decomposition were inhibited by the presence of water. In contrast, The decomposition of CH3CCl3 does not related to H2O directly. The difference in the forms of H2O or OH on the clay surface may relate to the reactivity against the decomposition of CH3CCl3,

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CHF2OCH2CF3 and CHF2OCH2C2F5. This may be a possible reason.

Page 1858, line 22:

The weighting factor of each data is s2 of it. The two values of Ar and dEr /R were fitted. A non-linear least-squares method was performed by a commercial software of Origin ver. 7 using the Levenberg-Marquardt method.

Equation 9 (p.1862, line 9):

It is more possible than Eq. 9 that gaseous CH3CCl3 is first adsorbed and then it travels from a surface state to pores. Since the surface outside clay materials is much smaller than the surface in pores, the effect of this adsorption on the flux into pores and the reaction is expected to be small. This discussion will be added in the revised manuscript.

Technical corrections

Figures:

Readiness of Figures will be increased.

Reference:

WMO (Scientific Assessment of Ozone Depletion: 2002, 2003) was cited.

Page 1846, line 13: "Some of us" is changed to "Kutsuna et al. (2000a)".

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 1843, 2003.

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