Atmospheric Chemistry and Physics Discussions

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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According to the referees' comments, the manuscript has been revised. In addition to the revisions reported on May 26 and 27, there are new revisions. Some of them are related to mistakes in the calculation. Additional revisions are as follows.

1. The wrong numbers and the wrong calculation results have been corrected. Two data of k_1 and most of K in Table 1 are corrected. Lifetimes in Table 4 are corrected. The corrections are listed later [R1] .

2. New section '2.4 Data analysis' has been added. In Section 2.4, parameters of t, t_r, k_1, K, k_{clay}, Γ and f_{MC} were defined. How to derive these parameters and lifetime in sections 3.2, 3.3 and 3.4 are overviewed. The content of this section is shown later

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[R2].

3. The row of k_1/s is eliminated from Table 1. Two rows of k_{clay} and Γ are added in Table 1. k_{clay} means the overall surface rate constant and Γ means reaction probability at steady states. The k_{clay} and Γ values in Table 1 are listed in [R3]. Physical meaning of k_{clay} and Γ are described in Section 2.4. The activities of clay materials are compared via Γ instead of k_1/s. Fig. 6 plots Γ instead of k_1/s.

4. Eqs. 9-12 on page 1862 and the explanation have been revised. This is shown in [R4]. Flux of CH_3CCl_3 to the surface of the clay samples is described to be proportional to $k_{clay}f_{MC}$ as mentioned in Section 2.4, although it was reported to be proportional to k_1 in the revisions on May 26 and 27.

5. Section 3.4.2: Additional explanation has been added concerning the calculation of a in Eq. 21 on page 1866. The corresponding average mass concentration of clays in air below 1 m high on the ground surface (n'_m) has been explained. I had underestimated n'_m by a factor of 10, which resulted in wrong lifetimes in Table 4. The lifetimes corrected in Table 4 are listed in [R1].

[R1] Corrections of k_1 and K in Table 1 (page 1875): 10^5 k_1 for blank: -0.01 ± 0.08. An additional blank experiment was done. N is 2 for 'blank'.

$10^5 k_1$ for API no. 12: 12.9 (0.2).

(from the top column to the bottom column) $10^3 K$: $-12\pm$ 3, 42(15), 15(14), 8(16), 213(13), 35(14), -16(12), 171 ± 23, 253(20), 300(16), 286(17), 241(20), 93(18), 18(16), 10(25), 23 ± 10, 157(15), 266(32), 96(17), 84(17), 170(16), 218(17), 0 ± 28, 149 ± 50, 206 ± 60, 60 ± 8, -18(18), 7(16), 91(14), 14(14), 98(15).

The slopes k_1/s, K/s and $k_1(1 + K)$ deduced in Fig. 5 are 5.7×10^{-5} s^{-1} m^{-2} (R= 0.72), 5.4×10^{-2} m^{-2} (R = 0.85) and $(6.8 \pm 0.7) \times 10^{-10}$ s^{-1} (R = 0.78).

Corrections of lifetimes in Table 4 (page 1878):

case (i): (from the top to the bottom column) 2, 2, 2, 2 for the 1st row; 6, 6, 6, 6 for the 2nd row; 20, 20, 20, 20 for the 3rd row; 40, 20, 9, 5 for the 4th row; 100, 50, 20, 10 for the 5th row; 400, 200, 90, 50 for the 6th row; 400, 200, 80, 40 for the 7th row; 1000, 400, 200, 100 for the 8th row; blank, blank, 800, 400 for the 9th row.

case (ii): (from the top to the bottom column) 20, 8, 5, 3 for the 1st row; 40, 20, 10, 6 for the 2nd row; 200, 80, 50, 30 for the 3rd row; blank, 700, 300, 200 for the 4th row; blank, blank, 800, 400 for the 5th row; the others are blank.

case (iii): (from the top to the bottom column) 9, 5, 3, 3 for the 1st row; 20, 10, 8, 6 for the 2nd row; 90, 50, 30, 30 for the 3rd row; 800, 300, 200, 80 for the 4th row; blank, 800, 400, 200 for the 5th row; blank, blank, blank, 800 for the 6th row; blank, blank, blank, 800 for the 7th row; the others are blank.

[R2] New section '2.4 Data analysis' has been inserted after Section 2.3 (line 14, page 1850) as follows.

In Section 3.2, time course of partial pressure of CH_3CCl_3 was measured using the closed circulation reactor. Three measurements were carried out during 30 min before the CH_3CCl_3 - air mixture flowed over a clay sample. Let P_{init} (Pa) be the mean of partial pressures measured during this period. The CH_3CCl_3 - air mixture began to flow over the clay sample at 30 min. The sudden decrease in partial pressure of CH_3CCl_3 was observed by changing the gas circulation path. This was caused by gas adsorption on the clay sample and by changes in the circulation route that led to changes in the reactor volume. The volume change was calculated to correspond to a 23% decrease in partial pressure. The reaction time (t_r in minute) is defined as follows:

$$t_r = t - 30, \tag{1}$$

where t is time in minute after the CH_3CCl_3 - air mixture is introduced to the reactor without contact to the clay sample. The initial partial pressure of CH_3CCl_3 at $t_r = 0$ (P_{0init} in Pa) was calculated as follows:

$$P_{0init} = 0.77 \times P_{init} \tag{2}$$

The value of P_{0init} was used to estimate the equilibrium coefficient of CH_3CCl_3 between on the clay sample and in air as mentioned later [Eq. (4)]. After contact with the clay sample, CH_3CCl_3 decreased approximately according to first-order kinetics as

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shown in Section 3.2. The decay rate was evaluated by using the quasi-first-order rate constant k_1 in s^{-1}. That is, the k_1 value for each experiment was calculated by fitting the data at reaction time t_r (ranging from 14 to 114 min) to Eq. (3). The data at t_r = 4 min was not used because it did not obey first-order kinetics. The equilibrium did not seem to be achieved at t_r = 4 min.

$$P(t_r) = P_{0init} \exp[-k_1(60t_r)] \tag{3}$$

where $P(t_r)$ is the partial pressure of the CH$_3$CCl$_3$ at reaction time t_r; and P_{0init} in Pa is a fitting parameter. P_{0init} means the partial pressure of CH$_3$CCl$_3$ at t_r = 0 that is estimated by extrapolation of Eq. (3). The value is defined by Eq. (4), and the K value is given as an indication of the adsorptive activity of the clay samples for CH$_3$CCl$_3$:

$$K = (P_{0init} - P_{0fit})/P_{0fit} \tag{4}$$

The K value is the estimate of the equilibrium mole ratio of the amount of CH$_3$CCl$_3$ adsorbed to gaseous CH$_3$CCl$_3$ at t_r = 0. In Section 3.2, the activity of clay samples was evaluated by means of two new parameters (k_{clay} in s^{-1} and Γ) as well as k_1 and K. The parameter k_{clay} is the first-order overall rate constant of CH$_3$CCl$_3$ adsorbed on the surface and in the pores of clay materials [Eq. (5)].

$$da_{MC}/dt = -k_{clay}a_{MC} \tag{5}$$

where a_{MC} in molecules is the total amount of CH$_3$CCl$_3$ adsorbed on the surface and in the pores of the clay sample. The parameter Γ represents reaction probability at the steady state under the experimental condition. The k_{clay} and Γ values are expressed as Eqs. (6) and (7), respectively.

$$k_{clay} = \frac{1 + K}{K}k_1 \tag{6}$$

$$\Gamma = \frac{4V}{sv}(1 + K)k_1 \tag{7}$$

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where V is the volume of the closed circulation reactor used (8.5×10^{-4} m^3); s is the surface area of the clay sample (m^2); and v is the mean molecular velocity of CH$_3$CCl$_3$ (m s^{-1}). Eqs. (6) and (7) are derived as follows. Let f_{MC} be the mole fraction of a_{MC} to CH$_3$CCl$_3$ in air (outside the clay sample) under equilibrium condition. On the assumption of the steady state and a linear process, k_{clay} is written as Eq. (8).

$$k_{clay} = \frac{1 + f_{MC}}{f_{MC}} k_1 \qquad (8)$$

The product $k_{clay}f_{MC}$ value is proportional to a flux of gaseous CH$_3$CCl$_3$ to the clay surface at the steady state. The k_{clay} value and the reaction probability (γ) satisfies Eq. (9);

$$V k_{clay} f_{MC} = \frac{1}{4} \gamma s v \qquad (9)$$

Substituting Eq. (8) into Eq. (9) gives Eq. (10).

$$\gamma = \frac{4V}{sv}(1 + f_{MC})k_1 \qquad (10)$$

In Section 3.2, f_{MC} was approximately replaced by K. Substituting $f_{MC} = K$ into Eqs. (8) and (10) gives Eqs. (6) and (7), respectively. Γ was used instead of γ because Γ was the reaction probability obtained on the above assumption. On the other hand, in Section 3.3, k_{clay} and γ were calculated by Eqs. (8) and (10), respectively. That is, it was not assumed that $f_{MC} = K$. The amount of CH$_3$CCl$_3$ adsorbed (a_{MC}) on illite (API no. 35*) samples was plotted against partial pressure of CH$_3$CCl$_3$ (P_{MC}) at t_r = 4 - 174 min. It was found that a_{MC} was almost proportional to P_{MC} in the reaction on the illite (API no. 35*) except for the data during initial reaction periods. The f_{MC} value was given as the slope a_{MC}/P_{MC}. Temperature dependence of k_{clay} and f_{MC} was also determined for the reaction on the illite (API no. 35*). In Section 3.4, the lifetime of CH$_3$CCl$_3$ through the reaction on dusts or on ground surfaces was estimated. The estimation was based on the k_{clay} and f_{MC} values determined for the illite (API no.

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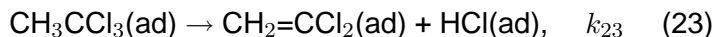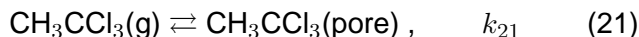Print Version

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35*) in Section 3.3. The lifetime was estimated on the assumption that the equilibrium of CH_3CCl_3 between in air and on clay minerals was achieved. Since the reactions of CH_3CCl_3 on clay minerals were slow ($\gamma \approx 10^{-9}$), this assumption was reasonable.

[R3] New rows (k_{clay} and Γ) in Table 1 (page 1875).

10^5 k_{clay} : (from the top to the bottom) blank, 67(25), 190(186), 121(242), 74(5), 109(42), -3(8), 281±108, 145(13), 72(5), 79(5), 137(12), 76(15), 58(54), 107(272), 75±34, 25(3), 59(8), 84(16), 67(14), 112(11), 117(10), blank, 144±57, 151±70, 51±8, 14(17), 40(96), 41(6), 41(43), 386(59).

10^{10} Γ: (from the top to the bottom) blank, 4.6(0.2), 3.2(0.1), 3.4(0.4), 8.4(0.2), 3.0(0.1), 0.8(1.8), 13.8±5.0, 11.1(0.4), 7.6(0.3), 7.3(0.3), 13.6(0.5), 6,4(0.3), 1.7(0.4), 1.2(0.3), 2.6±0.3, 3.3(0.3), 6.7(0.3), 7.5(0.3), 9.7(0.6), 14.9(0.4), 11.7(0.3), 34±16, 10.3±2.1, 13.4±4.9, 2.0±0.2, -4.6(3.2), 0.5(0.2), 3.8(0.1), 0.9(0.2), 4.7(0.1).

[R4] Revisions for Eqs. 9 - 12 and the explanation (page 1862) are as follows. In order to consider the temperature-dependence of adsorption and surface reaction separately, we simplified the reaction scheme as follows:

CH_3CCl_3(g) $\rightleftarrows$ CH_3CCl_3(pore) , k_{21} (21)

CH_3CCl_3(pore) $\rightleftarrows$ CH_3CCl_3(ad) , K_{22} (22)

CH_3CCl_3(ad) $\rightarrow$ CH_2=CCl_2(ad) + HCl(ad), k_{23} (23)

CH_2=CCl_2(ad) $\rightleftarrows$ CH_2=CCl_2(g),   (24)

where k_{21} is a constant originating from diffusion of CH_3CCl_3 in pores; K_{22} is the adsorption equilibrium coefficient of CH_3CCl_3 in pores; k_{23} is the first-order surface reaction rate constant in pores; CH_3CCl_3(g) and CH_3CCl_3(pore) are gaseous CH_3CCl_3 outside and in pores, respectively; CH_3CCl_3(ad) is CH_3CCl_3 adsorbed on the surfaces in pores; and CH_2=CCl_2(ad) and HCl(ad) are CH_2=CCl_2 and HCl, respectively, adsorbed on the surfaces in pores. 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. Since the k_{23} value is much smaller than the adsorption rate and the desorption rate, equilibrium of CH_3CCl_3 between in air and on the surface can be expected to be determined by K_{22}. The steady state flux of CH_3CCl_3 to pores by diffusion (F_{diff}) is represented by Eq. (25).

$$F_{diff} = k_{21} \left(P_{MC(g)} - P_{MC(pore)} \right), \qquad (25)$$

where $P_{MC(g)}$ and $P_{MC(pore)}$ are partial pressures 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. (26).

$$\text{d } P_{MC(pore)}/\text{dt} = - k_d P_{MC(pore)}, \qquad (26)$$

where $k_d = k_{23} K_{22}$. Since $F_{diff} = - \text{d}P_{MC(pore)}/\text{dt} = - k_{clay} f_{MC} P_{MC(g)}$ at steady state, where k_{clay} and f_{MC} are defined in Section 2.4, Eq. (27) is obtained:

$$(k_{clay} f_{MC})^{-1} = k_{21}^{-1} + k_d^{-1} . \qquad (27)$$

Substituting Eq. (8) to Eq. (27) gives Eq. (28):

$$(1 + f_{MC})^{-1} k_1^{-1} = k_{21}^{-1} + k_d^{-1} . \qquad (28)$$

The k_{21} value is estimated to be $> 10^{-3}$ 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 $k_1 << k_{21}$ and that $(1 + f_{MC}) k_1$ is nearly equal to k_d. Physical meaning of k_1 is represented by Eq. (28) on the assumption of the steady state and linear processes as shown in schemes 21 - 24. In this scheme, under quasi-equilibrium conditions, the equilibrium mole ratio f_{MC}, which is defined in Section 2.4, is represented as follows:

$$f_{MC} = 1.71 \times 10^{-17} \, K_H^{MC}, \qquad (29)$$

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where the factor 1.71×10^{-17} in m^2 Pa is a result of the units used in Eq. (29). Substituting Eq. (29) to Eq. (8) gives Eq. (30):

$$k_{clay} = (1 + 5.85 \times 10^{16}\ K_H^{MC-1})\ k_1. \qquad (30)$$

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