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Atmospheric
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Discussions

Interactive comment on “Aqueous-phase ozonolysis of methacrolein and methyl vinyl ketone: a potentially important source of atmospheric aqueous oxidants” *by* Z. M. Chen et al.

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We thank Prof. Herrmann very much for his constructive comments. Here are our responses to the comments:

The rate constants for OH and NO_3 reactions with unsaturated first-generation oxidation products of isoprene can well be estimated as near-diffusion controlled. The concentration levels of either radical could be taken from any aqueous phase modeling study. With both parameters available, lifetimes and sink strengths can be compared and should be discussed.

This is a good suggestion. Our comparison and discussion are complemented as following.

In the atmospheric aqueous phase, MAC and MVK may be oxidized potentially by O_3, OH radicals, and NO_3 radicals. On the basis of the rate constants and concentration levels of these oxidants, their relative importance in the oxidation of MAC and MVK can be compared with the lifetimes, as shown in Table 1.

From the lifetimes in the bulk of droplets estimated in Table 1, it seems to be seen that in the daytime, the OH radicals would dominate the oxidation of MAC and MVK, and in the nighttime when the OH concentration is very low, the O_3 would dominate or compete with NO_3 radicals. As can be seen from the abovementioned data, however, up to date, there are no enough studies for the aqueous-phase rate constants for the oxidation of MAC and MVK(Lilie and Henglein, Ber. Bunsenges. Phys. Chem. 74, 388-393, 1970; Kumar et al., J. Macromol. Sci. Chem. A27, 299-308, 1990; Pedersen and Sehested, Int. J. Chem. Kinet. 33, 182-190, 2001). Obviously, more studies for the accurate aqueous-phase rate constants are needed to evaluate the relative importance of the three kinds of oxidants in the oxidation of MAC and MVK in the atmospheric aqueous phase.

The aqueous-phase reaction includes not only the reaction in the bulk of droplets but also the reaction on the surface of droplets, as shown in Fig. 6 in the text, and especially, the latter may be more important and more ubiquitous than the former in the atmosphere. Based on the aqueous-phase reaction rate constants and the mass accommodation coefficients (α) of oxidants, the lifetimes of MAC and MVK reaction with oxidants on the surface of droplets may be estimated as following.

The uptake rate of the absorbate OX (r_a=d{OX}/dt; here OX indicates an oxidant) by droplets can be given in eq. (1):

$$r_a = \frac{d\{OX\}}{dt} = \alpha Z \tag{1}$$

$$Z = \frac{1}{4}\bar{c}A_s[OX] \tag{2}$$

$$\bar{c} = \sqrt{\frac{8RT}{\pi M_{OX}}} \tag{3}$$

where Z is the rate of collisions between the gaseous molecules and droplet surface, α is the mass accommodation coefficient of oxidant, $\bar{c}$ is the mean molecular velocity of the gas molecules, A$_s$ is the effective surface area of droplets, R is the gas constant, T is the temperature and M$_{OX}$ is the molecular weight of the oxidant. {OX} indicates the concentration of oxidant on the surface of droplets, whereas [OX] indicates the gas-phase concentration of oxidant.

We can obtain:

$$r_a = \frac{d\{OX\}}{dt} \propto \alpha\frac{[OX]}{\sqrt{M_{OX}}} \tag{4}$$

If at the beginning the surface concentration of oxidant were zero, then the concentration at time t is

$$\{OX\} \propto \frac{[OX]}{\sqrt{M_{OX}}}t \tag{5}$$

By combining the aqueous-phase rate constants in Table 2 with eq. (5), the ratio of the lifetimes of MAC and MVK reaction with different oxidants on the surface of droplets can be estimated as:

$$\tau_{MAC-O3}:\tau_{MAC-OH}:\tau_{MAC-NO3}=$$

$$\frac{1}{\{O_3\}k_{MAC-O3}} : \frac{1}{\{OH\}k_{MAC-OH}} : \frac{1}{\{NO_3\}k_{MAC-NO3}} \tag{6}$$

τ_{MVK-O3}:τ_{MVK-OH}:$\tau_{MVK-NO3}$=

$$\frac{1}{\{O_3\}k_{MVK-O3}} : \frac{1}{\{OH\}k_{MVK-OH}} : \frac{1}{\{NO_3\}k_{MVK-NO3}} \tag{7}$$

The lifetime ratio results are shown in Table 1. It can be seen, unlike the case in the bulk, that the O_3 oxidation is comparable with the OH oxidation for MAC and MVK on the surface of droplets, whereas the NO_3 oxidation is negligible. Obviously, this conclusion should be further evaluated using the more accurate parameters such as mass accommodation coefficients and aqueous-phase rate constants. Although there is a great uncertainty, we suggest that the O_3 oxidation of MAC and MVK is significant in the atmospheric aqueous phase.

We will add these discussions and references into the revised manuscript.

Table 1: Comparison of atmospheric lifetimes of MAC and MVK reaction with different oxidants on the surface and in the bulk of droplets.

	MAC			MVK		
	O_3	OH	NO_3	O_3	OH	NO_3
$[OX]_g(cm^{-3})$	7e11	1.6e6	5e8	7e11	1.6e6	5e8
$H(M\ atm^{-1})^a$ 298K	1.14e-2	25	0.6	1.14e-2	25	0.6
$[OX]_{a,e}(M)^g$	3.4e-11	1.8e-12	7.6e-13	3.4e-11	1.8e-12	7.6e-13
α^b	0.05	0.05	4e-3	0.05	0.05	4e-3
Molecular weight	48	17	62	48	17	62
$k(M^{-1}\ s^{-1})$	$2.1e4^c$	$5.8e9^d$	1e3–1e6^f	$4.4e4^c$	$8.5e9^e$	1e3–1e6^f
τ_{bulk}(h)	340	0.027	365–365000	186	0.018	365–365000
τ_{surf} ratio	1	1.1	4.8e2–4.8e5	1	1.4	8.8e2–8.8e5

where $[O_3]_g$, the 24 h daytime and nighttime average concentration of O_3 in the troposphere; $[OH]_g$, the 12 h daytime average concentration of OH radicals in the troposphere; $[NO_3]_g$, the 12 h nighttime average concentration of $[NO_3]$ radicals in the troposphere. [a], Ervens et al., J. Geophys. Res. 108 (D14), 4426, 2003; [b], Ervens et al., 2003; [c], Pedersen and Sehested, Int. J. Chem. Kinet., 33, 182–190, 2001; [d], In analogy with $CH_3CH{=}CHCHO$, (Lilie and Henglein, 1970); [e], Lilie and Henglein, 1970; [f], estimated from other organic compounds, Herrmann et al.,Atmos. Environ. 39, 4351–4363, 2005 ; [g], $[OX]_{a,e}$ aqueous-phase concentrations of oxidants at the gas-aqueous equilibrium.