Heterogeneous Reactions of Methacrolein and Methyl Vinyl Ketone on α -Al₂O₃ Particles

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The heterogeneous reactions of methacrolein (MAC) and methyl vinyl ketone (MVK) on α-Al₂O₃ surfaces have been studied in a flow reactor using transmission-Fourier Transform Infrared (T-FTIR) spectroscopy to monitor the reaction progress. Unlike SiO₂ particles where MAC and MVK are weakly physisorbed, the results in this work demonstrate that on α-Al₂O₃ particles MAC and MVK are irreversibly adsorbed and can rapidly react on the surface to form various products such as aldehydes, organic acids, hydrogen peroxide, and even higher molecular weight compounds. The initial uptake rates and initial uptake coefficients for MAC and MVK on α -Al₂O₃ under dry conditions were determined to explore the reactivity of the particles. Furthermore, the effect of water vapor on the heterogeneous reactions was also investigated as a function of relative humidity. Both the heterogeneous uptake and transformation of MAC and MVK on α -Al₂O₃ were largely suppressed under humid conditions due to the depletion of surface active sites by water molecules. On the basis of experimental results, atmospheric implications of heterogeneous reactions of MAC and MVK were discussed. Our work suggests that heterogeneous reactions on α -Al₂O₃ can be important sinks for MAC and MVK as well as possible contributors to atmospheric organic aerosol.

Introduction

Mineral dust represents a major component of atmospheric aerosol in the troposphere (1). A lot of attention has been paid to mineral particles due to its potential effect on atmospheric heterogeneous chemistry and climate change (2, 3). Mineral particles can encounter various environments through long-range transport in the atmosphere. Field observations have shown that there exist strong interactions between the mineral particles and various gaseous species, and sulfate and nitrate as well as organic coatings are often observed in the mineral particles or agglomerates (4-6). These findings indicated that heterogeneous reactions appear to play a critical role in atmospheric processing of mineral particles. In recent years, a number of laboratory studies have focused on the heterogeneous reactions of SO_x and NO_x on various types of mineral particles, and significant advances have been made in both kinetics and mechanisms of these reactions and their global impacts (see the reviews in refs 2 and 7).

However, little is known about the heterogeneous reactions of organic compounds with mineral particles. Quite recently, a few laboratory studies have begun to explore the heterogeneous chemistry of several simple volatile organic compounds (VOCs) on mineral particles (8–13). These works suggested that heterogeneous reactions of simple VOCs on mineral particles may play an important role in atmospheric chemistry.

As two major first-generation products in the oxidation of isoprene, methacrolein (MAC) and methyl vinyl ketone (MVK) are of great interest due to their large global abundance (14, 15) and high reactivity (16). However, previous studies on MAC and MVK mainly focused on their gas-phase and aqueous phase reactions (16–20), and their heterogeneous fates on atmospheric aerosols are still unclear although these processes are expected to have potentially significant impact on the Earth's atmosphere.

In the present study, we explored the heterogeneous reactions of MAC and MVK on the surface of α -Al $_2$ O $_3$ particles, a major oxide constituent of mineral dust, at room temperature and various relative humidity (RH) values. To the best of our knowledge, there have been no reports regarding heterogeneous reactions of these two unsaturated carbonyls on the surface of active mineral constituents, such as α -Al $_2$ O $_3$.

Experimental Section

Experimental Apparatus. The heterogeneous reactions of MAC and MVK were carried out in a flow reactor using transmission-Fourier Transform Infrared (T-FTIR) spectroscopy to monitor the reaction progress. A 250-mesh stainless steel circular grid coated with particle sample was mounted in the center of the reactor to provide the location of the heterogeneous reaction. A FTIR spectrometer (Nicolet Nexus, USA) equipped with a MCT-B detector was used to collect the infrared spectra of the particle phase throughout the frequency range between 4000 and 600 cm⁻¹. IR spectra were recorded at a resolution of 4 cm⁻¹, and 64 scans were averaged for each spectrum. More details about the experimental apparatus can be found in our previous study (*21*).

Data Analysis. In the present study, the carbonyl compounds were analyzed by determining their derivatives of 2,4-dinitrophenyhydrazine (DNPH) with high-performance liquid chromatography (HPLC) instrument (Agilent 1100, USA) equipped with an ultraviolet detector. The peroxide compounds were determined on the basis of fluorescent analysis by another HPLC instrument (Agilent 1100, USA) with postcolumn derivation, involving the hemin-catalyzed oxidation of peroxides to a fluorescent derivative using hydroxyphenylacetic acid. The organic acids were analyzed using ion chromatography (IC) (DIONEX 2650, USA) with an ED50 conductivity detector. The details about the analysis methods can be found in our previous work (*21*), and the detection limits are presented in the Supporting Information.

In addition, a HP 1100 LC-MS Trap SL System (Agilent, USA) consisting of a series 1100 HPLC and an ion trap mass spectrometer equipped with electro-spray interface (ESI) was used to determine the higher molecular weight compounds (HMCs) extracted from the particle phase. The chromatographic separations were performed on a Zorbax Eclipse XDB-C₁₈ LC column (Agilent 150 \times 2.1 mm, particle size 5 μ m, pore size 80 Å) at 40 °C, and the mobile-phase was a methanol/water mixture (40/60, v/v) at a flow rate of 1.2 mL min $^{-1}$. The electro-spray ionization was performed in the positive ion mode under optimum conditions as follows: capillary voltage 3500 V, nebulizer pressure 35.0 psi, dry gas flow rate 8.0 L min $^{-1}$, and dry gas temperature 330 °C. Full

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scan mode was used to acquire the MS spectra of the HMCs with a scan range of m/z from 35 to 300.

Experimental Procedures. The α -Al₂O₃ powder (Alfa Aesar, 99.9%), ~15 mg, with a Brunauer-Emmett-Teller (BET) surface area of 32.8 m²/g and mean particle diameter around 40 nm, was evenly coated onto a 250-mesh stainless steel circular grid, which was then mounted inside the reactor. At the beginning of all experiments, the α -Al₂O₃ powder on the grid inside the reactor was evacuated at room temperature for \sim 1 h to remove the physisorbed impurities. Then, the dry or humid synthetic air was introduced into the reactor at a rate of 400 standard cubic centimeters per minute (sccm). After the surface of α-Al₂O₃ particles was saturated by the dry or humid air, a background spectrum of the particle sample was collected. Subsequently, the uptake experiments for MAC and MVK were performed. The dry or humid organic reactant-containing airflow was introduced into the reactor at a rate of 400 sccm. The in situ T-FTIR spectra of α-Al₂O₃ particles were recorded to monitor the reaction progress until the surface saturation was achieved. All of the experiments were carried out at room temperature and in the dark. After the reaction was completed, the grid with the α-Al₂O₃ particles was quickly immersed in 5 mL of an acetonitrile solution to extract the carbonyl compounds or HMCs. Similarly, instead of the acetonitrile solution, the 1 mM H₃PO₄ solution or ultrapure water was used to trap the peroxides or organic acids. The gas-phase products was collected with the Horibe tube in the cold trap of ethanol-liquid nitrogen at \sim -90 °C and then was eluted using 10 mL of the corresponding solvents. The resulting solutions were then analyzed by the methods described above. The sources and purity grades of all chemicals used in this work are presented in the Supporting Information.

Results and Discussion

Uptake of MAC and MVK onto α-Al₂O₃ Particles in Dry Air. The heterogeneous uptake of MAC and MVK onto the surface of α-Al₂O₃ particles was investigated at first in dry air (RH <1%). Figure 1 shows the infrared spectra of $\alpha\text{-}Al_2O_3$ particles following exposure to 1.5×10^{15} molecules cm⁻³ gaseous MAC and 1.1×10^{15} molecules cm⁻³ gaseous MVK. In contrast to the spectrum for adsorption of MAC onto SiO₂ particles (see Figure 1 a3), where the MAC molecules are physisorbed without chemical transformation (21), several new adsorption bands were observed in the spectra for adsorption of MAC onto α-Al₂O₃ particles. These new absorption bands increased continuously in intensity with the exposure time, while the characteristic MAC absorption bands at 1679 cm⁻¹ and 1314 cm⁻¹ gradually decreased. This suggests that MAC can transform into other species when adsorbed onto α-Al₂O₃ particles. Similar striking changes also occurred during the adsorption of MVK onto α -Al₂O₃ particles. As shown in Figure 1b, in addition to the characteristic adsorption bands of MVK at 1670 cm⁻¹, 1617 cm⁻¹, 1409 cm⁻¹, and 1371 cm⁻¹, there are many new adsorption bands in the spectra of α-Al₂O₃ particles following exposure to MVK, indicating that MVK can also undergo heterogeneous reactions on the surface of α-Al₂O₃ to yield various products. The infrared spectra of α-Al₂O₃ particles appear not to change any more after 180 and 60 min of exposure to MAC and MVK, respectively, when the heterogeneous reactions were completed.

We determined the three kinds of products offline, namely, low molecular weight carbonyls, organic acids, and peroxides, collected in both particle and gas phase, using HPLC and IC. The absolute yields of products formed in the heterogeneous reactions of MAC and MVK on $\alpha\text{-Al}_2O_3$ are listed in Table 1. The absolute yield here is expressed as the amount of each product produced by unit surface area (the BET surface area of particles was used here) of $\alpha\text{-Al}_2O_3$ particles. As will be discussed below, the formation of these various species on

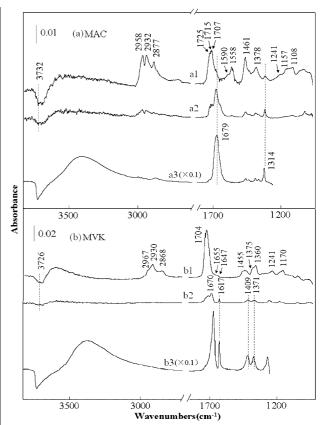


FIGURE 1. T-FTIR spectra of α -Al $_2O_3$ particles following exposure to (a) MAC and (b) MVK in dry air. The spectra of these two carbonyl compounds on SiO $_2$ particles under similar conditions are given as a comparison. a1. 180 min exposure of α -Al $_2O_3$ to MAC; a2. 2 min exposure of α -Al $_2O_3$ to MAC; a3. 150 min exposure of SiO $_2$ to MAC; b1. 60 min exposure of α -Al $_2O_3$ to MVK; b2. 2 min exposure of α -Al $_2O_3$ to MVK; b3. 150 min exposure of SiO $_2$ to MVK.

 $\alpha\text{-}\mathrm{Al}_2\mathrm{O}_3$ particles can be further confirmed by the spectroscopic data.

The intense absorption bands between 1700 cm⁻¹ and 1730 cm⁻¹ in the spectra are associated with C=O stretching vibrations, suggesting that aliphatic carbonyl compounds such as aldehydes and organic acids are significant products of heterogeneous reactions of MAC and MVK on α-Al₂O₃. In the spectra of α-Al₂O₃ following exposure to MAC, the absorption bands at 1590 cm⁻¹ and 1378 cm⁻¹ are assigned to $v_{as}(COO)$ and $v_{s}(COO)$ of formate species (11, 22), respectively, and the bands at 1558 cm⁻¹ and 1461 cm⁻¹ can be attributed to $v_{as}(COO)$ and $v_{s}(COO)$, respectively, for adsorbed acetate (23, 24). The weak bands between 1675 cm⁻¹ and 1600 cm⁻¹ with features at 1655 cm⁻¹ and 1647 cm⁻¹ observed in the spectra for adsorption of MVK on α-Al₂O₃ can be attributed to the C=O and C=C stretching vibrations of adsorbed crotonaldehyde (8, 24, 25). There is also evidence for aliphatic carbon in various adsorbed species on α-Al₂O₃. Absorption bands between 2800 cm⁻¹ and 3000 cm⁻¹ are assigned to aliphatic C-H stretching vibrations, and the absorption bands at 1375 cm⁻¹ and 1455 cm⁻¹ are assigned to aliphatic C-H bending vibrations (22-24). Absorption bands below 1300 cm⁻¹ may be associated with C-C or C-O bonds of adsorbed species (24, 25).

Previous studies have shown that the carbonyl compounds adsorbed onto $\alpha\text{-}Al_2O_3$ surfaces can undergo heterogeneous reactions due to the high reactivity of surface sites (8, 9, 11, 22). In addition to surface hydroxyl groups, two types of surface defect sites, i.e. oxygen and aluminum vacancies, are found on $\alpha\text{-}Al_2O_3$ surfaces. However, in dry air the clean $\alpha\text{-}Al_2O_3$

TABLE 1. Absolute Yields of Products Measured on the Particles and in the Gas Phase from Heterogeneous Reactions of MAC and MVK on the Surface of α -Al₂O₃ at Various RH Values

	dry (<1% RH)		20% RH		60% RH					
	P ^a	G ^b	Р	G	Р	G				
Absolute Yields (10 ¹⁶ molecules m ⁻²) of Products Formed during Heterogeneous Reactions of MAC										
CH ₃ CH ₂ CHO	0.483 ± 0.112	136 ± 17	0.155 ± 0.012	107 ± 21	_c	62.9 ± 7.1				
HCHO	_	36.1 ± 15.1	_	27.2 ± 8.3	_	18.5 ± 5.2				
CH ₃ CH ₂ COOH	2.31 ± 0.07	1.13 ± 0.12	0.371 ± 0.039	_	0.047 ± 0.033	_				
CH₃COOH	1.05 ± 0.51	1.17 ± 0.66	0.251 ± 0.095	_	0.032 ± 0.016	_				
НСООН	$\textbf{5.82} \pm \textbf{0.02}$	3.41 ± 1.51	$\textbf{0.724} \pm \textbf{0.072}$	$\textbf{0.063} \pm \textbf{0.030}$	$\textbf{0.083} \pm \textbf{0.025}$	_				
Absolute Yields (10 ¹⁶ molecules m ⁻²) of Products Formed during Heterogeneous Reactions of MVK										
CH ₃ CH=CHCHO	0.409 ± 0.070	103 ± 26	0.332 ± 0.081	52.1 ± 17.2	0.130 ± 0.046	18.8 ± 6.2				
СНОСНО	0.850 ± 0.244	8.78 ± 1.07	0.212 ± 0.047	2.82 ± 0.25	0.164 ± 0.053	2.13 ± 0.35				
CH₃CHO	0.613 ± 0.242	4.99 ± 0.90	0.207 ± 0.066	1.35 ± 0.44	_	1.01 ± 0.48				
НООССООН	0.012 ± 0.009	_	0.008 ± 0.003	_	_	_				
CH₃COOH	1.79 ± 0.68	7.40 ± 2.03	0.853 ± 0.141	0.216 ± 0.068	0.618 ± 0.081	0.124 ± 0.053				
H_2O_2	$\textbf{0.516} \pm \textbf{0.042}$	_	$\textbf{0.262} \pm \textbf{0.059}$	_	0.317 ± 0.022	_				

^a The absolute yields of products measured in the particle phase. ^b The absolute yields of products measured in the gas phase. ^c No products formed or below the detection limit of techniques.

surface is dominated by aluminum atoms (namely, oxygen vacancies) showing Lewis acidic properties (26–28), and carbonyl compounds adsorbed on acidic aluminum sites can react with surface active O atoms to yield various species (11, 22). On the basis of the above mechanism and products analysis, we postulate that surface active O atoms are likely to attack the C=C group of MAC molecules adsorbed on acidic aluminum sites to form formaldehyde and propionaldehyde as follows:

$$\begin{aligned} \mathrm{CH_2} &= \mathrm{C(CH_3)CHO_{ads}} + \mathrm{O_{ads}} + \mathrm{2Al} - \mathrm{OH_{ads}} \rightarrow \\ &\quad \mathrm{HCHO_{ads}} + \mathrm{CH_3CH_2CHO_{ads}} + \mathrm{2Al} - \mathrm{O_{ads}} \end{aligned} \tag{1}$$

It is reported that the adsorbed aldehydes on $\alpha\text{-}Al_2O_3$ particles can be oxidized to the corresponding carboxylates by active O atoms (11, 22), through reaction 2 and 3. Thus, formic and propionic acids are expected to be formed through further oxidation of adsorbed formaldehyde and propionaldehyde on $\alpha\text{-}Al_2O_3$, respectively. In addition, considerable amounts of acetic acid were also observed both in the gas phase and on the particles, but its formation pathway needs to be further studied.

$$R - CHO_{ads} + O_{ads} \rightarrow R - HC(O)O_{ads}$$
 (2)

$$R - HC(O)O_{ads} + O_{ads} \rightarrow RC(O)O_{ads} + OH_{ads}$$
 (3)

Surprisingly, MVK molecules appear not to undergo similar reaction proposed for MAC on $\alpha\text{-}Al_2O_3$ since the expected formaldehyde, acetone, or methylglyoxal were not observed during the reaction. Instead, the crotonaldehyde was detected as the predominant carbonyl product in the MVK— $\alpha\text{-}Al_2O_3$ reaction. After excluding its formation by the possible gas phase reaction based upon the $\alpha\text{-}Al_2O_3\text{-}free$ blank experiment and by the isomerization of MVK during the derivatization reaction with DNPH for HPLC analysis (29), we propose that crotonaldehyde is probably formed through the MVK isomerization on the surface of $\alpha\text{-}Al_2O_3\text{:}$

$$\mathrm{CH_2} = \mathrm{CHC(O)CH_{3(ads)}} \xrightarrow{\mathrm{isomerization}} \mathrm{CH_3CH} = \mathrm{CHCHO_{ads}}$$

(4)

However, MVK isomerization cannot occur on SiO_2 because of its much lower surface reactivity than α -Al₂O₃ (21).

As shown in Table 1, acetaldehyde and glyoxal are also generated from the heterogeneous reactions of MVK on

 α -Al₂O₃, possibly arising from the further oxidation of crotonaldehyde by surface active O atoms:

$$\label{eq:chochade} \text{CH}_3\text{CH} = \text{CHCHO}_{\text{ads}} + 2\text{O}_{\text{ads}} \rightarrow \text{CH}_3\text{CHO}_{\text{ads}} + \\ \text{CHOCHO}_{\text{ads}} \quad (5)$$

As expected, acetaldehyde and glyoxal remaining on the surface of $\alpha\text{-}Al_2O_3$ can also further transform into acetic acid and oxalic acid, respectively. In addition, hydrogen peroxide is also produced by the heterogeneous reactions of MVK on $\alpha\text{-}Al_2O_3$, probably due to the combination of surface OH groups.

The relative molar yields of the products from heterogeneous reaction of MAC and MVK on α-Al₂O₃ in dry air were summarized in Table 2. Here the relative molar yield is defined as the molar amount of the reaction products versus the molar amount of the consumed MAC/MVK. It should be noted that the amount of MAC/MVK consumed during the reaction is nearly equal to that taken up by α-Al₂O₃ particles since the amount of MAC/MVK observed on the particles was negligible when the heterogeneous reaction was completed, according to the spectroscopic data and HPLC analysis. By combining the carbon number and the molar yield of the reaction products, we calculated the carbon mass balance of the products from heterogeneous reactions of MAC and MVK to be 48.9 \pm 7.4% and 41.4 \pm 10.7%, respectively. This indicates that a large portion of reaction products is missing.

Previous studies have shown that carbonyl compounds can undergo carbon-carbon bond formation reactions known as Aldol condensation reactions on the surface of oxide particles with either acidic or basic properties or both (23-25, 30). When carbonyl compound adsorbs onto the oxide particles, surface basic oxygen anion abstracts a hydrogen atom from the α carbon position of the compound to form a nucleophilic negative carbon ion (-CH(R)CHO), which can attack the electrophilic carbonyl carbon of another compound to form an aldol, followed by dehydration to produce olefin aldehyde (23, 24, 30). Thus, it is expected that aldol condensation reactions can also occur for carbonyl compounds on $\alpha\text{-}Al_2O_3$ due to the existence of both Lewis acid sites and basic oxygen anions on the surface. Here we presume that aldol condensation reaction probably occurs for MVK to yield HMCs, while MAC cannot undergo this type of reaction since there are no hydrogen atoms in the α -carbon position of the molecule. However, propionaldehyde, one of major products in the heterogeneous reaction of MAC, is expected to undergo aldol condensation reaction on α-Al₂O₃

TABLE 2. Relative Molar Yields of Products (%) from Heterogeneous Reactions of MAC and MVK on α -Al₂O₃ in Dry Air (<1% RH)

products	P ^a MAC	MVK	G" MAC	MVK	total MAC	MVK
products	IVIAU	IVIV	IVIAU	IVIV	IVIAG	IVIV
CH ₃ CH=CHCHO	_c	0.2 ± 0.1	_	$\textbf{36.3} \pm \textbf{9.1}$	_	36.5 ± 9.2
CH ₃ CH ₂ CHO	0.3 ± 0.1	_	54.6 ± 6.6	_	54.9 ± 6.7	_
СНОСНО	_	0.4 ± 0.2	_	3.5 ± 0.5	_	3.9 ± 0.7
CH ₃ CHO	_	0.3 ± 0.1	_	2.2 ± 0.4	_	2.5 ± 0.5
HCHO	_	_	17.6 ± 7.3	_	17.6 ± 7.3	_
CH₃CH₂COOH	1.3 ± 0.1	_	0.6 ± 0.2	_	1.9 ± 0.3	_
НООССООН	_	0.1 ± 0.1	_	_		0.1 ± 0.1
CH₃COOH	0.6 ± 0.3	0.8 ± 0.2	0.7 ± 0.4	2.5 ± 1.3	1.3 ± 0.7	3.2 ± 1.7
НСООН	3.1 ± 0.1	_	1.9 ± 0.8	_	5.0 ± 0.9	_
H_2O_2	_	0.1 ± 0.1	_	_	_	0.1 ± 0.1

^a The yields of products measured in the particle phase. ^b The yields of products measured in the gas phase. ^c No products formed or below the detection limit of techniques.

suggested by Li et al. (8). Thus, MAC adsorbed onto $\alpha\text{-Al}_2O_3$ also has the potential to form the HMCs.

LC-MS analysis of the extracted solution of the particle samples was performed to determine the HMCs probably formed by the heterogeneous reactions. The average mass spectra of some products were obtained as expected. As illustrated in Figure S1 in the Supporting Information, three main product ions at m/z 98, m/z 126, and m/z 43, one main product ion at m/z 181, two major product ions at m/z 181 and m/z 251, and two evident product ions at m/z 233 and m/z 193 were observed, respectively, in the average mass spectra of the four products from the heterogeneous reactions of MAC and MVK. This suggests that the heterogeneous reactions of MAC and MVK on $\alpha\text{-Al}_2O_3$ do yield some HMCs. However, the formation mechanisms of these compounds are extremely complicated, leading to the difficulties in deducing their structures. In addition, no information is available in the literature regarding the HMCs formed by the heterogeneous reactions of MAC and MVK on the solid surface. Thus, it is a big challenge to identify these compounds, and further studies are highly required.

Uptake of MAC and MVK onto α-Al₂O₃ Particles in **Humid Air.** Water vapor is ubiquitous in the troposphere. It is well-known that adsorbed water significantly affects the physical and chemical properties of mineral oxide surfaces and thus the heterogeneous chemistry (28, 31, 32). Therefore, it is important to explore the heterogeneous reactions of MAC and MVK on α-Al₂O₃ under humid conditions. Two relative humidity (RH) values, 20% and 60%, were selected in the present study. Figure 2 shows the T-FTIR spectra collected after exposure of α-Al₂O₃ particles to MAC and MVK at various RH values. It can be seen that the frequencies of absorption bands in the spectra obtained under different RH were correspondingly similar, suggesting that the same species seemed to be present with humidity as without humidity. However, as the RH increased, the intensity of each absorption band decreased sharply. This indicates that water appears to significantly suppress the heterogeneous reactions of MAC and MVK on α-Al₂O₃ by depleting the surface active sites. As discussed above, in dry air the clean α -Al₂O₃ surface is aluminum terminated with Lewis acid sites (26), which is highly reactive and can adsorb organic molecules followed by oxidation with basic oxygen anions. While under humid conditions, basic Al-O groups are hydrated to form Al-OH by adsorbed water, changing aluminum terminated surface to hydroxyl terminated one, even with an overlayer of molecularly adsorbed water at high RH (26, 28, 33). It should be noted that the heterogeneous reactions at >60% RH were not investigated in this study. However, Al-Abadleh and Grassian (28) reported that a liquidlike water layer could be formed on the surface of α-Al₂O₃ when the RH was greater than 70%. Thus, it can be

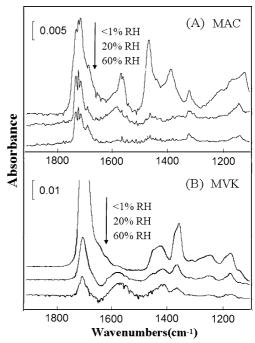


FIGURE 2. T-FTIR spectra obtained from heterogeneous reactions of MAC and MVK on α -Al $_2$ O $_3$ after 90 and 60 min exposure to organic vapors, respectively, at various RH values.

expected that heterogeneous reactions may be suppressed to a larger extent at higher RH.

Using HPLC and IC, we measured the yields of products at various RH values (Table 1). The results indicate that the yields of products apparently decreased with increasing RH. This further supports the conclusions based on the spectroscopic evidence mentioned above. It is interesting to note that under humid conditions organic acid products were observed almost only on the particles. This is distinct from the results under dry conditions where organic acids were simultaneously observed on the particles and in the gas phase, suggesting that adsorbed water can enhance the uptake of organic acids onto $\alpha\text{-Al}_2\text{O}_3$. This finding agreed well with the water-assisted uptake of organic acids onto mineral dust particles reported previously (5, 12).

Kinetics of the Uptake of MAC and MVK onto α -Al₂O₃ Particles. Because MAC and MVK can undergo adsorption and transformation simultaneously on α -Al₂O₃ particles, it is difficult to directly monitor the uptake of MAC and MVK onto the surface of α -Al₂O₃. To resolve this problem, we carried out the indirect measurements as follows. Collecting gaseous samples with the Horibe tube in the cold trap of ethanol-liquid nitrogen at \sim -90 °C and then processing and

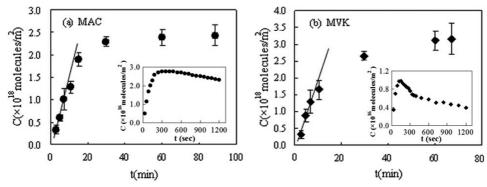


FIGURE 3. Kinetic curves of MAC (a) and MVK (b) uptake onto α -Al₂O₃ particles in dry air as a function of exposure time. The inset shows the surface concentrations of MAC/MVK as a function of time within 20 min of the exposure.

analyzing them with the method described in the Experimental Section, we obtained the total amount of gaseous organic reactant in the outflow of the reactor in the absence (1) and presence (2) of α -Al₂O₃ particles within the same time scales. The discrepancy between the amount (1) and (2) represents the amount of MAC/MVK taken up by the surface of α-Al₂O₃ particles through both adsorption and reaction. Figure 3 shows the uptake of MAC/MVK onto α-Al₂O₃ particles in dry air as a function of the exposure time. The error bars represent the variability in the data based on multiple experiments performed under similar conditions. It can be seen that the amount of MAC/MVK taken up by α -Al₂O₃ particles appear to increase linearly at the beginning of exposure. After 10 min of exposure, the uptake of both MAC and MVK onto the particles increased slightly and then appeared to keep at a stable level after 30 min for MAC and 60 min for MVK. From the linear fit of the data points at the beginning of the exposure, the initial uptake rates on α -Al₂O₃ are calculated to be (2.2 \pm 0.5) \times 10^{15} molecule m^{-2} s^{-1} for MAC and (3.1 \pm 0.6) \times 10¹⁵ molecule m⁻² s⁻¹ for MVK. In addition, the surface concentrations of MAC and MVK on α-Al₂O₃ varying as a function of exposure time were determined based upon the adsorption bands of MAC at 1679 cm⁻¹ and MVK at 1617 cm⁻¹ in the T-FTIR spectra (not displayed here). As shown in the insets of Figure 3, the growth rates of surface concentration (namely, the accumulation rate) of these two carbonyls on α -Al₂O₃ surfaces maintained at a stable state at the beginning of the exposure, with the values of $(1.9 \pm 0.2) \times 10^{14}$ molecule m⁻² s⁻¹ for MAC and $(1.1 \pm 0.1) \times 10^{14}$ molecule m⁻² s⁻¹ for MVK. Notably, there is a large gap between the initial uptake rate and initial accumulation rate for both MAC and MVK. These large gaps are mainly attributed to their rapid chemical transformations on α -Al₂O₃ particles.

For further understanding the uptake ability of MAC and MVK on $\alpha\text{-}Al_2O_3$ particles, the uptake coefficient should be taken into account. Here we assess the uptake ability of MAC and MVK on $\alpha\text{-}Al_2O_3$ particles by initial uptake coefficient (γ_0) , which is defined as the initial uptake rate of the adsorbate $(d\{C\}/d\mathit{t})$ divided by the total number of gas-surface collisions per unit time (Z), as given in eq 1 (21, 34):

$$\gamma = \frac{\mathrm{d}\{C\}/\mathrm{d}t}{Z} \tag{1}$$

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

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

where $\{C\}$ is the concentration of MAC or MVK taken up by particle surfaces at the beginning of exposure, [C] is the

concentration of MAC or MVK in gas phase, Z is the rate of collisions of MAC or MVK molecules with the particle surfaces, \bar{c} is the mean molecular velocity of MAC or MVK in the gas phase, M_C is the molecular weight of MAC or MVK, and A_s is the effective surface area of the particles. Since the organic reactant-containing airflow introduced into the reactor is capable of penetrating the bulk powder sample, the entire sample mass is available for the uptake of MAC or MVK. Thus, the BET surface area of the sample is used to calculate the γ_0 here.

The γ_0 values are estimated to be $(2.0 \pm 0.5) \times 10^{-8}$ and $(3.8 \pm 0.8) \times 10^{-8}$ for heterogeneous uptake of MAC and MVK, respectively, on α-Al₂O₃ particles in 1 atm dry air. To the best of our knowledge, no published data can be directly compared with the results reported here due to different adsorbates or substrates. However, our previous study found reversible uptake of MAC and MVK with γ_0 values of (2.2 \pm 0.2) \times 10⁻⁹ and (1.1 \pm 0.2) \times 10⁻⁹ respectively, on the surface of SiO2 under similar conditions (21). These values were lower by about an order of magnitude compared to γ_0 on α -Al₂O₃. Similar scales of the discrepancies were also observed for γ_0 values of small carbonyl compounds, such as formaldehyde, acetaldehyde, acetone, and propionaldehyde, between on SiO2 and on α -Al₂O₃ from Knudsen cell measurements (8, 9). We conclude that the discrepancy in measured initial uptake coefficients mainly result from the different reactivity of mineral oxides, since α-Al₂O₃ is expected to be more reactive than SiO₂ due to its greater basic and acidic properties of surface sites (8, 9). Previous studies of various carbonyls adsorbed on α-Al₂O₃ also found chemical transformation of the adsorbates. However, the measured uptake coefficients were distinct. The Knudsen cell studies by Grassian's group (8, 9) have shown that the initial uptake coefficients of formaldehyde, acetaldehyde, acetone, and propional dehyde on α -Al₂O₃ under dry conditions was 7.7× 10^{-5} , 3.2×10^{-5} , 2.0×10^{-5} , and 4.7×10^{-5} , respectively, about 3 orders of magnitude larger than the γ_0 values for both MAC and MVK reported in this work. Such a large gap between the two studies may be partly caused by the discrepancy in reactivity of the adsorbates but is more likely due to the limitations of the respective methods. Knudsen cell is a low-pressure reactor where only the gaseous reactant molecules are exposed to the particles, while the reactor used here runs under atmospheric pressure, thus the number of surface reactive sites for reactant molecules adsorption greatly decreases because of significantly competitive depletion by other gaseous species such as N_2 , O_2 , and H_2O .

Atmospheric Implications. Here we propose that under dry conditions heterogeneous reactions on mineral particles appear to represent another significant sink for MAC and

MVK in the atmosphere. These reactions also provide a potential source for the carbonyl compounds, organic acids and hydrogen peroxide in the atmosphere. Thus, heterogeneous reactions of MAC and MVK may have the potential to impact the atmospheric chemical composition. Considering the formation of organic acids and some HMCs, the heterogeneous reactions of MAC and MVK may also represent a source of secondary organic aerosols. Obviously, further studies regarding the reaction mechanisms and the identification of the HMCs are required.

It is interesting to note that under humid conditions adsorbed water on mineral particles can enhance the uptake of organic acids. In turn, the uptake of organic acids onto the surface can significantly alter the hygroscopicity of mineral particles, which may have significant effects on their optical properties and their ability to act as cloud condensation nuclei (CCN) (12).

It is well-known that MAC and MVK are toxic to human beings. These two carbonyl compounds can be accumulated onto atmospheric particles and then enter into the human respiratory system, resulting in a major adverse effect in lung cells (35). Moreover, several products of heterogeneous reactions of MAC and MVK are also toxic, such as crotonal-dehyde, which is recognized as a mutagen and a carcinogen and can cause liver tumors (36). In addition, heterogeneous reactions of MAC and MVK can largely alter the physico-chemical properties of mineral dust aerosol, such as particle size, hygroscopicity, and composition, which may lead to the modification of health effects of mineral dust. Thus, the heterogeneous aging of mineral dust aerosol by organic compounds should be considered for the study on their health effects.

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Supporting Information Available

Information on sources and purity grades of chemicals used in this work; the detection limits of HPLC and IC method; and Figure S1 with average mass spectra of HMCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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