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Temperature dependence of the heterogeneous uptake of acrylic acid on Arizona test dust

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ABSTRACT

In this study, the temperature dependence of the heterogeneous uptake of acrylic acid on Arizona test dust (ATD) has been investigated within a temperature range of 255–315 K using a Knudsen cell reactor. Combined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiment, it was found that acrylic acid could adsorb on ATD via surface OH groups and convert to carboxylate on the particle surface. The kinetics study suggests that the initial true uptake coefficient (γ_t) of acrylic acid on ATD decreases from $(4.02 \pm 0.12) \times 10^{-5}$ to $(1.73 \pm 0.05) \times 10^{-5}$ with a temperature increase from 255 to 315 K. According to the temperature dependence of uptake coefficients, the enthalpy (ΔH_{obs}) and entropy (ΔS_{obs}) of uptake processes were determined to be $-(9.60 \pm 0.38)$ KJ/mol and $-(121.55 \pm 1.33)$ J·K/mol, respectively. The activation energy for desorption (E_{des}) was calculated to be (14.57 \pm 0.60) KJ/mol. These results indicated that the heterogeneous uptake of acrylic acid on ATD surface was sensitive to temperature. The heterogeneous uptake on ATD could affect the concentration of acrylic acid in the atmosphere, especially at low temperature. © 2016 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Mineral dust, originating from the arid and semi-arid areas, is emitted into the atmosphere at a rate of 1000–3000 Tg/year (Dentener et al. 1996). It has been realized that it could significantly impact on climate change, hydrological cycle, and marine ecosystem at local and global scales (Crowley et al. 2010; Cwiertny et al. 2008; George et al. 2015; Usher et al. 2003). During the long-range transport, mineral dust can influence the climate system either directly by scattering and absorbing solar radiation or indirectly, by serving as cloud

condensation nuclei (Usher et al. 2003). In addition, it provides reactive surfaces for heterogeneous reactions of trace gases, thereby producing a substantial effect on atmospheric chemistry (George et al. 2015; Usher et al. 2003).

In the past decades, researchers have paid much attention to the heterogeneous reactions of atmospheric trace gases on mineral dust, because they not only influence the sinks of trace gases but also account for the alteration of the particulate composition and surface properties (Aubin and Abbatt 2006; Jacob 2000). Acrylic acid, one of organic acids with the structure of CH₂—CHCOOH, is released to the troposphere by numerous

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sources such as manufacturers of plastics, production of acrylate, aircraft and electronic components (Graedel 1978). It can also be emitted by natural sources including marine algae and the rumen fluid of sheep (Howard 1990). Acrylic acid has been confirmed as one of the 189 hazardous air pollutants by the US Congress in the Clean Air Act Amendments. To the best of our knowledge, little quantitative data are available for environmental levels of acrylic acid in ambient air. As for the acrylic acid air quality guideline, the World Health Organization (WHO) recommended an ambient air guidance value of 54 μ g/m³ for the general population. The concentration of emitted vapor of acrylic acid in the plume from factories producing acrylic acid or manufacturing its polymers was found to vary from 22 to 183 mg/m³ (Grudzinski 1988). Previous studies have investigated the homogeneous reactions of acrylic acid with several oxidants such as OH radicals and ozone. For example, the rate coefficients for the reactions of OH radicals, Cl atoms with acrylic acid were measured to be 1.75×10^{-11} and 3.99×10^{-10} cm³/(molecule·sec), respectively (Teruel et al. 2007). Schöne et al. (2014) studied the kinetics and products for the atmospheric aqueous phase radical chemistry of acrylic acid. However, the knowledge of mechanism and kinetics for heterogeneous uptake of acrylic acid on typical mineral dust is limited. Furthermore, the temperature of the Earth's atmosphere varies with altitude, latitude and longitude, as well as with season and time of day. For instance, the atmospheric temperatures for latitude 40°N during June increase from 220 K to room temperature with the decrease of the altitude (Smith 2003). The experimental determination of rate constants for important atmospheric reactions and how temperature affects the rate constants remain an important part of atmospheric sciences. Therefore, the study for the temperature dependence of heterogeneous uptake of acrylic acid on typical mineral dust is necessary.

In this work, the heterogeneous uptake of acrylic acid on Arizona test dust at 255–315 K was examined by a Knudsen cell reactor. Arizona test dust has been identified as a common mineralogical component of dust sample. It was used as a proxy of mineral dust in the present study. A series of uptake coefficients for the heterogeneous uptake of acrylic acid on the surface of Arizona test dust in the investigated temperature range were obtained. This range is close to the temperature of the Earth's surface in the atmospheric boundary layer, and can reflect the effects of temperature on the reactions in ambient. The measured uptake coefficients at different temperatures could provide basic data for atmospheric chemistry modeling studies.

1. Materials and methods

Arizona test dust (nominal 0–10 μ m) and acrylic acid (99.5%) were purchased from Powder Technology Inc. and Acros Organics, respectively. Nitrogen Brunauer–Emmett–Teller (BET) physisorption measurement was performed using a Quantachrome Autosob-1-C instrument. The total surface area of the ATD sample was measured to be 7.135 m²/g.

The Knudsen cell reactor used for the present study has been described in detail elsewhere (Wang et al. 2011; Zhou et al. 2014). Here is a brief introduction. A stainless steel

chamber equipped with a Hiden (HAL 3F 501) quadrupole mass spectrometer (QMS) was used to measure the gas phase reactant and product. The Arizona test dust samples were dispersed evenly on the sample holder with ethanol and then dried at 423 K for 2 hr. The pretreated samples and reactor chamber were then evacuated at 298 K for 12 hr to reach a base pressure of approximately $5.0\times10^{-5}\,\text{Pa}.$ The temperature of the sample holder could be controlled from 255 to 315 K within ±0.1 K by using a refrigerated circulator (DHJF-4005, Zhengzhou scientific instrument Co. Ltd., China). The sample covers were closed after the temperature of this system reached a set value. The gaseous acrylic acid was introduced into the chamber through a leak valve. Prior to each experiment, the reactor chamber was passivated with acrylic acid for at least 80 min. When a stable QMS signal was achieved, the isolation cover was retracted to expose the ATD sample to the gas phase reactant. The mass channel m/e = 72(C₂H₃COOH⁺) was monitored with the QMS online. The uptake coefficients were calculated based on the QMS data.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was applied to monitor the products formed on the surface of ATD particles during the heterogeneous uptake. Detailed description about the equipment and gas supply has been elaborated previously (Tong et al. 2010; Wu et al. 2011), thus only some experimental processes are listed here. In the DRIFTS experiment, ATD powder was in situ pretreated by heating in synthetic air (20% O₂ + 80% N₂) at 573 K for 3 hr and then cooled to room temperature. A DRIFTS spectrum of unreacted ATD powder was recorded as a background spectrum. When gaseous acrylic acid diluted in N2 with the concentration of (1.23 \pm 0.02) \times 10¹⁴ molecules/cm³ was introduced into the DRIFTS chamber and interacted with ATD surface, DRIFTS spectra of the ATD surface were collected in the spectral range from 4000 to 650/cm with a resolution of 4/cm.

2. Results and discussion

2.1. Uptake behavior of acrylic acid on Arizona test dust

Fig. 1a shows the typical uptake curves of acrylic acid on 24.4 mg ATD at 300 K. The concentration of acrylic acid in the Knudsen cell reactor was estimated to be around 6.75×10^{-1} ¹¹ molecules/cm³. The initial concentration of gaseous acrylic acid is first established in the chamber, and then the powder sample was exposed to contact with the reactant. As shown in Fig. 1a, the mass spectral signal intensity of acrylic acid (m/e = 72) decreased dramatically after the sample cover was opened. Then the QMS signal recovered to its original baseline value owing to the saturation adsorption of acrylic acid on the surface. There was no obviously steady-state uptake, indicating that the adsorption of acrylic acid on ATD was the main process of this uptake system. Previous literatures have reported the heterogeneous uptake of several simple gaseous monocarboxylic acids (such as formic acid, acetic acid and propionic acid) on α -Al₂O₃ and SiO₂ particles (Carlos-Cuellar et al. 2003; Tong et al. 2010; Wu et al. 2012), they suggested that surface hydroxyl groups are the reactive sites for these heterogeneous uptake systems. ATD is mainly composed of SiO₂ and Al₂O₃, with mass

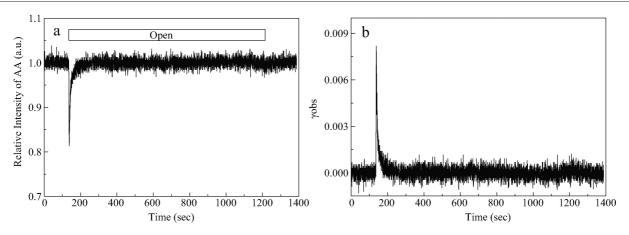


Fig. 1 - (a) Uptake curves and (b) observed uptake coefficients of acrylic acid on 24.4 mg Arizona test dust at 300 K.

percentage of 69% and 17%, respectively (Teipel et al. 2009). It seems reasonable to deduce that surface OH groups on ATD surface can play a role in its heterogeneous interactions with acrylic acid. To learn more about the nature of the uptake process, the uptake of acrylic acid on ATD surface was investigated by DRIFTS.

DRIFTS spectrum for the heterogeneous uptake of acrylic acid on ATD surface at 300 K is shown in Fig. 2. The positive and negative absorption bands in the spectrum indicate the formation and the loss of the corresponding species on the surface, respectively (Tong et al. 2010; Wen et al. 2010). The negative hydroxyl bands at 3743 and 3718 cm⁻¹ suggest that surface hydroxyl groups of ATD were consumed upon acrylic acid adsorption. Meanwhile, the positive bands at 3102, 3045 and 3015 cm which were assigned with C-H stretching were identified as acrylic acid adsorption on ATD surface (Cinar et al. 2011). In the carboxylate region, four bands at 1372, 1439, 1560 and 1700 cm⁻¹ were also observed. According to previous studies of the identification of absorption bands in the DRIFTS spectrum of organic acids on mineral oxides, these bands can be assigned in detail. That is, the band at about 1560 cm⁻¹ can be attributed to the OCO antisymmetric stretching mode $(v_{as}(OCO))$ in dissociated acrylate (Kirwan et al. 2003). The

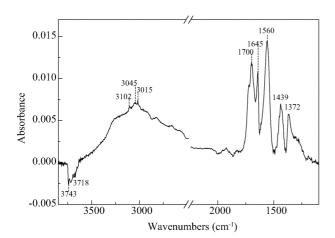


Fig. 2 – In situ DRIFTS spectrum for the heterogeneous uptake of acrylic acid on ATD surface at 300 K.

bands at 1372 and 1439/cm are associated with C–H in plane bend and symmetric stretching mode ($\nu_{\rm s}({\rm OCO})$), respectively (Kirwan et al. 2003). The band at 1645 cm⁻¹ belongs to surface-adsorbed water. The peak at 1700 cm is assigned to the stretching of $\nu({\rm C}\!\!=\!\!0)$ of molecularly adsorbed acrylic acid (Kirwan et al. 2003). DRIFTS spectral features indicate that acrylic acid can adsorb onto ATD surface via surface hydroxyl groups and form adsorbed acrylic acid and acrylate on the surface.

To determine whether this gas adsorption is reversible or irreversible, Knudsen cell and DRIFTS experiments have been performed. In the Knudsen cell experiments, when the uptake experiment was finished, the sample cover and leak valve were closed so that the reactant gas was pumped out by the pumping system. After gaseous acrylic acid was evacuated from the Knudsen cell reactor, the sample cover was opened again and no desorption of acrylic acid was observed. In the DRIFTS experiments, after the heterogeneous uptake for 140 min, the acrylic acid flow was cut off and the ATD particles were purged by synthetic air at 300 K for 60 min. The intensity of the acrylate peak at 1560/cm⁻¹ did not change during this process. In addition, the reacted particles after DRIFTS experiments were sonicated in 1.5 mL ultrapure water for 20 min. The filtered solution was then analyzed by an ion chromatography (IC) system. Acrylate ion was detected by the IC measurement. These results indicate that acrylic acid can adsorb onto ATD surface via surface hydroxyl groups and irreversibly convert to acrylate on the surface.

2.2. Uptake kinetics of acrylic acid on Arizona test dust at $300 \ K$

Based on the changes of QMS signal, the observed uptake coefficient, $\gamma_{\rm obs}$, of acrylic acid on ATD characterized by the loss of gaseous acrylic acid can be derived from the Knudsen cell equation (Underwood et al. 2001a):

$$\gamma_{\text{obs}} = \frac{A_h}{A_s} \left(\frac{I_0 - I}{I} \right) \tag{1}$$

where, A_h (cm²) is the effective area of the escape aperture, A_s (cm²) is the geometric area of the sample holder, and I_0 and I are the mass spectral intensities of acrylic acid with the sample holder covered and exposed, respectively. The escape aperture,

 A_h , was measured according to previously described methodology (Li et al. 2002). It was about 0.16 cm² in our experiments.

Fig. 1b shows the evolution of γ_{obs} as a function of exposure time. For 24.4 mg of ATD sample, the initial observed uptake coefficient for the maximal value, $\gamma_{\text{max,obs}}$, was 8.19×10^{-3} . It decreased quickly with an increase in exposure time, which corresponded to the increase in the QMS signal of acrylic acid. The decrease in the uptake coefficient occurs for the reason that the surface becomes saturated with adsorbed molecules. γ_{obs} can be determined by using the geometric surface area of the sample, with the assumption that the gassurface collisions only take place on the external layer. In fact, as for the multilayer powder samples, the reactant molecules can diffuse into the underlying layers of powder samples. Consequently, there is an increase in the number of collisions using the total surface area. Considering this important factor, Underwood et al. (2001a) has developed a linear mass dependent (LMD) model, which is widely used for the data analysis in Knudsen cell experiments. That is,

$$\gamma_t = Slope \times \left(\frac{A_s}{S_{RFT}}\right) \tag{2}$$

where, γ_t is the true uptake coefficient, Slope is the slope of the plot of $\gamma_{\rm obs}$ versus sample mass in the linear regime (mg⁻¹), and S_{BET} is specific surface area of the particle sample (cm²/mg). It can be seen from Fig. 3 that γ_{obs} is linearly dependent on the sample mass for ATD in the mass range of 0-32 mg (R = 0.994). This implies that gaseous acrylic acid molecules can diffuse into the underlying layers of Arizona test dust particles. As a result, a smaller true uptake coefficient is obtained (compared to the observed uptake coefficients). Previous publications have reported this linear dependence for many reaction systems, such as SO2, NO2, H2O2 and COS on typical mineral oxides (Liu et al. 2008b; Underwood et al. 2001b; Zhou et al. 2012, 2014). Using Eq. (2), the true uptake coefficient of acrylic acid on ATD at 300 K was measured to be (2.06 \pm 0.06) \times 10⁻⁵. The γ_t values for each experiment done in the linear regime are given in Table 1. At present, no other kinetics data are available regarding the uptake of acrylic acid on mineral dust particles. Hatch et al. (2007) investigated the heterogeneous uptake of the C1 to C4 organic acids on a swelling clay mineral, the BET area-corrected

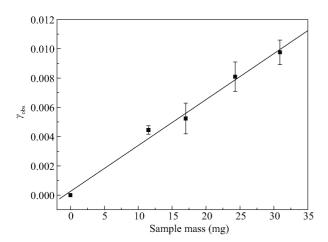


Fig. 3 – Mass dependence of initial observed uptake coefficients for acrylic acid on Arizona test dust.

Table 1-Initial true uptake coefficients and desorption rate constants of acrylic acid on Arizona test dust at different temperatures.

T (K)	$\gamma_{\rm t} \ (\times 10^{-5})$	$k_{\rm des} \ (\times 10^{-3})$
315	1.73 ± 0.05	13.8 ± 2.37
300	2.06 ± 0.06	9.80 ± 1.06
285	2.62 ± 0.10	7.34 ± 0.25
270	3.29 ± 0.16	5.05 ± 0.64
255	4.02 ± 0.12	3.73 ± 0.13

initial uptake coefficients were measured to be 1.3×10^{-5} 5.4×10^{-5} under dry conditions. As reported by Carlos-Cuellar et al. (2003), the measured true uptake coefficient for acetic acid on SiO_2 was 2.4 \times $10^{-4}.$ Thus, the range of γ_t calculated from this work is consistent with those reported uptake coefficients of monocarboxylic acids on a swelling clay (Hatch et al. 2007), while it is one order of magnitude lower than the value for the heterogeneous uptake of acetic acid on SiO2. The influence of reactant concentration on the uptake coefficient was also taken into account by changing the initial concentration of acrylic acid (Fig. S1). There was no obvious dependence of initial uptake coefficient on different acrylic acid concentrations ranging from 3.64×10^{11} to 1.75×10^{12} molecules/cm³. When the QMS signal intensity was calibrated with molecular flow rate (molecule/sec), the adsorption capacity could be calculated using the integrated area from the acrylic acid uptake curves. It was \sim 4.64 \times 10¹² molecules/cm for acrylic acid on Arizona test dust at 300 K.

2.3. Effect of temperature on uptake of acrylic acid on Arizona test dust

The temperature dependence for the uptake coefficients of heterogeneous uptake of acrylic acid on ATD was further investigated within a temperature range of 255–315 K. This temperature region is a common scope in the atmosphere, and may reflect the real effects of temperature on this reaction near the Earth's surface.

Table 1 lists the initial true uptake coefficients and desorption rate constants measured at different temperatures. The γ_t was in the range of $(1.73 \pm 0.05) \times 10^{-5}$ – $(4.02 \pm 0.12) \times 10^{-5}$. It was evident that the uptake coefficients of acrylic acid on Arizona test dust decreased with an increase in temperature. For example, the initial true uptake coefficient at 255 K was approximately two times larger than that at 300 K. This trend of the uptake coefficients with temperature agrees well with the physical adsorption process. Previous studies have also reported this negative temperature dependence for a series of heterogeneous uptake systems, such as formic acid on α -Al₂O₃, carbonyl sulfide on kaolinite, sulfur dioxide on Inner Mongolia desert dust and hydrogen peroxide on calcium carbonate (Liu et al. 2010; Wu et al. 2012; Zhou et al. 2012, 2014). On the basis of temperature dependence of uptake coefficients, the changes of observed entropy (ΔS_{obs}) and enthalpy (ΔH_{obs}) for acrylic acid adsorption on Arizona test dust can be calculated using the following equation:

$$ln\left(\frac{\gamma_t}{1-\gamma_t}\right) = -\frac{\Delta H_{obs}}{RT} + \frac{\Delta S_{obs}}{R} \tag{3} \label{eq:3}$$

where, T is the temperature (K). Therefore, from a plot of the left side of Eq. (3) versus inverse temperature, as shown in Fig. 4a, the $\Delta H_{\rm obs}$ and $\Delta S_{\rm obs}$ were determined to be $-(9.60 \pm 0.38)$ KJ/mol and $-(121.55 \pm 1.33)$ J·K/mol, respectively. In Fig. 4 the true uptake coefficients and desorption rate constants in Table 1 were used. Using the thermodynamic values obtained, the initial true uptake coefficient, $\gamma_{\rm t}$, can be fit to the following equation (obtained by rearranging Eq. (3)):

$$\gamma_{t} = \frac{exp(1154.2/T - 14.6)}{1 + exp(1154.2/T - 14.6)} \tag{4} \label{eq:tautotau}$$

This empirical formula can represent the acrylic acid uptake data on ATD well from 255 to 315 K.

As for the desorption rate constants, it can be calculated according to the flux balance equation based on the uptake profile shown in Fig. 1a (Liu et al. 2008a; Seisel et al. 2004):

$$F_{des}(t) = F(t) \bigg(1 + \frac{k_{ini}}{k_{esc}} \bigg) - F_0 \eqno(5)$$

$$F_{des}(t) = k_{des}N_{ads}(t) \tag{6}$$

where, $F_{des}(t)$ represents the desorption flux of acrylic acid from the particle surface at time t (molecules/sec), F_0 is the flow into the reactor (molecules/sec), k_{des} is desorption rate constant (sec⁻¹), k_{ini} is the initial rate constant and equal to k_{ads} (sec⁻¹), and k_{esc} is the escape rate constant of the Knudsen cell (sec⁻¹). $k_{esc} = \omega A_h$, where ω represents the collision frequency of acrylic acid on ATD. The number of adsorbed molecules on the particle surface, N_{ads} (t), can be determined by integrating the QMS signal between t=0 and the desired time t. As shown in Table 1, the calculated k_{des} values range from $(3.73 \pm 0.13) \times 10^{-3}$ to $(13.8 \pm 2.37) \times 10^{-3}$, they increase with increasing temperature. Fig. 4b illustrates the temperature dependence of k_{des} . On the basis of the slope of this plot, the activation energy for desorption (E_{des}) was calculated to be (14.57 ± 0.60) KJ/mol.

3. Discussion and conclusions

In this work, the heterogeneous uptake kinetics and mechanism of acrylic acid on ATD were studied. DRIFTS experiment

indicated that acrylic acid could absorb on ATD surface via OH groups and resulted in carboxylate formation. The uptake kinetics were investigated at a temperature scope from 255 to 315 K using a Knudsen cell reactor. The initial true uptake coefficient changes significantly with temperature, it increases with a decrease in temperature. For example, the initial uptake coefficient at 255 K is approximately two times larger than that at 300 K. The uptake coefficients within the investigated temperature region can be expressed as Eq. (4). According to the temperature dependence of uptake coefficients, $\Delta H_{\rm obs}$ and $\Delta S_{\rm obs}$ during the uptake process were measured to be – (9.60 ± 0.38) KJ/mol and –(121.55 ± 1.33) J·K/mol, respectively. The activation energies for desorption ($E_{\rm des}$) of acrylic acid on ATD was calculated to be (14.57 ± 0.60) KJ/mol.

The rate of removal of acrylic acid by uptake on ATD can be estimated using a simple model. The lifetime of acrylic acid owing to uptake on ATD can be calculated by the following equation:

$$\tau = 4/\gamma_t \overline{\upsilon} \sigma$$

where, γ_t is the initial true uptake coefficient, σ is the dust surface area density (m²/m³) and $\bar{\nu}$ is the mean molecular speed of acrylic acid (m/sec). Since the loading of ATD in the atmospheric particles is unavailable, it is hard to accurately estimate the flux of acrylic acid causing by the uptake on ATD. Assuming that the dust loading is 150 µg/m³ during the high pollution events (Li et al. 2012), we can obtain $\sigma \approx 1.1 \times 10^{-3} \text{ m}^2/\text{m}^3.$ The lifetime of acrylic acid owing to heterogeneous uptake on ATD is calculated to be 6.8 days at 300 K, which is longer than the lifetime of gas phase oxidation by OH radical (8 hr), but much shorter than that by O₃ (25 days) (Teruel et al. 2007). It should be pointed out that the uptake coefficient value increases significantly at the lower temperature. Considering that the temperature in the troposphere can reach values much lower than 300 K, which may lead to a larger uptake coefficient and a shorter lifetime. Therefore, the interaction between acrylic acid and ATD may influence the concentration of acrylic acid in the atmosphere, especially in very low temperature regions with a high concentration of ATD.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.03.027.

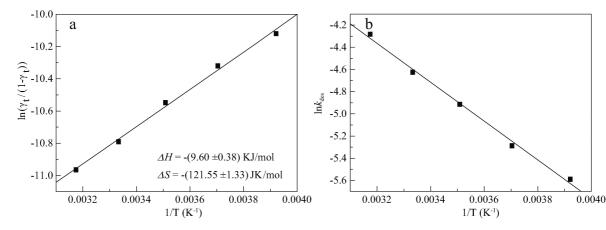


Fig. 4 – Plot to determine (a) the enthalpy ($\triangle H_{obs}$) and entropy ($\triangle S_{obs}$) of acrylic acid on Arizona test dust using the initial true uptake coefficients, and (b) the dependence of desorption rate (k_{des}) constants on temperature.

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REFERENCES

- Aubin, D.G., Abbatt, J.P., 2006. Laboratory measurements of thermodynamics of adsorption of small aromatic gases to n-hexane soot surfaces. Environ. Sci. Technol. 40 (1), 179–187.
- Carlos-Cuellar, S., Li, P., Christensen, A.P., Krueger, B.J., Burrichter, C., Grassian, V.H., 2003. Heterogeneous uptake kinetics of volatile organic compounds on oxide surfaces using a Knudsen cell reactor: adsorption of acetic acid, formaldehyde, and methanol on α-Fe₂O₃, α-Al₂O₃, and SiO₂. J. Phys. Chem. A 107 (21), 4250–4261.
- Cinar, M., Coruh, A., Karabacak, M., 2011. FT-IR, UV-vis, ¹H and ¹³C NMR spectra and the equilibrium structure of organic dye molecule disperse red 1 acrylate: a combined experimental and theoretical analysis. Spectrochim. Acta A 83 (1), 561–569.
- Crowley, J.N., Ammann, M., Cox, R.A., Hynes, R.G., Jenkin, M.E., Mellouki, A., et al., 2010. Evaluated kinetic and photochemical data for atmospheric chemistry: volume V heterogeneous reactions on solid substrates. Atmos. Chem. Phys. 10 (18), 9059–9223
- Cwiertny, D.M., Young, M.A., Grassian, V.H., 2008. Chemistry and photochemistry of mineral dust aerosol. Annu. Rev. Phys. Chem. 59, 27–51.
- Dentener, F.J., Carmichael, G.R., Zhang, Y., Lelieveld, J., Crutzen, P.J., 1996. Role of mineral aerosol as a reactive surface in the global troposphere. J. Geophys. Res. 101 (D17), 22869–22889.
- George, C., Ammann, M., D'Anna, B., Donaldson, D.J., Nizkorodov, S.A., 2015. Heterogeneous photochemistry in the atmosphere. Chem. Rev. 115 (10), 4218–4258.
- Graedel, T.E., 1978. Chemical Compounds in the Atmosphere. Academic Press, New York.
- Grudzinski, U.J., 1988. Substantiation of single maximum permissible levels of acrylic acid in the air of populated regions. Gig. Sanit. 9, 64–65 (in Russian).
- Hatch, C.D., Gough, R.V., Tolbert, M.A., 2007. Heterogeneous uptake of the C1 to C4 organic acids on a swelling clay mineral. Atmos. Chem. Phys. 7 (16), 4445–4458.
- Howard, P.H., 1990. Handbook of Environmental Fate and Exposure for Organic Chemicals, vols. 1–4. Lewis Publishers, Chelsea, Michigan.
- Jacob, D.J., 2000. Heterogeneous chemistry and tropospheric ozone. Atmos. Environ. 34 (12), 2131–2159.
- Kirwan, L.J., Fawell, P.D., van Bronswijk, W., 2003. In situ FTIR-ATR examination of poly(acrylic acid) adsorbed onto hematite at low pH. Langmuir 19 (14), 5802–5807.
- Li, P., Al-Abadleh, H.A., Grassian, V.H., 2002. Measuring heterogeneous uptake coefficients of gases on solid particle surfaces with a Knudsen cell reactor: complications due to surface saturation and gas diffusion into underlying layers. J. Phys. Chem. A 106 (7), 1210–1219.
- Li, J., Wang, Z.F., Zhuang, G., Luo, G., Sun, Y., Wang, Q., 2012. Mixing of Asian mineral dust with anthropogenic pollutants

- over East Asia: a model case study of a super-duststorm in March 2010. Atmos. Chem. Phys. 12 (16), 7591–7607.
- Liu, Y.C., He, H., Ma, Q.X., 2008a. Temperature dependence of the heterogeneous reaction of carbonyl sulfide on magnesium oxide. J. Phys. Chem. A 112 (13), 2820–2826.
- Liu, Y.C., He, H., Mu, Y.J., 2008b. Heterogeneous reactivity of carbonyl sulfide on α -Al $_2$ O $_3$ and γ -Al $_2$ O $_3$. Atmos. Environ. 42 (5), 960–969.
- Liu, Y., Ma, J., Liu, C., He, H., 2010. Heterogeneous uptake of carbonyl sulfide onto kaolinite within a temperature range of 220–330 K. J. Geophys. Res. 115, D24311.
- Schöne, L., Schindelka, J., Szeremeta, E., Schaefer, T., Hoffmann, D., Rudzinski, K.J., et al., 2014. Atmospheric aqueous phase radical chemistry of the isoprene oxidation products methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid kinetics and product studies. Phys. Chem. Chem. Phys. 16 (13), 6257–6272.
- Seisel, S., Lian, Y., Keil, T., Trukhin, M.E., Zellner, R., 2004. Kinetics of the interaction of water vapour with mineral dust and soot surfaces at T = 298 K. Phys. Chem. Chem. Phys. 6 (8), 1926–1932.
- Smith, I.W.M., 2003. Laboratory studies of atmospheric reactions at low temperatures. Chem. Rev. 103 (12), 4549–4564.
- Teipel, U., Winter, H., Caesar, J., 2009. Product qualification using test dust: characterization of dust. Gefahrstoffe Reinhalt. Luft 69 (1), 43–48.
- Teruel, M.A., Blanco, M.B., Luque, G.R., 2007. Atmospheric fate of acrylic acid and acrylonitrile: rate constants with Cl atoms and OH radicals in the gas phase. Atmos. Environ. 41 (27), 5769–5777.
- Tong, S.R., Wu, L.Y., Ge, M.F., Wang, W.G., Pu, Z.F., 2010. Heterogeneous chemistry of monocarboxylic acids on α -Al $_2$ O $_3$ at different relative humidities. Atmos. Chem. Phys. 10 (16), 7561–7574.
- Underwood, G.M., Li, P., Al-Abadleh, H., Grassian, V.H., 2001a. A Knudsen cell study of the heterogeneous reactivity of nitric acid on oxide and mineral dust particles. J. Phys. Chem. A 105 (27), 6609–6620.
- Underwood, G.M., Song, C.H., Phadnis, M., Carmichael, G.R., Grassian, V.H., 2001b. Heterogeneous reactions of NO₂ and HNO₃ on oxides and mineral dust: a combined laboratory and modeling study. J. Geophys. Res. 106 (D16), 18055–18066.
- Usher, C.R., Michel, A.E., Grassian, V.H., 2003. Reactions on mineral dust. Chem. Rev. 103 (12), 4883–4939.
- Wang, W., Ge, M., Sun, Q., 2011. Heterogeneous uptake of hydrogen peroxide on mineral oxides. Chin. J. Chem. Phys. 24 (5), 515–520.
- Wen, B., Li, Y., Chen, C.C., Ma, W.H., Zhao, J.C., 2010. An unexplored O₂ involved pathway for the decarboxylation of saturated carboxylic acids by TiO₂ photocatalysis: an isotopic probe study. Chem. Eur. J. 16 (39), 11859–11866.
- Wu, L.Y., Tong, S.R., Wang, W.G., Ge, M.F., 2011. Effects of temperature on the heterogeneous oxidation of sulfur dioxide by ozone on calcium carbonate. Atmos. Chem. Phys. 11 (13), 6593–6605.
- Wu, L.Y., Tong, S.R., Hou, S.Q., Ge, M.F., 2012. Influence of temperature on the heterogeneous reaction of formic acid on α -Al₂O₃. J. Phys. Chem. A 116 (42), 10390–10396.
- Zhou, L., Wang, W.G., Ge, M.F., 2012. Temperature dependence of heterogeneous uptake of hydrogen peroxide on silicon dioxide and calcium carbonate. J. Phys. Chem. A 116 (30), 7959–7964.
- Zhou, L., Wang, W.G., Gai, Y.B., Ge, M.F., 2014. Knudsen cell and smog chamber study of the heterogeneous uptake of sulfur dioxide on Chinese mineral dust. J. Environ. Sci. 26 (12), 2423–2433.