

Xu Gang^{1,2}
Lee XinQing²
Shao HongBo^{1,3}
Lv YingChun¹

¹CAS Key Laboratory of Coastal Environmental Processes/Shandong Provincial Key Laboratory of Coastal Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, P. R. China

²State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, P. R. China

³Institute for Life Sciences, Qingdao University of Science and Technology, Qingdao, P. R. China

Short Communication

Does Aqueous-Phase Oxidation of HCHO Opens a Pathway to Formic Acids in Atmosphere?

Formic acid is the major contributor to acid rain in some regions but its sources are not fully understood. We investigated the aqueous-phase reactions of HCHO (aq) and OH⁻ radicals at enlarged rainwater pH values (2.49–5.89) in Guiyang, China from May 2006 to April 2007. Our results show that there were no significant correlation between the $[HCOOH]_t/[HCHO]$ (aq) and the rainwater pH. The ratio did not appear to vary consistently as a function of rainwater pH as predicted by theoretical model. In addition, we saw no clear evidence that oxidation of HCHO (aq) would produce significant HCOOH (aq) which indicates this reaction may be only a minor contribution to the budget of HCOOH (g) in atmosphere. Further investigation is strongly suggested to be carried out in field cloud water, fog water, or rainwater because the ratios would be diverged from equilibrium value as a result of other chemical or physical processes.

Keywords: Air quality; Aqueous phase; HCOOH; HCHO; Oxidation

Received: April 7, 2010; *revised:* June 22, 2010; *accepted:* August 24, 2010

DOI: 10.1002/clen.201000103

1 Introduction

Acid rain is a serious environmental problem on a world wide scale. Generally, sulfur dioxide (SO₂) and nitrogen oxides (NO_x) are the primary sources of acid rain in urban or industrial regions. However, many researches found that formic acid is the major contributor to acid rain in some areas of the world. It was shown that formic acid could be responsible for up to 64% of the rainwater acidity in remote areas [1] and up to 30% of the acidity of wet deposition in polluted areas [2].

Extensive studies have been conducted to study the sources of inorganic anions in rainwater. However, the atmospheric sources of HCOOH (aq) in rainwater have not been well established up to now. The aqueous oxidation of HCHO (aq) is proposed as an important source for formic acid [3]. The theoretical production of HCOOH (aq) was in good agreement with the observed concentration level of formic acid in rainwater with mean value of 1–10 μmol/L [3]. However, we still lack field evidence to support this hypothesis as yet.

Guiyang city is serious acid rain polluted in China. The rainwater pH ranges from 2.49 to 5.89. The enlarge rainwater acidity proposes an excellent example for us to study the correlation between HCOOH (aq) and HCHO (aq). So the purpose of this study is to investigate the relationship of HCOOH and HCHO in rainwater in field condition.

2 Description of the study area

Guiyang City (26°34', 106°43'), the capital of Guizhou Province, locates in the southwest of China with an extension of 8049 km²

and more than 1.34 million people lived in urban sites. The city lies in a wide karst valley basin with an elevation of around 1000 m. The rainwater samples were collected on the roof of doctoral dormitory in the institute of Geochemistry, Chinese Academy of Sciences (CAS). The collector was mounted at 1.5 m on an iron stand on roof of the sample building. No specific pollution sources or point sources are adjacent to the sampling site.

3 Materials and methods

The rain water samples were collected with 1.5 m × 2 m polyethylene bottles, which had been cleaned with 2–3 N HCl and thoroughly rinsed with Milli-Q water (18.2 MΩ) before sampling. In order to minimize the contamination from dry deposition, special attention was paid to opening the sampler as soon as possible after the onset of rainfall. Rainwater was collected on an event basis from May 2006 to April 2007. Immediately after collection, the samples were treated with chloroform and stored in the dark at 4 °C to minimize biological degradation in rainwater.

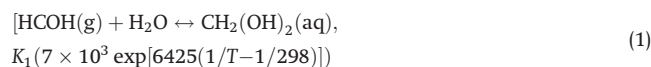
Formic acid was determined using Dionex ICS-90 ion chromatography. The separation column was AS11-HC (AG11-HC as guard column) and the gradient eluent KOH was generated from Dionex reagent free controller (RFC-30). HCHO in rainwater was analyzed according to the Nash method. This technique has been used successfully in the past [4–7]. The detection limit was 0.05 mg/L and the reproducibility defined as standard deviation of six consecutive measurements of the same sample was better than 5%.

Chameides proposed a theoretical model which was improved in our study. The model was used to investigate the chemistry of HCHO (aq) and HCOOH (aq) with a coupled gas and aqueous phase. They found that aqueous-phase reactions can both produce and destroy HCOOH (aq), controlling the levels of formic acid in rainwater [3].

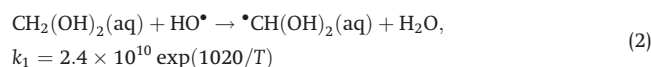
Correspondence: Dr. S. HongBo, Institute for Life Sciences, Qingdao University of Science and Technology, Qingdao 266042, P. R. China
E-mail: shaohongbochu@126.com

4 Results

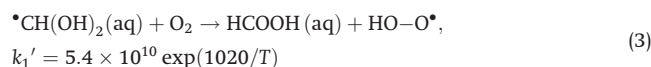
As shown in Fig. 1, there was a statistically significant correlation ($r = 0.68$, $p < 0.001$) between HCHO (aq) and HCOOH (aq) which indicates that the concentrations of the two species in rainwater are linked together [5]. Chameidies [3] suggested HCOOH (aq) could be produced from HCHO (aq) oxidation in aqueous phase. HCHO (g) is ubiquitous components of troposphere in urban and remote regions of the world. HCHO (g) is highly soluble in water to produce $\text{CH}_2(\text{OH})_2$.



where K_1 represents the solubility of Henrys Law constant for HCHO (aq) [8]. It is suggested that most of HCHO (aq) in aqueous phase was present in the form of hydrated HCHO (aq), which did not absorb solar radiation and therefore the lifetime of HCHO (aq) in aqueous phase was longer than that in gas phase. The more probable fate of hydrated HCHO (aq) was oxidation by OH radicals to form $\text{CH}(\text{OH})_2$ radicals [9].



$\text{CH}(\text{OH})_2$ radicals followed by a fast second H abstraction with molecular oxygen. It is important to note that this reaction appear to be faster than Eq. (2). Equation (2) was the rate-determining step that controlled the production of formic acid in aqueous phase [8].



In an aqueous phase such as cloud water or rainwater, $\text{CH}_2(\text{OH})_2$ reacts predominantly with O_2 to form formic acid. The formed HCOOH (aq) can evaporate to the gas phase through gas-aqueous equilibrium, see Eq. (4):

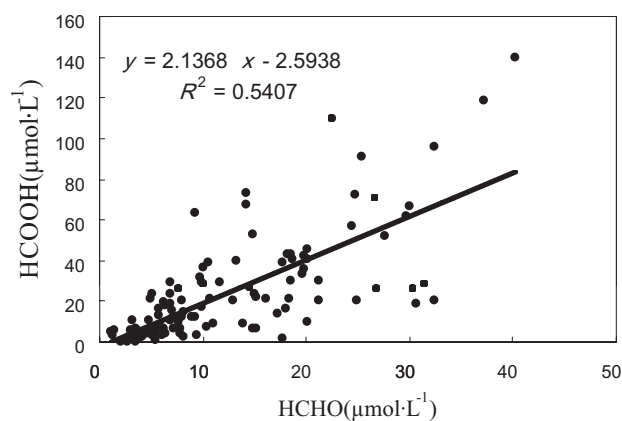
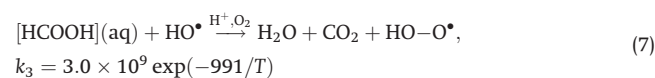
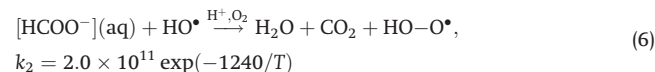
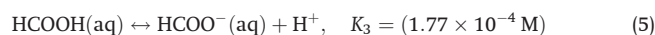


Figure 1. Relationship between HCHO and formic acid in rainwater in Guiyang.

On the other hand, HCOOH (aq) can dissociate to form the formate ion. Finally HCOOH (aq) and HCOO^- can be further oxidized by OH radicals to form CO_2 and H_2O then evaporated into atmosphere [8].



Assume r_f represent the ratio of formic acid production to destruction rate, then r_f is given by (I):

$$r_f = \frac{k_1[\text{CH}_2(\text{OH})_2]}{k_2[\text{HCOO}^-(\text{aq})] + k_3[\text{HCOOH}(\text{aq})]} \quad (I)$$

$$= \frac{K_1 k_1 [\text{H}^+]}{K_2 (k_3 [\text{H}^+] + k_2 K_3)} \frac{p_{\text{HCHO}}}{p_{\text{HCOOH}}}$$

The ratio r_f depends on the pH, the relative availability of HCHO (g), and HCOOH (g). The ratio of the gas-phase partial pressures of HCHO (g) and HCOOH (g) almost always exceeds unity and usually is around 10, therefore for the pH range of atmospheric interest a net production of HCOOH (g) is expected (Fig. 2).

A steady state in aqueous phase is approached when formic acid production Eq. (3) is equal to consumption by Eqs. (6) and (7) after about 50 min [9], denoting a relatively rapid process. It is described in the following formula.

$$k_1[\text{CH}_2(\text{OH})_2(\text{aq})][\text{OH}] = k_2[\text{HCOO}^-(\text{aq})][\text{OH}] + k_3[\text{HCOOH}(\text{aq})][\text{OH}]$$

Assume $[\text{HCOOH}]_t + [\text{HCOO}^-(\text{aq})] + [\text{HCOOH}(\text{aq})]$, the formula was shorten:

$$\frac{[\text{HCOOH}]_t}{[\text{HCHO}(\text{aq})]} = \frac{k_1 \left(1 + \frac{[\text{H}^+]}{K_3}\right)}{k_2 + k_3 \frac{[\text{H}^+]}{K_3}} \quad (II)$$

According to (II), the $[\text{HCOOH}]_t$ concentration becomes independent of the initial gas-phase HCOOH (g) level after the stationary state is reached. Because formic acid is both produced and destroyed

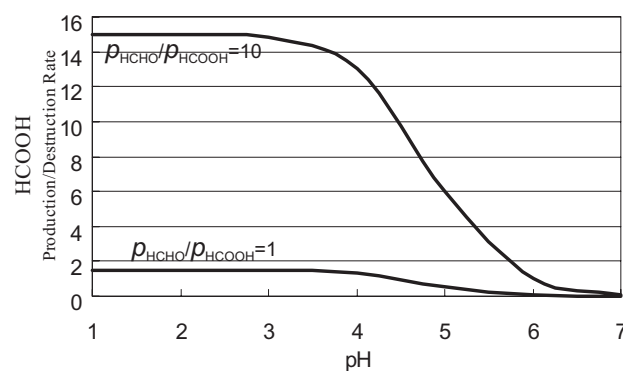


Figure 2. Ratio of formic acid production to destruction rates in cloud as a function of pH and the ratio of the pressures of HCHO and HCOOH.

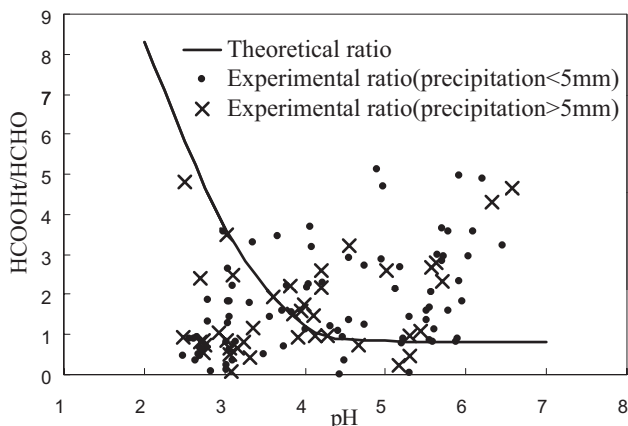


Figure 3. Variation of the ratio $[HCOOH]_t/[HCHO]$ with the rainwater pH in Guiyang.

by OH radicals, it is not strongly dependent on OH radicals or the initial HCOOH (g) level but is sensitive to rainwater pH, temperature, and the initial HCHO (g) level. At the same temperature and initial HCHO (g) concentrations, the variations of $[HCOOH]_t/[HCHO]$ (aq) as a function of pH was described in Fig. 3. It can be seen that the ratio of $[HCOOH]_t/[HCHO]$ (aq) was equal to 0.8 since the $pH > 4$. However, the ratio increased significantly with decreased pH of the aqueous phase when the $pH < 4$. It is suggested that the aqueous-phase pH have significant influence on the ratio of $[HCOOH]_t/[HCHO]$ (aq) in term of theoretical calculation especially for those samples with $pH < 4$.

The chemical composition of heavy rains may be more representative of the chemical character of cloud water because a significant amount of evaporation occurs and the washout of gases and particles is larger during a light rainfall [10]. As a result, the ratios of $[HCOOH]_t/[HCHO]$ (aq) was plotted against pH for rainwater > 5 mm or < 5 mm as described in Fig. 3. From above theoretical calculation, the ratio of $[HCOOH]_t/[HCHO]$ (aq) depend on the aqueous-phase pH especially for the acidic rainwater ($pH < 4$). To our disappointed, there was no such variations between the ratio of $[HCOOH]_t/[HCHO]$ (aq) and pH on basis of our field experiment results regardless of light or heavy rainfall. On the contrary, a weak positive correlation ($r = 0.02$, $p = 0.76$) was observed between the ratio and pH from the experiment data as presented in Fig. 3.

5 Discussion

Aqueous-phase oxidation of HCHO (aq) has been hypothesized as an important source to atmosphere HCOOH (g). The model indicate that the oxidation of HCHO (aq) by peroxides and OH radicals can serve as an cloud source of 0.2–1.2 μM formic acid and a source of from 4 to 170 ppt gas phase HCOOH (g) over the lifetime of the cloud [3]. Similar reactions for aqueous-phase production of acetic and other carboxylic acids were also suggested [9]. Therefore, aqueous-phase oxidation may open a pathway, or even more importantly to be the main sources for carboxylic acids in atmosphere. So it is important to address the possible contribution of the reaction to the sources of the acids. In a simulated experiment, Lelieveld has investigated the detailed kinetic and mechanism of the oxidation of HCHO (aq) by the OH radical in aqueous solution. The results showed that formic acid

was the only significant product of the aqueous oxidation [11]. Arakaki et al. [12] have detected the formation of formic acid in solutions containing hydrated HCHO (aq) ($\text{CH}_2(\text{OH})_2$), HOOH, and Fe(III) or Cu(II). These experiments suggest that formic acid was a product of the oxidation of HCHO (aq) in aqueous solutions in experimental condition.

However, we still lack field evidence to support this model until now. In a field experiment, Keene et al. [13] examined the pH dependence of the ratio of total HCOOH (aq) to HCHO (aq), and they saw no evidence of significant HCOOH (aq) production from aqueous-phase oxidation of HCHO (aq). So this reaction made at most only a minor contribution to the HCOOH (aq) budget at the site. In our present work, HCOOH (aq) and HCHO (aq) were simultaneously measured in rainwater in Guiyang. Although a net production of HCOOH (aq) from oxidation of HCHO (aq) is expected in field condition according to the model calculation, our experimental ratios of $[HCOOH]_t/[HCHO]$ (aq) were almost independent of pH values of rainwater which was contradict with theoretical calculations. Consequently, we saw no significantly contribution of HCOOH (aq) from aqueous-phase oxidation of HCHO (aq) from our experimental data, but we noted that this conclusion may be tentative because the ratio of $[HCOOH]_t/[HCHO]$ (aq) would be diverged from equilibrium value as a result of aqueous-phase chemical or physical processes [14–16]. Further work is needed to better characterize the relationship between HCOOH (aq) and HCHO (aq) in aqueous phase, their formation chemistry, and relevant controlling factor through simultaneously determination of HCOOH (aq) and HCHO (aq) in aqueous phase and gas phase.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (grant no. 40573048; 41001137), One Hundred-Talent Plan of CAS, the CAS/SAFEA International Partnership Program for Creative Research Teams, the Important Direction Project of CAS (KZCX2-YW-JC203), and CAS Young Scientists Fellowship (2009Y2B211). We thank Rongsheng Huang and Qing Wu for helping maintain the experimental site and for providing the meteorological data. We also thank Daikuan Huang and Hongguang Cheng for their invaluable support.

The authors have declared no conflict of interest.

References

- [1] J. N. Galloway, W. C. Keene, G. E. Likens, J. M. Miller, The Composition of Precipitation in Remote Areas of the World, *J. Geophys. Res.* **1982**, *87 (C11)*, 8771–8786.
- [2] A. Fornaro, I. G. R. Gutz, Wet Deposition and Related Atmospheric Chemistry in the Sao Paulo Metropolis, Brazil. Part 2: Contribution of Formic and Acetic Acids, *Atmos. Environ.* **2003**, *37*, 117–128.
- [3] W. L. Chameides, D. D. Davis, Aqueous-Phase Source of Formic Acid in Clouds, *Nature* **1983**, *304 (4)*, 427–429.
- [4] E. Sanhueza, Z. Ferrer, J. Romero, M. Santana, HCHO and HCOOH in Tropical Rains, *Ambio* **1991**, *20 (3)*, 115–118.
- [5] P. Khare, G. S. Satsangi, N. Kumar, K. M. Kumar, S. S. Srivastava, HCHO, HCOOH and CH_3COOH Air and Rain Water at a Rural Tropical Site in North Central India, *Atmos. Environ.* **1997**, *31 (23)*, 3867–3875.
- [6] C. Economou, N. Mihalopoulos, Formaldehyde in the Rainwater in the Eastern Mediterranean: Occurrence, Deposition and Contribution to Organic Carbon Budget, *Atmos. Environ.* **2002**, *36*, 1337–1347.

- [7] R. Seyfioglu, M. Odabasi, E. Cetin, Wet and Dry Deposition of Formaldehyde in Izmir, Turkey, *Sci. Total Environ.* **2006**, 366 (2–3), 809–818.
- [8] M. Chin, P. H. Wine, in *Aquatic and Surface Photochemistry* (Eds: G. R. Helz, R. G. Zepp, D. G. Crosby), Lewis Publishers, Boca Raton **1994**, 85–96.
- [9] D. J. Jacob, Chemistry of OH in Remote Clouds and Its Role in the Production of Formic Acid and Peroxymonosulfate, *J. Geophys. Res.* **1986**, 91, 9807–9826.
- [10] E. Sanhueza, Z. Ferrer, J. Romero, M. Santana, HCHO and HCOOH in Tropical Rains, *Ambio* **1991**, 20 (3–4), 115–118.
- [11] J. Lelieveld, P. J. Crutzen, Influences of Cloud Photochemical Processes on Tropospheric Ozone, *Nature* **1990**, 343, 227–233.
- [12] T. Arakaki, M. Shibata, T. Miyake, T. Hirakawa, H. Sakugawa, Enhanced Formation of Formate by Freezing in Solutions of Hydrated Formaldehyde–Metal–Hydrogen Peroxide, *Geochem. J.* **2004**, 38 (4), 383–388.
- [13] W. C. Keene, B. W. Mosher, D. J. Jacob, J. W. Munger, R. W. Talbot, R. S. Artz, J. R. Maben, et al., Carboxylic Acids in Clouds at a High-Elevation Forested Site in Central Virginia, *J. Geophys. Res.* **1995**, 100 (D5), 9345–9357.
- [14] S. Ozcan, M. E. Aydin, Organochlorine Pesticides in Urban Air: Concentrations, Sources, Seasonal Trends and Correlation with Meteorological Parameters, *Clean: Soil, Air, Water* **2009**, 37 (4–5), 343–348.
- [15] A. Monod, A. Chebbi, R. Durand-Jolibois, P. Carlier, Oxidation of Methanol by Hydroxyl Radicals in Aqueous Solution under Simulated Cloud Droplet Conditions, *Atmos. Environ.* **2000**, 34 (29–30), 5283–5294.
- [16] L. Saylan, H. Toros, O. Sen, Back Trajectory Analysis of Precipitation Chemistry in the Urban and Forest Areas of Istanbul, Turkey, *Clean: Soil, Air, Water* **2009**, 37 (2), 132–135.