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Research Highlight

Promoting Cl₂O generation from the HOCl + HOCl reaction on aqueous/frozen air–water interfaces[☆]Weina Zhang^{a,b}, Dayuan Zheng^{a,b}, Haolin Han^{a,b}, Zhengyi Wan^{c,e}, Jie Zhong^d, Yuemeng Ji^{a,b}, Guiying Li^{a,b}, Joseph S. Francisco^e, Taicheng An^{a,b,*}^a Guangdong-Hong Kong-Macao Joint Laboratory for Contaminants Exposure and Health, Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China^b Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, Key Laboratory for City Cluster Environmental Safety and Green Development of the Ministry of Education, School of Environmental Science and Engineering, Guangdong University of Technology, Guangzhou 510006, China^c Sinopec (Beijing) Research Institute of Chemical Industry, Beijing 10003, China^d School of Petroleum Engineering, China University of Petroleum (East China), Qingdao 266580, China^e Department of Earth and Environmental Science and Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6316, United States

Hypochlorous acid (HOCl) is a temporary reservoir of reactive chlorine species, such as Cl and ClO_x (chlorine oxides with strong oxidation) [1,2]. These reactive chlorine species are responsible for polar ozone depletion at extremely low temperatures (such as 243–273 K) [3–5]. Previous experimental studies have demonstrated that the reaction Cl₂O + H₂O ⇌ HOCl + HOCl reaches equilibrium under controlled conditions [6,7], confirming that HOCl + HOCl could produce Cl₂O in the gaseous phase. However, the traditional point of view is that the Cl₂O yield rate in the gas phase is extremely low, and therefore, it is not considered a source of atmospheric Cl₂O. Previous studies have reported the Cl₂O generation caused by the decomposition of chloronitric acid (ClONO₂) [8,9], but little is known about the process of Cl₂O generation by HOCl + HOCl at the air–water interface.

To understand the impact of the air–water interface on the generation of Cl₂O, under the National Natural Science Foundation of China (NSFC), we studied the specific mechanism of HOCl + HOCl on aqueous/frozen air–water interfaces using *ab initio* molecular dynamics (AIMD) simulations. First, HOCl + HOCl is simulated without any catalyst at aqueous/frozen air–water interfaces. As shown in Fig. 1a, two HOCl molecules rapidly separate from each other even though they are artificially placed at very close distances. MTD result (Fig. 1b) shows that the energy barrier (ΔG^\ddagger) on aqueous/frozen interfaces is 35.3/40.7 kcal/mol, and the corresponding reaction rate constant (k) is $8.04 \times 10^{-14}/8.81 \times 10^{-18} \text{ M}^{-1}\text{s}^{-1}$ (Table 1), which is 18/14 orders of magnitude greater than that of ($3.31 \times 10^{-32} \text{ M}^{-1}\text{s}^{-1}$) in gas phase [10]. Although the k of HOCl + HOCl on aqueous/frozen interfaces are significantly improved compared with that in the gas phase, the BOMD results and the small k still imply that the reaction is difficult to proceed without any catalyst assistance, which cannot explain the Cl₂O formation observed in reported experimental studies [8].

Therefore, it is speculated that the presence of some catalysts on aqueous/frozen air–water interfaces may promote the production of

Cl₂O. The catalysis effect by water is first investigated. Unlike the one-step reaction of HOCl + HOCl proposed in previous experimental and theoretical calculation studies [6,7,10], a two-elementary-step reaction was found to be included in the MTD results (Fig. 2), and the results also show that the HOCl + HOCl reaction was catalyzed by H₂O molecules on aqueous/frozen interfaces. Specifically, i) one HOCl is deprotonated by H₂O (Fig. 2a), producing ClO[−], and ii) the other HOCl participates in Cl-abstraction by ClO[−] (Fig. 2b), generating Cl₂O. Due to ΔG^\ddagger (28.4 kcal/mol) of the HOCl deprotonation step being larger than the Cl-abstraction step (7.0 kcal/mol), the former step is the rate-limiting step. Therefore, the total k of the HOCl + HOCl on aqueous/frozen interfaces is approximately $9.23 \times 10^{-9}/3.20 \times 10^{-7} \text{ M}^{-1}\text{s}^{-1}$ (Table 1), which is 5/11 orders of magnitude greater than that as compared without catalysis. However, these small k cannot explain the rapid Cl₂O generation. In summary, the above results suggest that the proposed two-step reaction under water catalysis conditions still contributes little to Cl₂O generation, although it is promoted compared with that in the gas phase.

According to the experiment, ClONO₂ hydrolyzed to generate HOCl and nitric acid, and subsequently Cl₂O from HOCl + HOCl [8]. Thus, the promotional effect of the acid catalyst (nitric acid) on the HOCl + HOCl reaction is investigated. Similar to water catalysis, the MTD results show that it just includes two steps, such as HOCl deprotonation and Cl-abstraction steps, and the former is found to be the rate-limiting step. Under catalyzed by nitric acid, the ΔG^\ddagger for HOCl deprotonation at aqueous air–water interface decreases to 17.5 kcal/mol. Therefore, the total k of HOCl + HOCl under nitric acid catalysis increases to $9.10 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1}$ (Table 1), which is 8 orders of magnitude greater than that under water catalysis. At the frozen air–water interface, the total k increases to $4.10 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ (Table 1), which is 4 orders of magnitude greater than that under water catalysis. These results show that nitric acid can accelerate Cl₂O generation from the HOCl + HOCl reaction at aqueous/frozen air–water interfaces by accelerating the rate-limiting step

[☆] Peer review under the responsibility of Editorial Board of Fundamental Research.

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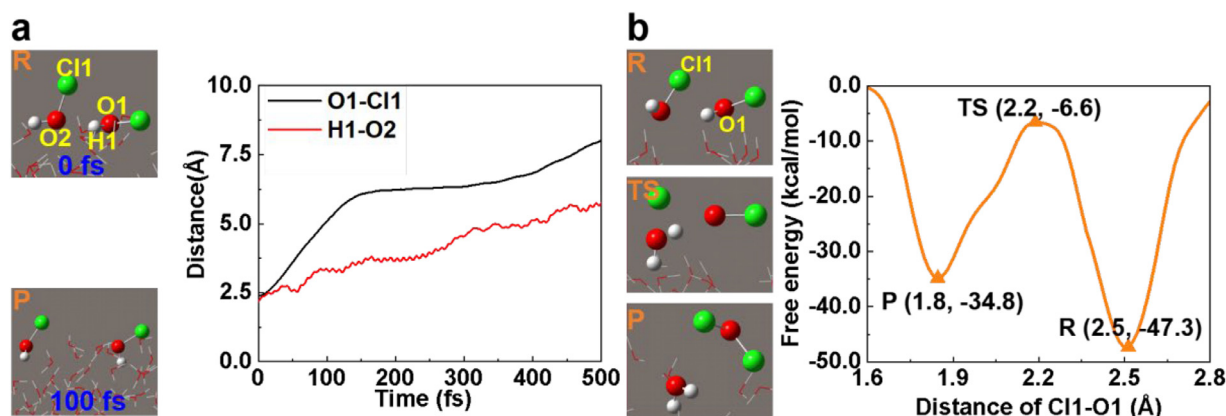


Fig. 1. HOCl + HOCl without any catalyst at the aqueous air–water interface. (a) Key bond evolution and related structures determined by BOMD and (b) Free energy profiles and corresponding structures determined by MTD, respectively. Reprinted with permission from W. Zhang, D. Zheng, H. Han, et al., Promoting Cl₂O generation from the HOCl + HOCl reaction on aqueous/frozen air–water interfaces, *J. Am. Chem. Soc.* (2024), 31935–31944. Copyright 2024 American Chemical Society.

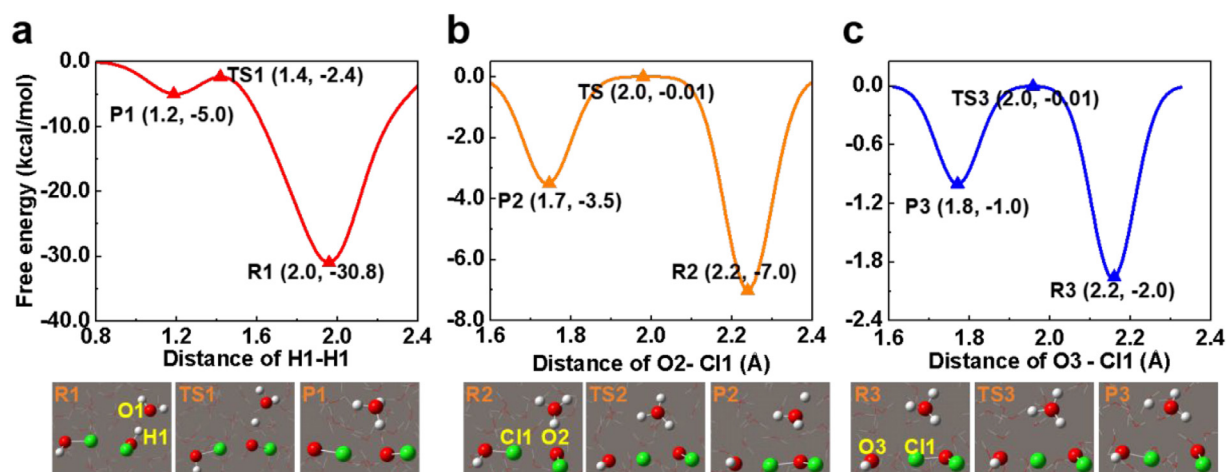


Fig. 2. HOCl + HOCl catalyzed by interfacial water at aqueous air–water interface. Free energy profiles and related structures of (a) HOCl deprotonation, (b) positive Cl⁻ abstraction and (c) reversible Cl⁻ abstraction simulated by MTD. Reprinted with permission from W. Zhang, D. Zheng, H. Han, et al., Promoting Cl₂O generation from the HOCl + HOCl reaction on aqueous/frozen air–water interfaces, *J. Am. Chem. Soc.* (2024), 31935–31944. Copyright 2024 American Chemical Society.

Table 1
The *k* of HOCl + HOCl under different catalysis conditions on aqueous/frozen air–water interfaces.

Catalysis from	<i>k</i> _{deprotonation} (M ⁻¹ s ⁻¹)		<i>k</i> _{Cl⁻abstraction} (M ⁻¹ s ⁻¹)		<i>total k</i> (M ⁻¹ s ⁻¹)	
	aqueous	frozen	aqueous	frozen	aqueous	frozen
Catalyst-free	/	/	/	/	8.04 × 10 ⁻¹⁴	8.81 × 10 ⁻¹⁸
Water	9.23 × 10 ⁻⁹	3.20 × 10 ⁻⁷	4.57 × 10 ⁷	1.40 × 10 ⁷	9.23 × 10 ⁻⁹	3.20 × 10 ⁻⁷
Nitric acid	9.10 × 10 ⁻¹	4.10 × 10 ⁻³	1.18 × 10 ⁷	4.29 × 10 ⁶	9.10 × 10 ⁻¹	4.10 × 10 ⁻³
Ammonia	4.43 × 10 ¹²	3.74 × 10 ¹²	1.66 × 10 ⁷	8.43 × 10 ⁶	1.66 × 10 ⁷	8.43 × 10 ⁶
Methylamine	5.52 × 10 ¹²	5.61 × 10 ¹²	1.40 × 10 ⁷	7.12 × 10 ⁶	1.40 × 10 ⁷	7.12 × 10 ⁶
Dimethylamine	5.90 × 10 ¹²	5.90 × 10 ¹²	8.97 × 10 ⁷	9.99 × 10 ⁶	8.97 × 10 ⁷	9.99 × 10 ⁶

of HOCl deprotonation, which explains Cl₂O formation observed in reported experimental studies [8].

Finally, the study emphasizes the promotional effect of base catalysts (ammonia, methylamine and dimethylamine) on the reaction of HOCl + HOCl. Base catalysts dramatically enhance Cl₂O formation from the HOCl + HOCl reaction. As shown in Fig. 3, ammonia catalysis follows the same two-step mechanism (HOCl deprotonation and Cl⁻ abstraction) as water or nitric acid, but with key differences. i) The deprotonation step is accelerated: Ammonia reduces the Δ*G*[‡] to 0.2 kcal/mol (Fig. 3e), and *k* increase to 4.43 × 10¹² M⁻¹s⁻¹ (Table 1). ii) The Cl⁻ abstraction

step becomes the rate-limiting step: Δ*G*[‡] is 7.6 kcal/mol (Fig. 3f) and *k* is 1.66 × 10⁷ M⁻¹s⁻¹ (Table 1). Accordingly, the total *k* for ammonia catalysis dramatically increases to 1.66 × 10⁷ M⁻¹s⁻¹ at the aqueous air–water interface, which is 16/8 orders of magnitude greater than that under water/acid catalysis. At the frozen air–water interface, a similar trend is observed, with ammonia catalysis increasing the total *k* by 13/9 orders of magnitude compared to water/acid catalysis. Notably, at the aqueous air–water interface, Cl₂O formation and decomposition are reversed: Cl₂O first rapidly formed through the Cl⁻ abstraction step (Fig. 3b), subsequently decomposed backwards to ClO⁻ within 2.2 ps

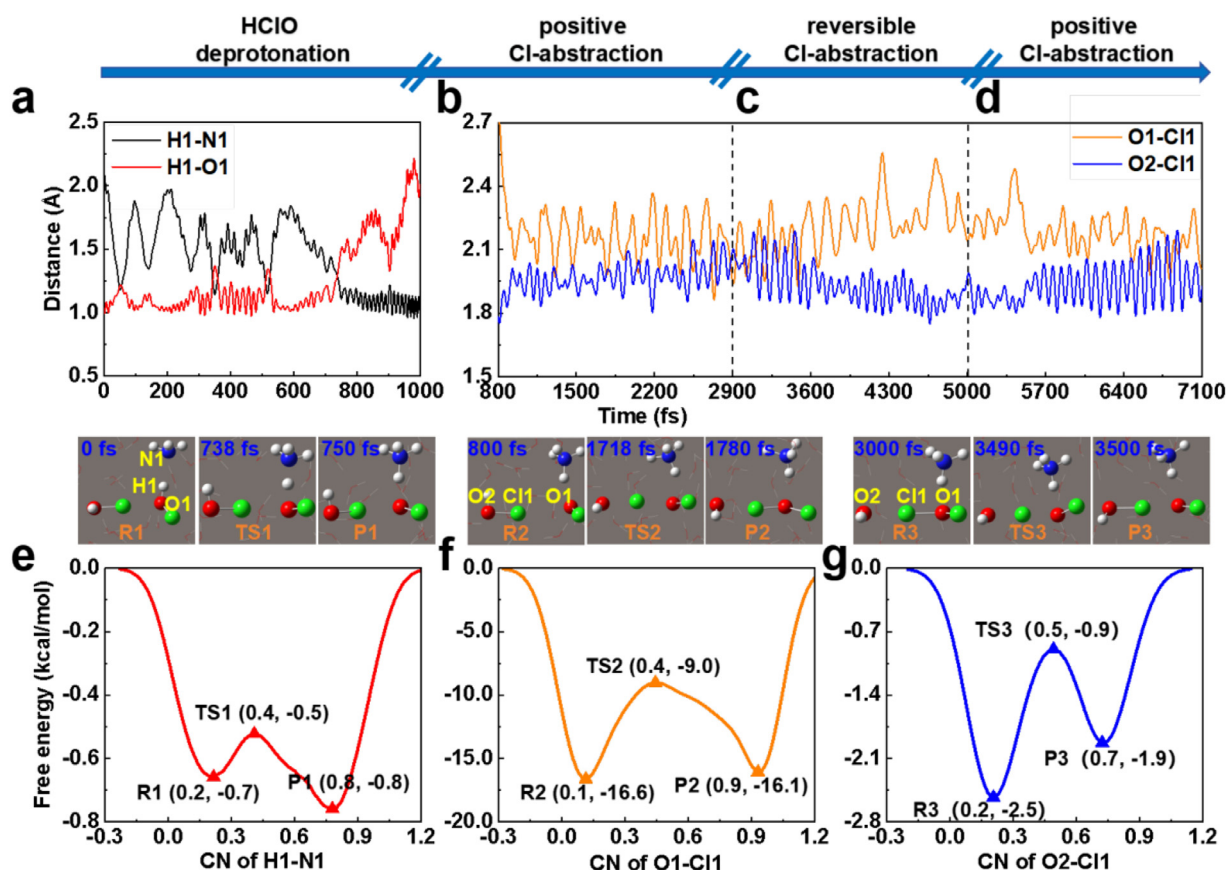


Fig. 3. HOCl + HOCl catalyzed by ammonia at aqueous air-water interface. (a)–(d) Key bond evolutions determined by BOMD for each elementary step. (e)–(g) Free energy profiles and corresponding structures determined by MTD for HOCl deprotonation step and positive and reversible Cl- abstraction formation steps, respectively. Reprinted with permission from W. Zhang, D. Zheng, H. Han, et al., Promoting Cl₂O generation from the hoCl + hoCl reaction on aqueous/frozen air–water interfaces, *J. Am. Chem. Soc.* (2024), 31935–31944. Copyright 2024 American Chemical Society.

(Fig. 3c), and quickly formed Cl₂O again within 2.8 ps (Fig. 3d). These results provide solid evidence that Cl₂O formation proceeds rapidly but reversibly, which is consistent with experimental observations of the equilibrium between Cl₂O and HOCl in the gas phase [6,7].

The study then compared the promoting effect between two organic bases (methylamine and dimethylamine) and an inorganic base (ammonia) on the HOCl + HOCl. At the aqueous air–water interface, the related BOMD results show similar reaction steps to those observed in the ammonia-catalyzed reaction. For methylamine catalysis, ΔG^\ddagger is 0.07 kcal/mol for the HOCl deprotonation and 7.7 kcal/mol for the Cl- abstraction. Thus, similar to the ammonia-catalyzed reaction, the Cl- abstraction is the rate-limiting step. This determines that the total k under methylamine catalysis is $1.40 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ at the aqueous air–water interface (Table 1), which is roughly the same order of magnitude as that of ammonia catalysis. The same is true of the reaction under dimethylamine catalysis, of which the k is $8.97 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ (Table 1). Therefore, at the aqueous air–water interface, the difference in the effect of different base catalysts on the total k for Cl₂O generation is small. This is also true of the reaction at frozen air–water interfaces, where the total k obtained from Cl₂O generation under catalysis of ammonia, methylamine and dimethylamine varies from 7.12×10^6 to $9.99 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ (Table 1). The only difference is the deprotonation time of HOCl with different base catalysts. The corresponding times were 0.75, 0.1 and 0.025 ps for ammonia, methylamine and dimethylamine, respectively, showing decreasing tendencies with increasing alkalinity. Moreover, the Cl₂O generation efficiency is greatly im-

proved under base catalysis conditions compared with neutral or acidic conditions.

The above findings were published in *Journal of the American Chemical Society* (2024, 146(46): 31935–31944). Reactive chlorine species are key contributors to polar ozone depletion [3–5]. Our findings suggest that interfacial reactions may serve as an unaccounted source of Cl₂O in cold environments, which can help to explain the high levels of Cl and ClO_x in polar regions. Thus, future atmospheric models should incorporate interfacial catalytic effects to better assess polar ozone depletion.

Declaration of competing interest

The authors declare that they have no conflicts of interest in this work.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (42020104001, 42277081 and 42077189), the Basic and Applied Basic Research Fund Project of Guangdong Province (2024A1515012691 and 2019B151502064), the Guangdong Provincial Key R&D Program (2022-GDUT-A0007), and the Basic and Applied Basic Research Project of Guangzhou (202201010496).

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