

Microdroplet-Mediated Multiphase Cycling in a Cloud of Water Drives Chemoselective Electrolysis

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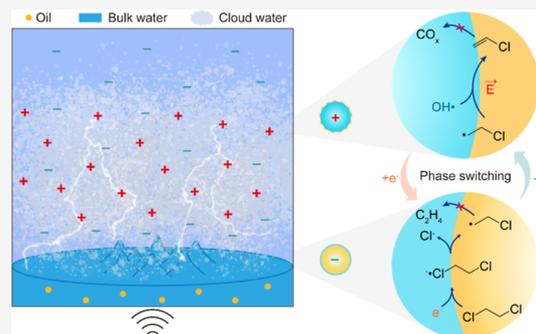


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ABSTRACT: Electrification of water in clouds leads to fascinating redox reactions on Earth. However, little is known about cloud electrochemistry, except for lightning, a natural hazard that is nearly impossible to harness. We report a controllable electrochemistry that can be enabled in microclouds by fast phase switching of water between the microdroplet, vapor, and bulk phase. Due to the size-dependent charge transfer between droplets during atomization, this process generates an alternating voltage arising from the self-electrification and discharging of microdroplets, vapor, and bulk phase by electron and ion transfer. We show that the microclouds with alternating voltage cause 1,2-dichloroethane ($\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}$) to be converted to vinyl chloride ($\text{H}_2\text{C}=\text{CHCl}$) at $\sim 80\%$ selectivity. These findings highlight the importance of controlled cloud electrochemistry in accelerating the removal of volatile organic compounds and treating contaminated water. We suggest that this work opens an avenue for harnessing cloud electrochemistry to solve challenging chemoselectivity problems in aqueous reactions of environmental and industrial importance.



INTRODUCTION

Phase change is often regarded as only a physical change. Yet the phase change of water in a cloud that occurs in nature strongly impacts the chemistry on Earth^{1,2} by causing atmospheric electrification.³ There has been a huge challenge to understand and harness the fascinating chemistry that goes with this capricious electrification phenomenon of cloud-water.⁴ Recent studies show that exotic chemical reactions exist once water microdroplets are generated during the liquid–vapor phase change by the spray of bulk-phase water^{5–10} or the coalescence of water vapor.^{11,12} The high electric field at the interface of water microdroplets^{13–16} combined with the inability to form a three-dimensional solvation shell around ions at the interface are able to ionize OH^- or an oxidizable solute to produce free electrons.^{17–24} Also, the high electric field can lower the activation barrier^{25,26} and increase successful collision rates,^{27,28} enabling water microdroplet interfaces to markedly accelerate chemical reactions compared with bulk-phase water. Another important contribution to microdroplet chemistry comes from the net charge of water microdroplets, which arises from the size-dependent transfer of electrons and ions during atomization.^{29,30} This net charge can alter the thermodynamics for redox reactions, thereby driving the spontaneous reactions that are impossible to occur in bulk-phase water, such as the formation of reactive oxygen species³¹ and reductive hydrogen species.³² There is debate regarding whether the charging mechanism of droplets is driven by ion or electron transfer. While early studies primarily focused on ion transfer, recent research suggests that electron transfer plays a

dominant role.^{29,33} Radical analyses during ultrasonic atomization showed that larger positively charged microdroplets predominantly contain hydroxyl radicals, while smaller negatively charged aerosol submicrodroplets mainly contain hydrogen radicals, suggesting that electron transfer is the primary charge transfer mechanism.³² The predominance of microdroplets in the phase change of cloudwater indicates an overlooked cloud electrochemistry paradigm besides hazardous lightning. Building water treatment using mild cloud electrochemical phenomena might offer the opportunity to address challenging problems of environmental and industrial importance.

1,2-Dichloroethane (DCE) is a widely produced chemical, predominantly used for the manufacture of the vinyl chloride (VC) monomer. Due to its negative impact on human health,³⁴ and long half-life (approximately 50 years in aqueous solutions),³⁵ the release of DCE waste leads to widespread and persistent groundwater contamination.^{36,37} In contrast to its persistence in groundwater, the half-life of atmospheric DCE is only ~ 73 days.³⁸ Cloud electrochemistry likely plays a role in the ~ 250 times faster degradation of DCE, which remains to

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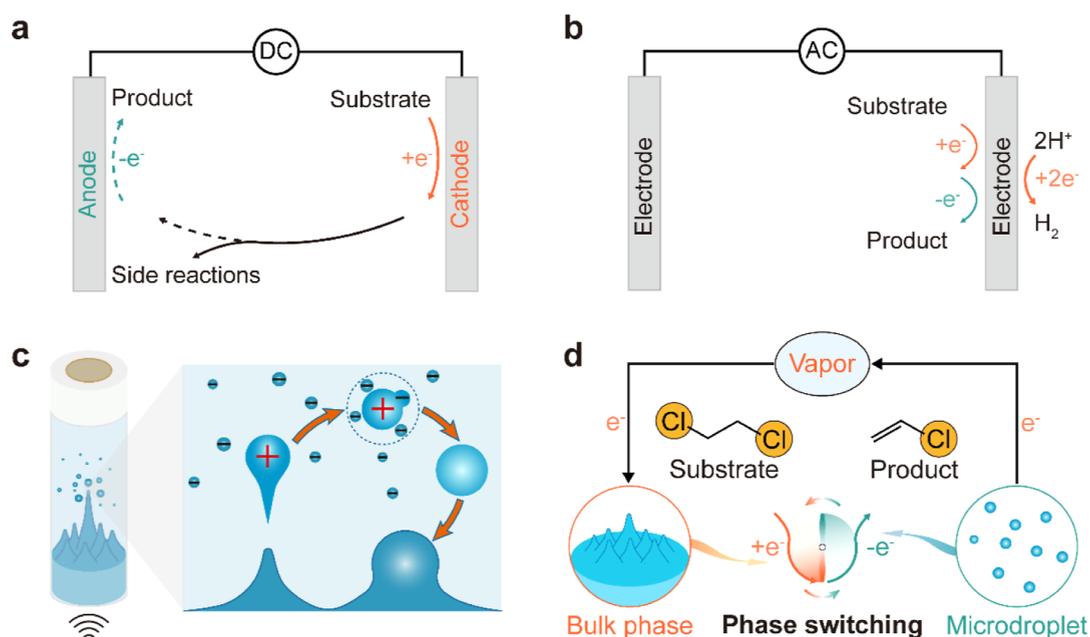


Figure 1. Schematics of paired electrolysis by (a) direct current, (b) alternating current (AC), (c) spray–coalescence cycles of charged water microdroplets and vapor, and (d) chemoselective electro-dechlorination of DCE driven by phase switched microcloud water.

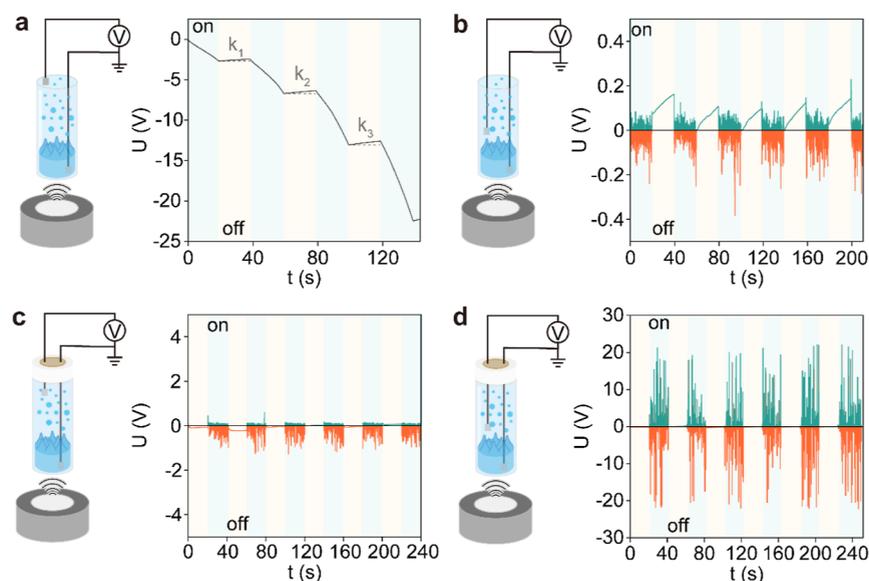


Figure 2. Measurements of the potential difference between the bulk phase and the above atmosphere of the phase switched water (a,b) in the open system and (c,d) in the closed system. “on” and “off” refer to activating and deactivating the spray, respectively. The slopes of voltage decay during the “off” phase are (a) $k_1 = 0.0124$ V/s, $k_2 = 0.0166$ V/s and $k_3 = 0.0253$ V/s.

be incorporated into Earth system models. Electrochemical processes have been proposed as the next-generation technologies for the treatment of contaminated water.^{39–42} Therefore, there is a more practical significance for testing the applicability of artificial cloud electrochemistry in the treatment of DCE-contaminated wastewater. From a waste upcycling perspective, the semidechlorination reaction of DCE to VC should be a preferred electrochemical process that can create economically added value⁴³ and mitigate the mineralization of organic chlorine. However, electrolysis of DCE in bulk-phase solution affords very low selectivity toward VC,⁴⁴ caused by the conflict between slow interelectrode mass transfer and the short-lived time of intermediates⁴⁵ (Figure 1a). We suggest that an elegant solution to mass transfer

limitation might arise from alternating current electrolysis, which can avoid the long-distance mass transfer process⁴⁵ (Figure 1b) and quench overreactions.⁴⁶ The application of alternating current electrolysis in bulk-phase water is still challenged by major problems, including the competing hydrogen evolution reaction and the relatively high cost of electrodes.

We report here the chemoselective electro-dechlorination of chlorine-containing wastewater driven by the phase switching among microdroplets, vapor composed of aerosol submicrodroplets, and bulk phase within a closed system of microcloud water (Figure 1c,d). To be specific, the ultrasonic spray of water in a closed system gives fast spray-coalescence cycles of charged water microdroplets and vapor, which are charac-

terized by an alternating voltage near the surface of bulk-phase water. During the spray, the vapor-mediated electron and ion transfer from water microdroplets to bulk-phase water enables the latter to reductively dechlorinate DCE to produce the chloroethyl radical intermediate. The electron-deficient microdroplets drive an accelerated dehydrogenation of the chloroethyl radical intermediate compared with that of bulk-phase water. Although the reduction and oxidation reactions are carried out heterogeneously, interphase mass transfer is not required because of the fast switching of water between microdroplets and the bulk phase, which is key to the high selectivity (~80%) for VC.

RESULTS

Voltage Measurement of Phase-Switched Water. The microcloud, characterized by fast switching back and forth of water between bulk phase, microdroplets, and vapor phase, was achieved by an external ultrasonic spray, as shown in Figures 2 and S1. The potential difference between the bulk phase and the above atmosphere that contains water vapor and microdroplets was investigated by an electrometer in voltmeter mode. Two platinum sheets that were attached to the electrometer were placed above and below the surface of water, respectively. The platinum sheet above the surface of the water was connected to the positive terminal of the electrometer, and its height from the water surface can be varied. The other platinum sheet in the bulk-phase water was connected to the negative terminal of the electrometer, and it was grounded. We first tested the potential difference generated by an ultrasonic spray of water in an open system. When measuring the potential difference between the bulk-phase water and the atmosphere approximately 5 cm above the surface of bulk-phase water, only the relatively small submicrodroplets in the vapor phase could reach the platinum sheet by diffusion, while the visible cloud containing larger microdroplets could not reach the platinum sheet, causing a negative voltage to continuously increase upon activating the spray (Figure 2a). After the spray was deactivated, it became relatively stable. This was due to the rapid dispersion of negatively charged submicrodroplets, which prevented further accumulation. Additionally, the air insulated the electrode, blocking charge dissipation, and larger positively charged microdroplets could not reach the electrode, so the voltage did not quickly return to zero. While the water vapor on the platinum sheet might gradually evaporate, carrying away some of the negative charge, resulting in a slight upward trend in the voltage. The rate of voltage growth in this upward trend increased as more water vapor accumulated on the platinum sheet ($k_3 > k_2 > k_1$), which should result from the more pronounced evaporation. Thus, the measured negative voltage relative to the bulk phase could be attributed to the enrichment of negative charges that were transferred by the vapor phase. The release of negatively charged vapor phase is consistent with our previous work that verified the positive charge of sprayed microdroplets and the negative charge of concomitant vapor due to the spontaneous electron extraction from sprayed water microdroplets to the vapor phase.³²

When the platinum sheet connected to the positive terminal of the electrometer was positioned within the visible cloud and at a distance of less than 0.5 cm from the surface of bulk-phase water, it could simultaneously interact with coexisting positively charged microdroplets and negatively charged vapor. This might account for the alternating voltage detected

near the water surface (Figure 2b). However, it should be noted that the microdroplets were generated in different sizes, primarily within the range 1–5 μm (Figure S2). Considering the existence of size-dependent charge transfer in sprayed microdroplets,²⁹ such instantaneous fluctuations of voltage may also be contributed by the collision and coalescence between microdroplets of different sizes. At intervals of spray, negatively charged vapor diffuses away from the vial opening and is not attracted back by electrostatic forces, while positively charged microdroplets settle, causing the voltage near the water surface to become positive. These results reflect a slow precipitation rate of the sprayed positively charged microdroplets relative to the diffusion rate of negatively charged vapor.

To verify the role of water vapor in the formation of alternating voltage, we sealed the vial and conducted the voltage measurements in this closed system (Figure 2c,d and S3). We first measured the potential difference between the bulk-phase water and the upper edge of the visible cloud, which was approximately 3 cm above the top of the bulk-phase water surface. It was found that the negative voltage, approximately -1 V, was significantly greater than the positive voltage in magnitude, indicating a higher proportion of negatively charged vapor compared to positively charged microdroplets at the upper edge of the visible cloud (Figure 2c). In comparison with the alternating voltage near the water surface in the open system (Figure 2b) and that well above the water surface in the closed system (Figure 2c), the closed system exhibited a greater amplitude of voltage alternation near the water surface (Figure 2d), with instantaneous voltages exceeding 20 V and more balanced positive and negative voltage. This indicates that the bulk-phase surface is the primary site for droplet fragmentation and charging. In the closed system, droplet motion such as convection was intensified relative to the open system, which might account for the higher magnitude of instantaneous voltage. The voltage immediately decreased to zero upon deactivating spray (Figure 2d), indicating a rapid electromigration and recombination of positively and negatively charged droplets into charge-neutral droplets (Figure 1c). We also conducted the current measurements in the closed system and found that the current exhibited alternating characteristics similar to the voltage (Figure S4), with a greater amplitude near the bulk-phase surface compared to farther regions. The above results unambiguously verified the contribution of vapor to the generation of alternating voltage.

To assess potential interference caused by noise from sonication or spray, we conducted voltage measurements under ultrasonic cavitation with the vial positioned horizontally. The voltage during ultrasonic cavitation showed an alternating voltage amplitude of only about 0.1 V (Figure S5), indicating that sonication has minimal impact on microcloud voltage measurements. Additionally, the reactor was also positioned horizontally, by which the horizontal spread of the cloud could neutralize the charged droplets and decrease the frequency of phase switching. The resultant voltage amplitude near the water surface at the atomization area decreased to approximately 5 V (Figure S6a). When the ungrounded platinum sheet was horizontally moved 3 cm from the atomization area, the voltage decreased further to about 1 V along with a reduction in the alternating frequency (Figures S6b and S7). These results suggest that the noise from sonication and spray is unlikely to interfere with the voltage

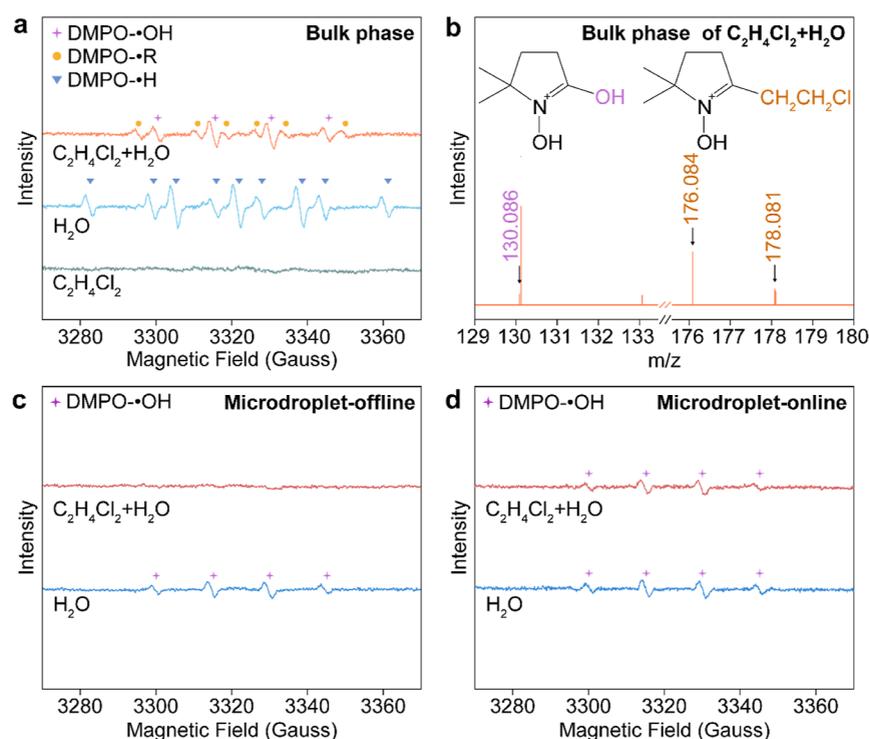


Figure 3. Observation of radicals formed in the electro-dechlorination of DCE in bulk phase as detected by (a) EPR spectroscopy and (b) liquid chromatography high-resolution mass spectrometry and in (c) offline-captured and (d) online-captured microdroplets, as detected by EPR spectroscopy.

measurements of the microcloud. When water breaks into tiny droplets, the formation of larger microdroplets with positive charge and smaller droplets with negative charge has been known as the Lenard effect.^{47,48} It is postulated that the smaller droplets that split off from the larger droplets are negatively charged, causing the larger droplets to be positively charged.³⁰ This assumption can rationalize the formation of positively charged microdroplets from a negatively charged water surface during the spray process.

Alternating voltage is typically applicable to paired electrolysis processes.^{49–51} As the alternating voltage in the microcloud is induced by the fast phase switching of water itself, one can expect a paired electrolysis by the microcloud without the need for interphase transfer of aqueous reactants and intermediates. This fact might avoid the limitations of mass transfer between electrodes or at solid–liquid interfaces of electrodes in traditional electrochemical cells,^{52,53} which would otherwise lead to side reactions in the case of unstable intermediates or products.

Phase Dependence Characteristic of Reduction and Oxidation Reactions in the Water Microcloud. We selected DCE as a model to test the feasibility of the paired electrolysis of organochlorine in a microcloud system. The radical intermediates generated during the spray were detected by electron paramagnetic resonance (EPR) spectrometry and high-resolution mass spectrometry using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a radical scavenger (Figure 3). The radicals in the bulk phase were investigated by introducing DMPO into the system prior to spraying, followed by analyzing the bulk phase after spray. The radicals in the microdroplets were investigated by either exporting the microdroplets into a centrifuge tube charged with DMPO under an Ar atmosphere, which was considered offline capture,

or by receiving them in a shallow glass container with DMPO inside the reactor, which was considered online capture. As shown in Figure 3a, the reaction conditions for spray could not generate detectable radicals for the pure DCE system in the absence of water. Under identical reaction conditions, EPR nonuple DMPO-•H peaks were observed in the bulk phase of the ultrapure water system, indicating the generation of hydrogen-atom radicals (•H). Meanwhile, the appearance of EPR quadruplet DMPO-•OH peaks in water microdroplets verified the generation of the hydroxyl radical (•OH), as shown in Figure 3c,d, which is consistent with our previous research showing the electron extraction from sprayed water microdroplets to vapor.³² The accumulation of •H rather than •OH in the bulk-phase water indicates preferential absorption of the electron-trapped vapor by the bulk phase.

However, with the addition of DCE into water, •H in the bulk phase disappeared and carbon-centered radicals (•R) and •OH were observed instead (Figure 3a). •R was subsequently identified as the chloroethyl radical (•CH₂CH₂Cl) by high-resolution mass spectrometry (Figure 3b). To be specific, two peaks were observed at *m/z* 176.084 and 178.081, consistent with the theoretical *m/z* 176.084 and 178.081 of oxidized [DMPO-•CH₂CH₂³⁵Cl + H]⁺ and [DMPO-•CH₂CH₂³⁷Cl + H]⁺, respectively. The chlorine removed in the dechlorination process was detected in the form of chloride ions (Figure S8). These results show the occurrence of a reductive dechlorination reaction in the bulk-phase water. Although •CH₂CH₂Cl and •OH coexisted in the bulk phase, •CH₂CH₂Cl disappeared in the microdroplets, and only •OH could be captured in situ (Figure 3d). When captured offline, neither could be detected (Figure 3c). This indicates that the oxidation reaction of •CH₂CH₂Cl by •OH can be significantly accelerated once the bulk-phase water is sprayed as microdroplets. If fast phase

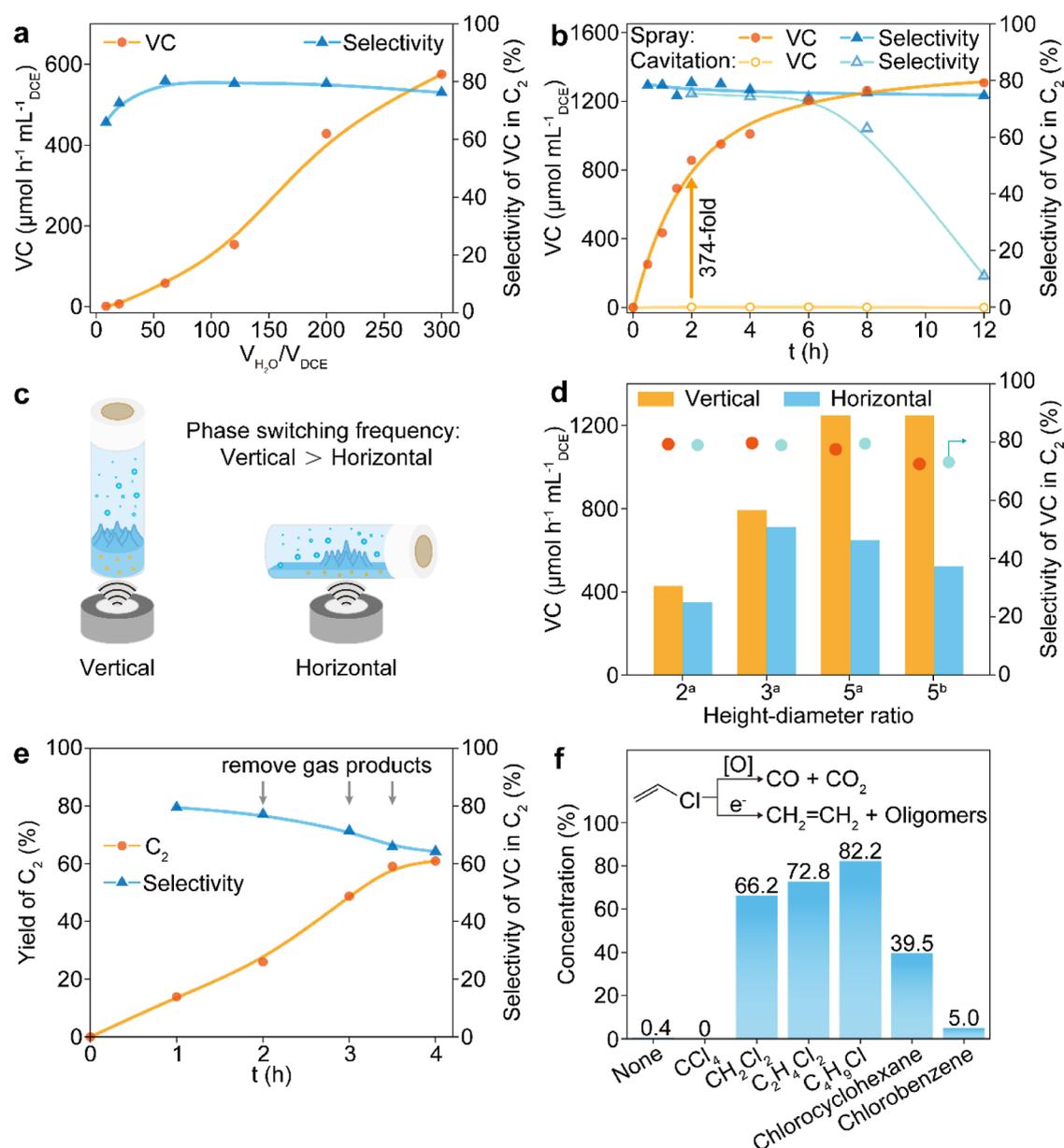


Figure 4. Evolution of VC in the DCE–water system under ultrasonic spraying. (a) Effect of water–DCE ratio on the generation of VC. (b) Time course of VC product generated by ultrasonic spraying and cavitation. (c,d) Effect of phase switching frequency on evolution of VC. (e) Time course of C_2 gas products generated in the reactor with a height–diameter ratio of 5. (f) Evolution of VC concentration in the presence of various organic chlorides. ^aConstant diameter for reactors of varied height–diameter ratios. ^bConstant height–diameter ratio of 5 while simultaneously increasing the height and diameter by 1.2-fold.

switching of water does not occur, then the excess $\bullet\text{OH}$ may directly attack DCE, leading to side reactions. In addition, studies have reported that the dehydrogenation of C–H bonds can be facilitated by $\bullet\text{H}$.^{54,55} An experiment using D_2O as the solvent was designed to explore the possibility of this alternative pathway. However, the result showed no detectable deuterated VC (Figure S9). The above results demonstrate a phase-dependence characteristic of reduction and oxidation reactions in a microcloud, with reductive dechlorination of organochlorine occurring over the bulk phase and subsequent oxidative dehydrogenation accelerated in microdroplets.

Evolution of VC from DCE–Water. We next analyzed the products of the cascade reduction–oxidation reaction in the DCE–water microcloud system. In contrast to the microcloud of ultrapure water that led to the formation of H_2 , H_2 was

hardly formed in this DCE–water microcloud system (Figure S10). This confirms the capability of the microcloud to preferentially reduce organochlorine rather than H^+ , which is consistent with the disappearance of $\bullet\text{H}$ and the appearance of chloroethyl radical with the addition of DCE into microcloud water (Figure 3a). As shown in Figures 4a and S11, VC was the main product with a selectivity of around 80% without the generation of CO_x . Its formation efficiency was positively related to the ratio of water to DCE. This implies that VC formation predominantly occurred at the DCE–water interface. Cl^- was detected and quantified after 2 h of the spray reaction, with the amount slightly exceeding the dechlorination amount corresponding to the generation of VC (Figure S8), indicating the presence of dechlorination intermediates in the solution. A selectivity of 96.3% was achieved for the

production of the C₂ gas products. In comparison with the ultrasonic spray system, the ultrasonic cavitation system without spray showed a 2 orders of magnitude lower rate of VC formation under identical reaction conditions (Figure 4b). Besides, a fast degradation of VC was observed in the ultrasonic cavitation system without spray, whereas the microcloud in the ultrasonic spray system could maintain a selectivity of 80% for VC in C₂ gas products (VC, ethylene, and acetylene) during 12 h of operation. In addition to the Ar atmosphere, we also tested the electro-dechlorination of DCE under N₂ and air atmospheres, finding no significant change in gas product selectivity but reduced reaction activity (Figure S12). Previous studies suggest that N₂ or O₂ may undergo redox reactions in microdroplets, consuming reactive oxygen species or electrons,^{8,30,56} which likely inhibits DCE degradation.

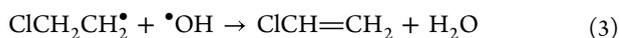
Scaling up the artificial cloud requires increasing the reactor volume, which might decrease the frequency of phase switching. Markedly, enlargement of the reactor by increasing the height-diameter ratio of the reactor without altering the diameter led to an obvious acceleration of VC formation (Figure 4c,d). The visible cloud composed of larger microdroplets remained unchanged in height upon increasing the reactor height (Figure S13). Thus, the contribution of the microdroplet to the phase switching was unaffected. The acceleration of VC formation should be ascribed to the enhanced charge separation caused by the spreading of the invisible, smaller microdroplets and the vapor phase. We also increased the reactor diameter and height simultaneously at a constant height-diameter ratio, which hardly inhibits the reactivity. Subsequently, we laid down the reactor in a horizontal direction, which enhanced a horizontal spread of the visible cloud but reduced the frequency of phase switching (Figure 4c). This horizontal spreading of the visible cloud led to a decreased formation rate of VC (Figure 4d). However, it is worth noting that in the 20 mL horizontal reactor with a height-diameter ratio of 2, although the alternating voltage near the atomization area dropped to about 5 V (Figure S6), only a slight decline in reaction activity was observed (Figure 4d), indicating that this voltage could still drive the electro-dechlorination of DCE. Similarly, in the case of a vertically positioned reactor, decreasing the voltage to about 1 V via the addition of the surfactant of SDS,³² could not decrease the reaction activity as well, despite the selectivity of C₂ gas products dropping to 75.7% (Figure S14). This indicates that the reduced activity observed in the horizontal reactor (Figure 4d) should be attributed to the decrease of the frequency of phase switching rather than the change of voltage magnitude. Furthermore, increasing the reactor volume enhanced the horizontal spread of the cloud, leading to a more pronounced decline in reaction activity. Based on the above results, we suggest that the reaction efficiency is predominantly controlled by the microdroplet-mediated phase switching frequency. Therefore, a reactor with an increased height-diameter ratio is likely to benefit the scaling up of the microcloud electrochemistry. We increased the yield of C₂ gas products from the degradation of DCE to 61% in a 60 mL vial reactor with a height-diameter ratio of 5 by intermittently removing gas products, achieving a selectivity of 64% for VC in C₂ gas products (Figure 4e). The final amount of Cl⁻ also slightly exceeded the dechlorination amount corresponding to the generation of C₂ gas products. Based on the concentration of

Cl⁻ in the aqueous phase, 70.2% of the DCE degraded, generating C₂ gas products in 86.7% selectivity (Figure S8).

It should be noted that the high selectivity for VC is not due to its own stability in microcloud water. In fact, when VC was introduced into the microcloud of pure water, it rapidly degraded via multiple pathways, including oxidation to CO_x and reduction to ethylene and oligomers (Figure S15). In contrast, in the presence of DCE or other aliphatic organochlorines such as dichloromethane, chlorobutane, and chlorocyclohexane, the degradation of VC can be effectively inhibited (Figure 4f). Especially, in the presence of chlorobutane, 82.2% of VC could remain intact after 2 h of spray reaction. Butylene product was detected through gas chromatography (Figure S16), indicating that both electrons and •OH were promptly captured by chlorobutane. However, no VC remained in the CCl₄-water system, despite the presence of C-Cl bonds capable of electron capture (Figure 4f). Instead, oxidation degradation products such as CO and CO₂ were detected in the gas phase (Figure S15). The CCl₄ molecule could not effectively consume •OH owing to the absence of a C-H bond, which might lead to an accumulation of reactive oxygen species and account for the oxidative degradation of VC. In addition, only 5% of VC remained intact after the reaction with chlorobenzene, accompanied by a noticeable yellow oligomer precipitate. This implies that chlorobenzene does not exhibit significant stabilizing effects on VC, likely owing to its inability to outcompete VC for electron and •OH capture. The above results indicate that the fast exhaustion of bulk-phase electrons by the C(sp³)-Cl bonds of DCE and the scavenging of microdroplet •OH by the C(sp³)-H bonds of •CH₂CH₂Cl are critical to protecting VC from degradation in the microcloud.

A schematic overview of the electro-dechlorination reaction of aliphatic organochlorine driven by back and forth phase switching of water can be delineated based on the above results (Figure S18). Electron extraction from the microdroplets to the vapor phase occurs spontaneously when the bulk-phase water undergoes spraying in the closed system. Then, due to the faster diffusion rate of vapor compared to the precipitation rate of microdroplets during phase switching, a net accumulation of electrons occurs on the surface of the bulk phase upon coalescence with microdroplets and with vapor. Thus, the spray-coalescence cycles of water can create a microcloud system where oxidation and reduction occur in the microdroplets and in the bulk-phase water, respectively. Owing to its large electron attachment cross section,^{57,58} DCE tends to capture the electron that is enriched in the bulk phase to form the anion radical ClCH₂CH₂Cl^{•-} (eq 1), which rapidly loses a chlorine ion to generate the dechlorinated intermediate •CH₂CH₂Cl (eq 2). The radicals formed following electron attachment to halogenated hydrocarbons are known to be highly reactive,⁵⁷ which is likely to lead to challenging chemoselectivity problems in subsequent reactions. The fast-phase switching of water continually replenishes exhausted DCE that could promptly consume electrons, thereby inhibiting the full reductive dechlorination of •CH₂CH₂Cl and VC to ethylene and oligomers. During the phase switching, spraying of the bulk phase as microdroplets leads to an accelerated oxidative dehydrogenation of •CH₂CH₂Cl by •OH at the interfaces of DCE-water microdroplets to generate VC (eq 3). This might be a result of the ordered solvent and reactant molecules oriented by the interfacial electric field, which can alleviate the steric effect of solvents and increase the

successful collision rates.²⁷ This also scavenges microdroplet •OH, thereby protecting VC from oxidative degradation at the microdroplet interfaces. In this way, the simultaneous reduction and oxidation reactions in the microcloud can be harnessed spatiotemporally to solve the challenging chemoselectivity problems in the upcycling of aliphatic chlorides.



CONCLUSIONS

In response to global warming, the amount of atmospheric water vapor and occurrence frequency of convective precipitation are escalating. In this regard, the cloud electrochemistry proposed in our work is expected to play an increasingly important role in the scavenging of volatile organic compounds. Apart from the natural attenuation, our results also reveal the applicability of an artificial water microcloud, achieved by the fast cycling between microdroplet, vapor, and bulk phase, as a promising upcycling approach for chlorine-containing wastewater treatment. The limitations of mass transfer of unstable intermediates could be neglected in the microcloud, thereby alleviating the challenging chemoselectivity problems found in conventional bulk-phase electrochemical processes. Further scaling up of the artificial cloud relying on renewable driving forces like hydro energy, wind energy, or solar energy is expected to bridge the gap between natural attenuation and industrial degradation of aqueous pollutants. Beyond water treatment, the cloud electrochemistry presented in this work could offer opportunities in broader applications, such as chemoselective electrosynthesis and air purification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c11224>.

Experimental methods, photographs of the experimental setup, particle distribution of microdroplets, potential measurements, quantification of chloride, CO_x and C₂H₄, and GC spectra supporting the data in the main text (PDF)

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Author Contributions

#X.C. and Y.X. contributed equally.

Notes

The authors declare no competing financial interest.

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REFERENCES

- Yung, Y. L.; McElroy, M. B. Fixation of nitrogen in the prebiotic atmosphere. *Science* **1979**, *203* (4384), 1002–1004.
- Navarro-González, R.; McKay, C. P.; Mvondo, D. N. A possible nitrogen crisis for Archaean life due to reduced nitrogen fixation by lightning. *Nature* **2001**, *412* (6842), 61–64.
- Levin, Z.; Borucki, W. J.; Toon, O. B. Lightning generation in planetary atmospheres. *Icarus* **1983**, *56* (1), 80–115.
- Gibb, B. C. Lightning-fast chemistry. *Nat. Chem.* **2019**, *11* (8), 677–679.
- Lee, J. K.; Walker, K. L.; Han, H. S.; Kang, J.; Prinz, F. B.; Waymouth, R. M.; Nam, H. G.; Zare, R. N. Spontaneous generation of hydrogen peroxide from aqueous microdroplets. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116* (39), 19294–19298.
- Lee, J. K.; Samanta, D.; Nam, H. G.; Zare, R. N. Micrometer-sized water droplets induce spontaneous reduction. *J. Am. Chem. Soc.* **2019**, *141* (27), 10585–10589.
- Ju, Y.; Zhang, H.; Jiang, Y.; Wang, W.; Kan, G.; Yu, K.; Wang, X.; Liu, J.; Jiang, J. Aqueous microdroplets promote C–C bond formation and sequences in the reverse tricarboxylic acid cycle. *Nat. Ecol. Evol.* **2023**, *7* (11), 1892–1902.
- Song, X.; Basheer, C.; Zare, R. N. Making ammonia from nitrogen and water microdroplets. *Proc. Natl. Acad. Sci. U.S.A.* **2023**, *120* (16), No. e2301206120.

- (9) Song, X.; Basheer, C.; Xia, Y.; Li, J.; Abdulazeez, I.; Al-Saadi, A. A.; Mofidfar, M.; Suliman, M. A.; Zare, R. N. One-step formation of urea from carbon dioxide and nitrogen using water microdroplets. *J. Am. Chem. Soc.* **2023**, *145* (47), 25910–25916.
- (10) Song, X.; Meng, Y.; Zare, R. N. Spraying water microdroplets containing 1,2,3-Triazole converts carbon dioxide into formic acid. *J. Am. Chem. Soc.* **2022**, *144* (37), 16744–16748.
- (11) Lee, J. K.; Han, H. S.; Chaikasetin, S.; Marron, D. P.; Waymouth, R. M.; Prinz, F. B.; Zare, R. N. Condensing water vapor to droplets generates hydrogen peroxide. *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117* (49), 30934–30941.
- (12) Pan, Y.; Zheng, X.; Zhao, G.; Rao, Z.; Yu, W.; Chen, B.; Chu, C. Water vapor condensation on iron minerals spontaneously produces hydroxyl radical. *Environ. Sci. Technol.* **2023**, *57* (23), 8610–8616.
- (13) Dang, L. X.; Chang, T.-M. Molecular mechanism of ion binding to the liquid/vapor interface of water. *J. Phys. Chem. B* **2002**, *106* (2), 235–238.
- (14) Xiong, H.; Lee, J. K.; Zare, R. N.; Min, W. Strong electric field observed at the interface of aqueous microdroplets. *J. Phys. Chem. Lett.* **2020**, *11* (17), 7423–7428.
- (15) Hao, H.; Leven, I.; Head-Gordon, T. Can electric fields drive chemistry for an aqueous microdroplet? *Nat. Commun.* **2022**, *13* (1), 280.
- (16) Kathmann, S. M.; Kuo, I. F. W.; Mundy, C. J. Electronic effects on the surface potential at the vapor–liquid interface of water. *J. Am. Chem. Soc.* **2008**, *130* (49), 16556–16561.
- (17) Heindel, J. P.; Hao, H.; LaCour, R. A.; Head-Gordon, T. Spontaneous formation of hydrogen peroxide in water microdroplets. *J. Phys. Chem. Lett.* **2022**, *13* (43), 10035–10041.
- (18) Gong, C.; Li, D.; Li, X.; Zhang, D.; Xing, D.; Zhao, L.; Yuan, X.; Zhang, X. Spontaneous reduction-induced degradation of viologen compounds in water microdroplets and its inhibition by host–guest complexation. *J. Am. Chem. Soc.* **2022**, *144* (8), 3510–3516.
- (19) Chen, H.; Wang, R.; Xu, J.; Yuan, X.; Zhang, D.; Zhu, Z.; Marshall, M.; Bowen, K.; Zhang, X. Spontaneous reduction by one electron on water microdroplets facilitates direct carboxylation with CO₂. *J. Am. Chem. Soc.* **2023**, *145* (4), 2647–2652.
- (20) Yuan, X.; Zhang, D.; Liang, C.; Zhang, X. Spontaneous reduction of transition metal ions by one electron in water microdroplets and the atmospheric implications. *J. Am. Chem. Soc.* **2023**, *145* (5), 2800–2805.
- (21) Zhao, L.; Song, X.; Gong, C.; Zhang, D.; Wang, R.; Zare, R. N.; Zhang, X. Sprayed water microdroplets containing dissolved pyridine spontaneously generate pyridyl anions. *Proc. Natl. Acad. Sci. U.S.A.* **2022**, *119* (12), No. e2200991119.
- (22) Jin, S.; Chen, H.; Yuan, X.; Xing, D.; Wang, R.; Zhao, L.; Zhang, D.; Gong, C.; Zhu, C.; Gao, X.; Chen, Y.; Zhang, X. The spontaneous electron-mediated redox processes on sprayed water microdroplets. *JACS Au* **2023**, *3* (6), 1563–1571.
- (23) Angelaki, M.; Carreira Mendes Da Silva, Y.; Perrier, S.; George, C. Quantification and mechanistic investigation of the spontaneous H₂O₂ generation at the interfaces of salt-containing aqueous droplets. *J. Am. Chem. Soc.* **2024**, *146* (12), 8327–8334.
- (24) Chen, H.; Wang, R.; Chiba, T.; Foreman, K.; Bowen, K.; Zhang, X. Designer “Quasi-benzynes”: The spontaneous reduction of ortho-diiodotetrafluorobenzene on water microdroplets. *J. Am. Chem. Soc.* **2024**, *146* (15), 10979–10983.
- (25) Zhu, C.; Pham, L. N.; Yuan, X.; Ouyang, H.; Coote, M. L.; Zhang, X. High electric fields on water microdroplets catalyze spontaneous and fast reactions in halogen-bond complexes. *J. Am. Chem. Soc.* **2023**, *145* (39), 21207–21212.
- (26) Gong, K.; Meng, Y.; Zare, R. N.; Xie, J. Molecular mechanism for converting carbon dioxide surrounding water microdroplets containing 1,2,3-Triazole to formic acid. *J. Am. Chem. Soc.* **2024**, *146* (12), 8576–8584.
- (27) Song, Z.; Liang, C.; Gong, K.; Zhao, S.; Yuan, X.; Zhang, X.; Xie, J. Harnessing the high interfacial electric fields on water microdroplets to accelerate Menshutkin reactions. *J. Am. Chem. Soc.* **2023**, *145* (48), 26003–26008.
- (28) Song, Z.; Zhu, C.; Gong, K.; Wang, R.; Zhang, J.; Zhao, S.; Li, Z.; Zhang, X.; Xie, J. Deciphering the microdroplet acceleration factors of Aza-Michael addition reactions. *J. Am. Chem. Soc.* **2024**, *146* (15), 10963–10972.
- (29) Lin, S.; Cao, L. N. Y.; Tang, Z.; Wang, Z. L. Size-dependent charge transfer between water microdroplets. *Proc. Natl. Acad. Sci. U.S.A.* **2023**, *120* (31), No. e2307977120.
- (30) Xia, Y.; Xu, J.; Li, J.; Chen, B.; Dai, Y.; Zare, R. N. Visualization of the charging of water droplets sprayed into air. *J. Phys. Chem. A* **2024**, *128* (28), S684–S690.
- (31) Heindel, J. P.; LaCour, R. A.; Head-Gordon, T. The role of charge in microdroplet redox chemistry. *Nat. Commun.* **2024**, *15* (1), 3670.
- (32) Chen, X.; Xia, Y.; Wu, Y.; Xu, Y.; Jia, X.; Zare, R. N.; Wang, F. Sprayed oil–water microdroplets as a hydrogen source. *J. Am. Chem. Soc.* **2024**, *146* (15), 10868–10874.
- (33) Chen, B.; Xia, Y.; He, R.; Sang, H.; Zhang, W.; Li, J.; Chen, L.; Wang, P.; Guo, S.; Yin, Y.; Hu, L.; Song, M.; Liang, Y.; Wang, Y.; Jiang, G.; Zare, R. N. Water–solid contact electrification causes hydrogen peroxide production from hydroxyl radical recombination in sprayed microdroplets. *Proc. Natl. Acad. Sci. U.S.A.* **2022**, *119* (32), No. e2209056119.
- (34) Huang, B.; Lei, C.; Wei, C.; Zeng, G. Chlorinated volatile organic compounds (Cl-VOCs) in environment - sources, potential human health impacts, and current remediation technologies. *Environ. Int.* **2014**, *71*, 118–138.
- (35) Vogel, T. M.; Criddle, C. S.; McCarty, P. L. ES&T Critical Reviews: Transformations of halogenated aliphatic compounds. *Environ. Sci. Technol.* **1987**, *21* (8), 722–736.
- (36) Falta, R. W.; Bulsara, N.; Henderson, J. K.; Mayer, R. A. Leaded-gasoline additives still contaminate groundwater. *Environ. Sci. Technol.* **2005**, *39* (18), 378A–384A.
- (37) Falta, R. W. The potential for ground water contamination by the gasoline lead scavengers ethylene dibromide and 1,2-dichloroethane. *Groundwater Monit. Rem.* **2004**, *24* (3), 76–87.
- (38) *Toxicological Profile for 1,2-Dichloroethane*; Registry, A. f. T. S. a. D., Ed.; US Department of Health and Human Services, 2022.
- (39) Scialdone, O.; Galia, A.; Filardo, G. Electrochemical incineration of 1,2-dichloroethane: Effect of the electrode material. *Electrochim. Acta* **2008**, *53* (24), 7220–7225.
- (40) Sonoyama, N.; Sakata, T. Electrochemical continuous decomposition of chloroform and other volatile chlorinated hydrocarbons in water using a column type metal impregnated carbon fiber electrode. *Environ. Sci. Technol.* **1999**, *33* (19), 3438–3442.
- (41) Radjenovic, J.; Sedlak, D. L. Challenges and opportunities for electrochemical processes as next-generation technologies for the treatment of contaminated water. *Environ. Sci. Technol.* **2015**, *49* (19), 11292–11302.
- (42) Choi, C.; Wang, X.; Kwon, S.; Hart, J. L.; Rooney, C. L.; Harmon, N. J.; Sam, Q. P.; Cha, J. J.; Goddard, W. A.; Elimelech, M.; Wang, H. Efficient electrocatalytic valorization of chlorinated organic water pollutant to ethylene. *Nat. Nanotechnol.* **2023**, *18* (2), 160–167.
- (43) Lin, R.; Amrute, A. P.; Pérez-Ramírez, J. Halogen-mediated conversion of hydrocarbons to commodities. *Chem. Rev.* **2017**, *117* (5), 4182–4247.
- (44) Liang, Y.; Lin, F.; Adeli, Y.; Jin, R.; Jiao, N. Efficient electrocatalysis for the preparation of (hetero)aryl chlorides and vinyl chloride with 1,2-dichloroethane. *Angew. Chem., Int. Ed.* **2019**, *58* (14), 4566–4570.
- (45) Zeng, L.; Wang, J.; Wang, D.; Yi, H.; Lei, A. Comprehensive comparisons between directing and alternating current electrolysis in organic synthesis. *Angew. Chem., Int. Ed.* **2023**, *62* (50), No. e202309620.
- (46) Rodrigo, S.; Gunasekera, D.; Mahajan, J. P.; Luo, L. Alternating current electrolysis for organic synthesis. *Curr. Opin. Electrochem.* **2021**, *28*, 100712.

- (47) Lenard, P. Ueber die electricität der wasserfälle. *Ann. Phys.* **1892**, 282 (8), 584–636.
- (48) Tammet, H.; Hörrak, U.; Kulmala, M. Negatively charged nanoparticles produced by splashing of water. *Atmos. Chem. Phys.* **2009**, 9 (2), 357–367.
- (49) Gunasekera, D.; Mahajan, J. P.; Wanzi, Y.; Rodrigo, S.; Liu, W.; Tan, T.; Luo, L. Controlling one- or two-electron oxidation for selective amine functionalization by alternating current frequency. *J. Am. Chem. Soc.* **2022**, 144 (22), 9874–9882.
- (50) Wang, D.; Jiang, T.; Wan, H.; Chen, Z.; Qi, J.; Yang, A.; Huang, Z.; Yuan, Y.; Lei, A. Alternating current electrolysis enabled formal C–O/O–H cross-metathesis of 4-alkoxy anilines with alcohols. *Angew. Chem., Int. Ed.* **2022**, 134 (18), No. e202201543.
- (51) Bortnikov, E. O.; Smith, B. S.; Volochnyuk, D. M.; Semenov, S. N. Stirring-free scalable electrosynthesis enabled by alternating current. *Chem. Eur. J.* **2023**, 29 (18), No. e202203825.
- (52) Zaky, A. M.; Chaplin, B. P. Porous substoichiometric TiO₂ anodes as reactive electrochemical membranes for water treatment. *Environ. Sci. Technol.* **2013**, 47 (12), 6554–6563.
- (53) Martínez-Huitle, C. A.; Rodrigo, M. A.; Sirés, I.; Scialdone, O. Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: A critical review. *Chem. Rev.* **2015**, 115 (24), 13362–13407.
- (54) Chen, X.; Xia, Y.; Zhang, Z.; Hua, L.; Jia, X.; Wang, F.; Zare, R. N. Hydrocarbon Degradation by Contact with Anoxic Water Microdroplets. *J. Am. Chem. Soc.* **2023**, 145 (39), 21538–21545.
- (55) Yuan, G.; Jin, Z.; Cao, Y.; Schulz, H.-M.; Gluyas, J.; Liu, K.; He, X.; Wang, Y. Microdroplets initiate organic-inorganic interactions and mass transfer in thermal hydrous geosystems. *Nat. Commun.* **2024**, 15 (1), 4960.
- (56) Kumar, A.; Avadhani, V. S.; Nandy, A.; Mondal, S.; Pathak, B.; Pavuluri, V. K. N.; Avulapati, M. M.; Banerjee, S. Water Microdroplets in Air: A Hitherto Unnoticed Natural Source of Nitrogen Oxides. *Anal. Chem.* **2024**, 96 (26), 10515–10523.
- (57) McCorkle, D. L.; Szamrej, I.; Christophorou, L. G. Electron attachment to halocarbons of environmental interest: Chloroethanes. *J. Chem. Phys.* **1982**, 77 (11), 5542–5548.
- (58) Walter, W. K.; Jones, R. G.; Waugh, K. C.; Bailey, S. The reaction of 1,2-dichloroethane with copper. *Catal. Lett.* **1994**, 24 (3–4), 333–342.