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Simultaneous degradation of 1,4-dioxane and 1,1,1-trichloroethane with a flowing water-film plasma reactor

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Abstract

In this work, a flowing water-film plasma reactor was used to simultaneously degrade 1,4-dioxane and 1,1,1-trichloroethane. Chemical oxidation of 1,4-dioxane and 1,1,1-trichloroethane with advanced oxidation has previous been achieved independently, however, simultaneous removal of both compounds in the same advanced oxidation reactor is a challenge due to the compounds dramatic differences in physical properties. 1,4-dioxane is highly miscible in water while, 1,1,1-trichloroethane has a very low solubility, easily partitioning into the gas phase. 1,4-dioxane was historically used as a stabilizer for 1,1,1-trichloroethane, a widely used chlorinated solvent, hence, water sources co-contaminated by 1,4-dioxane and 1,1,1-trichloroethane are common. In the flowing water-film reactor, plasma channels propagate in the gas phase along the water/gas interface, creating reactive species such as hydroxyl radicals, free electrons, and atomic hydrogen which can react in the gas phase to degrade 1,1,1-trichloroethane, as well as penetrate into liquid film to simultaneously degrade the 1,4-dioxane. Removal efficiency was shown to be independent of the presence of the other compound likely because degradation occurred in separate phases – water for 1,4-dioxane, and gas for 1,1,1-trichloroethane.

Keywords: Non-thermal plasma, nanosecond discharge, 1,1,1-trichlorethane, 1,4-dioxane.

1. Introduction

The removal of pollutants from gases and liquids by various types of plasma processes has been extensively studied over the past thirty or more years [1−7]. For example, volatile organic compounds including chlorinated hydrocarbons can be removed from the gas phase by plasma processes [8, 9] and, more generally, many air pollutants have been treated with plasma [7]. Water treatment has also been pursued using many types of plasma reactors including plasma formed directly in the liquid and plasma generated over the liquid [1, 5, 6, 10−12]. Some water pollutants, for example many chlorinated organics including 1,1,1-trichloroethane (TCA), are highly volatile and can rapidly transfer from the liquid to the gas. TCA frequently co-occurs with 1,4-dioxane, a highly water soluble contaminant [13], and therefore treatment technologies that can simultaneously degrade both gas and liquid contaminants are of major interest for such pollution problems.

TCA dissolved in water has been degraded, for example, with electron beams [14], sonication combined with persulfate [15], peroxone activated persulfate [16], and catalytic treatment of this contaminant followed by biotreatment has also been reported [17]. TCA in air at low concentrations was also decomposed by electron beam and corona discharge [18−20]. 1,4-dioxane can be degraded by ozone and catalytic ozonation [21] and other advanced oxidation processes combined with biotreatment [22]. However, only a few studies have reported the simultaneous degradation of TCA and 1,4-dioxane. In one example, Li *et al*. [23] showed that TCA and 1,4-dioxane can be degraded simultaneously by a sono-activated persulfate process.

Previous work has demonstrated that the flowing water film plasma reactor utilized in this study can degrade 1,4-dioxane dissolved in the liquid water [24] by reaction with hydroxyl radicals that reach the liquid phase after formation in the plasma channels that propagate along the gas-liquid interface. Hydroxyl radicals are formed through water dissociation and other reactions that occur in the plasma and some of these hydroxyl radicals recombine to form hydrogen peroxide (which transports easily into the liquid) and some of the hydroxyl radicals directly dissolve into the liquid [25, 26]. In addition, atomic hydrogen is formed in the plasma by the water dissociation, and as with the hydroxyl radicals, some atomic hydrogen recombines to form molecular hydrogen (which escapes into the flowing gas phase) and some atomic hydrogen may be available for reaction with contaminates in or near the plasma discharge [27]. There is also evidence of hydrated (aqueous) electrons reacting in the liquid phase in gas-liquid plasma reactors [28−30]. In the plasma phase, free electrons are also readily available and may react with volatile components that reach this phase. This complex mixture of oxidative (hydroxyl radical) and reductive (free electrons, atomic hydrogen and hydrated electrons) species can lead to degradation of components in both the gas and liquid phases. Since most of our previous work has focused on degradation of liquid phase [31] or interfacially active [32] compounds individually, the objective of this work is to analyze the simultaneous degradation of gas and liquid phase compounds. In addition, since TCA and 1,4 dioxane are both present in the liquid entering the system, but TCA is relatively more volatile, it is important to assess its transfer into the gas phase and determine where it is mainly reacting. The choice of 1,4-dioxane and TCA allows consideration of predominately gas phase and liquid phase species in a mixture that is of significant environmental applicability. The degradation pathway for TCA is also investigated by assessment of the intermediates generated in order to evaluate the roles of oxidative and reductive species.

2. Experimental

2.1 Plasma reactor

The plasma reactor used in the present study has been described previously [24, 33]. Fig. 1 shows a schematic of the system where liquid water solutions containing TCA and/or 1,4-dioxane are first pumped via a high-pressure reciprocating pump into to a mixing zone (0.125 in, 3.175 mm, Swagelok tee joint) where they combine with an argon carrier gas which is supplied at 60 psig (4 atm). The liquid and argon flow rates were constant for all experiments performed at 2 mL min^{-1} and 0.5 L min^{-1} respectively. Following the mixing zone, the high-pressure gas-liquid mixture enters the plasma reactor via a 0.25 mm ID stainless steel capillary where upon entering the discharge region the liquid phase forms a thin film along the walls of the reactor with a gas core flowing through the center. This annular flow pattern is caused by the large pressure drop between the inlet nozzle (4 atm) and the discharge region (2.5 atm) [34]. The residence time for the gas and liquid phases were investigated in previous work and estimated to be 2.5 and 150 ms, respectively, at the operating conditions utilized in this work [34]. The gas-liquid mixture exits the discharge region through a 1 mm ID stainless steel capillary and the liquid phase is collected in a beaker for further analysis.

The stainless-steel inlet and outlet capillary tubes also serve as the anode and cathode for plasma generation. A commercially available pulsed high voltage power supply (Eagle Harbor Technologies, LLC) capable of independent variation of output voltage (0−20 kV) pulse width (20−240 ns), and pulse frequency (single to 10 kHz) was utilized. The power supply settings were held constants for all experiments at 20 kV, 20 ns, and 10 kHz. It is also important to note that the plasma generated is a short lived “spark” in the gas phase which travels along the interface of the liquid film. The time averaged plasma properties for this system have been estimated in previous work and for an argon carrier gas the plasma gas temperature was 600 K with electron density of 2×10^{16} cm^{-3}, but independent of the input power in the range of 0.2 to 1.0 W [35].

Electrical diagnostics were performed with an oscilloscope (Tektronix, DPO 5204B) in conjunction with two HV probes (North Star, PVM-4 and Tektronix, DPO 5204B) and a Rogowski coil (Pearson Electronics, 6585). The leads of the HV probes were connected across the stainless-steel inlet and outlet capillaries and the grounds of the probes were connected in order to measure the electric potential between the electrodes. The Rogowski coil was centered around the plasma reactor body to measure current flow through the discharge region. The energy per pulse was calculated by multiplying the voltage and current and integrating the resulting power over the time period of a single pulse.

$$\text{Energy per pulse} = \int (V \times I) dt \tag{1}$$

V: Instantaneous voltage
I: Instantaneous current
t: Time

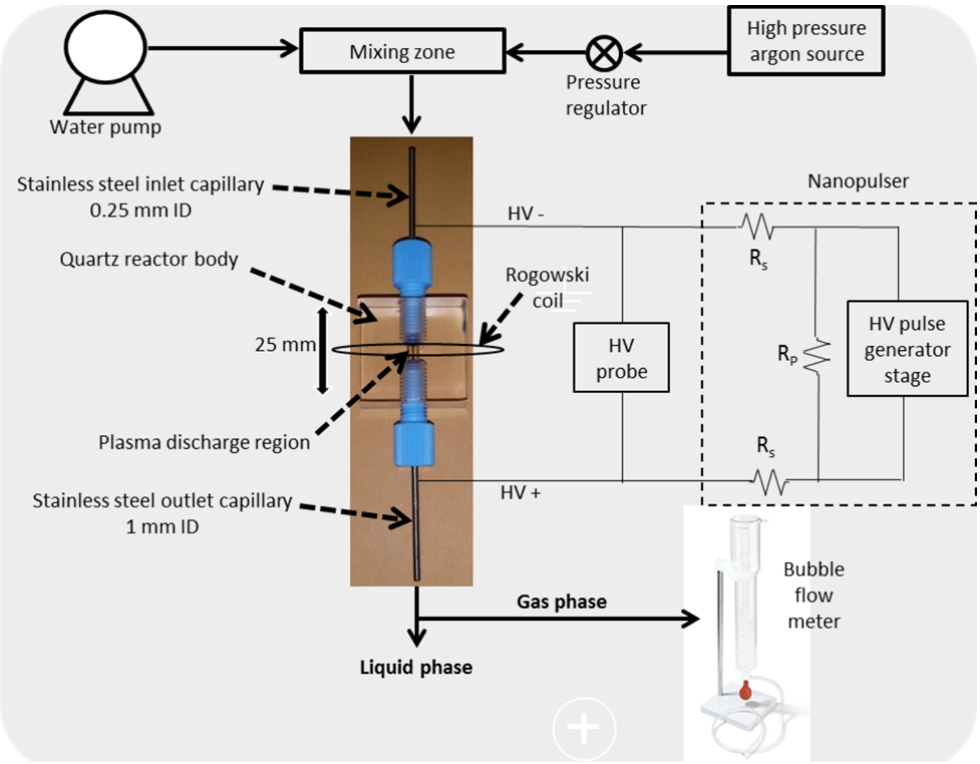

Fig. 1. Schematic of plasma reactor system showing feed of liquid via the water pump and gas via high pressured argon source.

Total discharge power was calculated by multiplying the energy per pulse by the pulse frequency. More information on the electrical diagnostics can be found in our previous publications [34].

2.2 Experimental design

Three sets of experiments were carried out. In the first set, the influent contained 50 mg L^{-1} TCA, while in the second set of experiments, the influent contained 50 mg L^{-1} 1,4-dioxane. In the third set of experiments, the influent contained 50 mg L^{-1} 1,4-dioxane and 50 mg L^{-1} TCA. A previous study has shown that the ratios of 1,4-dioxane to TCA in groundwater were as high as 0.08−5.89, notably much higher than found in commercial solvents in which 1,4-dioxane is used as a stabilizer at 1% relative amounts [36]. That can be explained by the fact that 1,4-dioxane is considered more recalcitrant to degradation than TCA in groundwater. Therefore, we used a 1,4-dioxane to TCA ratio of 1:1 in this study.

The influent was prepared by adding calculated amounts of pure 1,4-dioxane and/or TCA in sealed serum bottles filled with de-ionized water. When preparing influent containing TCA for experimental sets 1 and 3, the headspace was minimized, and magnetic stir bars were placed in the serum bottles to ensure proper mixing. The sealed serum bottles were then stirred on a magnetic stirrer for 48 hours to ensure that TCA was fully dissolved. Considering the stripping effects of the gas flow, the plasma reactor was operated with plasma off (as a control) and plasma on for each set of experiments.

2.3 Chemical analysis

Aqueous phase TCA was quantified using a static headspace method (modified from EPA SW-846 Test Method 5021A) with Agilent 6890 Gas Chromatography (GC) coupled with a OI Analytical Model 5360

Specific Detector (XSD™). Gaseous phase TCA was quantified by direct injecting 100 μL gaseous samples into the GC-XSD system. The GC oven temperature was maintained at 35 °C during the measurements, the temperature of the injection port and the detector was 200°C and 300°C, respectively. The detection limit was 10 μg L^{-1}.

Method details for quantifying aqueous phase 1,4-dioxane concentration have been described [24]. Because the Henry's Law constant for 1,4-dioxane is low [37], gaseous phase 1,4-dioxanae concentration was negligible and not quantified in the experiments.

The intermediates were identified using a Hewlett-Packard gas chromatography/mass spectrometry (GC-MS) (GC 5890 series II; MSD5971A) at the Scan mode. To analyze the intermediates generated in the aqueous phase, 10 mL of aqueous sample was transferred to a 20-mL vial and magnetically stirred (400 rpm) at 60°C for 30 min. 75 μm Carboxen /Polydimethylsiloxane (CAR/PDMS) fiber (Supelco, Bellefonte, USA) was immerged in the solution to extract 1,4-dioxane during the mixing, and then thermally desorbed for 5 min at the GC injector (225°C). The oven temperature was programmed from 35 to 80 (6 °C min^{-1}) and then from 80 to 120 (8 °C min^{-1}) holding for 3 min, then to 200 (12 °C min L^{-1}) [23]. The detector temperature was 150°C. The intermediates in the gaseous phase were analyzed at the same settings, except that the gaseous samples were directly injected to the GC-MS. Most of the intermediates were identified based on the fittings with the spectra library. To verify the generation of several key intermediates including 1,1-dichloroethene, 1,1-dichlorethane, 2,2,2-trichloroethanol, 1,1,1,2-tetrachloroethane and acetaldehyde, chemical standards were injected into the GC-MS at the same settings, the chemical standards' retention times and mass spectra were then compared against that of the samples.

Chloride (Cl^-) was measured in the first and third sets of experiments using ion chromatography (IC) (Dionex Aquion) with an IonPac™ AS22 column (4 × 250 mm), an AERS™ 500 carbonate suppressor and a conductivity detector. The eluent was 4.5 mM sodium carbonate mixed with 1.4 mM sodium bicarbonate and supplied to the IC system at an isocratic flow of 1.2 mL min^{-1}.

3. Results and discussion

3.1 Primary compound degradation

Figs. 2 and 3 show the degradation results for TCA (Fig. 2) and 1,4-dioxane (Fig. 3), respectively, for the three sets of experiments described previously. Regarding the experiments with TCA only, when the plasma was off, Fig. 2b shows that almost 100% of the influent TCA partitioned into the gas phase while the influent was flowing through the reactor. Fig. 2b also shows good mass balance for TCA in the plasma-off control. When the plasma was turned on, the concentration of TCA decreased in both the liquid phase and the gas phase compared to the plasma off control (Fig. 2a). The overall removal percentage of TCA in the reactor, including the gas-phase and liquid-phase removal, was 39.3%. Due to the vaporization of TCA, it can be inferred that degradation occurred mostly in the gas phase.

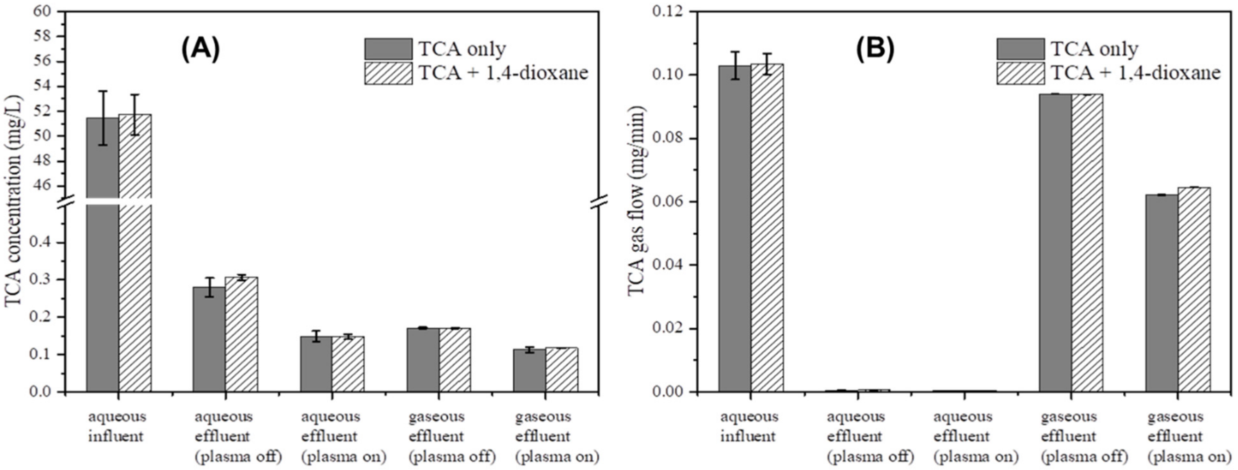

Fig. 2. (A) TCA concentration and (B) TCA mass flow for all cases. The liquid water flow was 2 mL min^{-1} and the argon gas flow was 0.5 L min^{-1}.

With respect to Fig. 3, with the plasma off, 98% of the 1,4-dioxane in the reactor influent stayed in the liquid phase and the remaining 2% partitioned into the gas phase. When the plasma was turned on, the liquid-phase 1,4-dioxane concentration in the reactor effluent dropped from ~50 to ~10 mg L^{-1}, corresponding to a 1,4-dioxane removal percentage of 78.8% in the liquid. This removal approximately represented the overall 1,4-dioxane removal in the reactor, including gas-phase and liquid-phase removal, because there was only 2% of 1,4-dioxane in the gas phase. From this result it can be inferred that 1,4-dioxane degradation occurs mostly in the liquid phase.

1,4-Dioxane and TCA did not significantly affect the removal of each other when they both were presented in the influent. The TCA removal was 39.3% in the set of TCA-only experiments and 37.3% in the set of combined TCA and 1,4-dioxane experiments. Similarly, the set of 1,4-dioxane-only experiments gave 78.8% removal of 1,4-dioxane and the set of combined 1,4-dioxane and TCA experiments gave 74.6% removal of 1,4-dioxane. This can be explained since the 1,4-dioxane degradation mainly occurred in the liquid phase, but the TCA degradation mainly occurred in the gas phase. Therefore, there was no competition for reactive species in the same phase. The previously reported pathway for 1,4-dioxane degradation in the same reactor [24] involves mainly oxidation through hydroxyl radicals in the liquid phase to form smaller organic acids before complete mineralization supports this hypothesis.

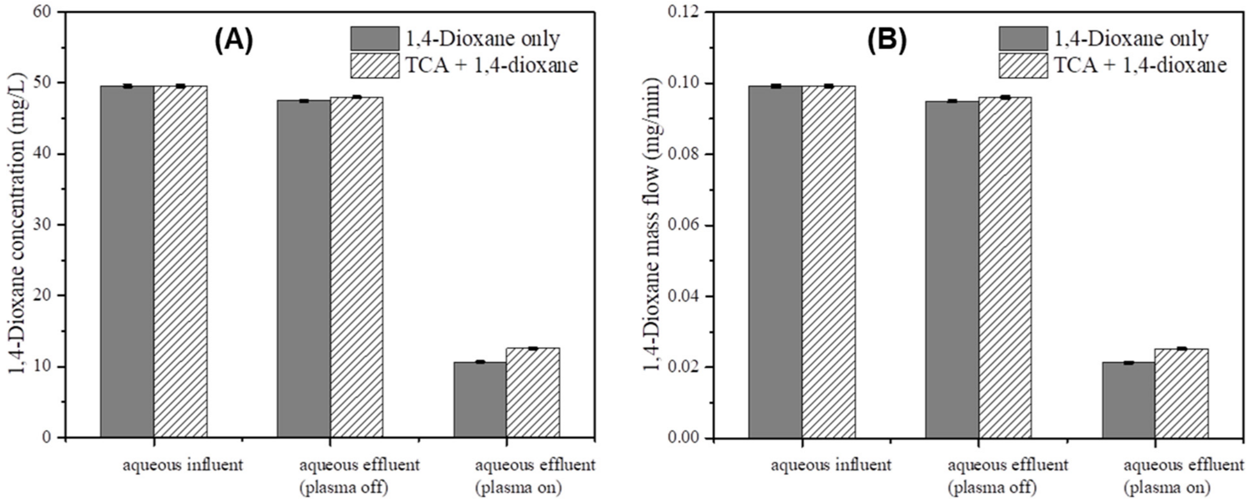

Fig. 3. (A) 1, 4-Dioxane concentration and (B) 1,4-Dioxane mass flow for all cases. The liquid water flow was 2 mL min^{-1} and the argon gas flow was 0.5 L min^{-1}.

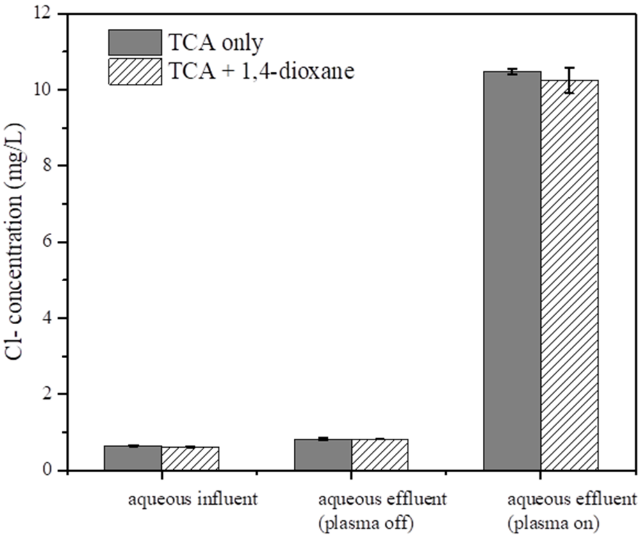

Fig. 4. V-I characteristic for various gas velocities at positive and negative voltages.

Fig. 4 shows the chloride (Cl^{-}) concentrations in the influent and effluent with only TCA in the influent, and with both TCA and 1,4-dioxane. The same concentrations of Cl^{-}, a mineralization product of TCA, was measured in the liquid phase with and without 1,4-dioxane present. From this result, the chloride must have been formed in the gas phase and rapidly dissolved back into the liquid phase. Since the effluent chloride concentration was ~10.5 mg L^{-1} and the influent contained TCA at 51.5 mg L^{-1} (= 41.1 mg-Cl^- L^{-1}), the chlorine removal efficiency was 25.5%, which was lower than the TCA removal efficiency of 37.3−39.3%. This was due to the formation of intermediates rather than complete mineralization.

3.2 Reaction products and mechanism

Table 1 shows reaction products from TCA detected in a) both gas and liquid samples, b) only the gas samples, and c) only the liquid samples. Many of these products were found in other studies dealing with TCA degradation by advanced oxidation. Six of these compounds are on the U.S. Environmental Protection Agency's Priority Pollutant List. Four of the six compounds are regulated by U.S. Environmental Protection Agency in drinking water. The maximum contaminant levels of the four compounds are also included in Table 1.

Table 1. Intermediates detected in liquid and/or gas samples using GC/MS-SPME[b].

	Retention Time (min)	Chemical	Fitting with the spectra library (%)	Priority Pollutant List [40]	Maximum Contaminant Level (mg L^{-1}) [41]
Detected in liquid samples and gas samples	7.3	Ethanol	80		
	7.5	1,1-Dichloroethene (Z/E)	96		
	8.5	Methylene chloride	91		
	10.0	1,1-Dichlorethane	91	✓	0.005
	11.0	1,1-Dichlorethene (Z/E)	96		
	11.4	Chloroform	90	✓	0.08 [a]
	12.8	1,2-dichloroethane	94	✓	0.005
	13.4	Trichloroethylene	83	✓	0.005
	17.6	1,1,2-trichloroethane	98	✓	
	19.8	1,1,1,2-Tetrachloroethane	91		
	22.6	1,1,2,2-Tetrachloroethane	90	✓	
	23.6	Pentachloroethane	78		
Only detected in gas samples		None			
Only detected in liquid samples	5.7	Acetaldehyde[c]	72		
	8.9	1,2-dichloroethene	93		
	15.3	2-chloroethanol	86		
	20.1	2,2-Dichloroethanol	90		
	23.1	2,2,2-Trichloroethanol	97		

[a] Chloroform is regulated as one of the total trihalomethanes (TTHMs) for which the MCL is 80 µg L^{-1}.
[b] Compounds that have more than two carbons are not included in this table because they are likely impurities in the chemicals used.
[c] Acetaldehyde may result from contaminants in the TCA feed solution.

Based upon the intermediates found and reactions with plasma generated reactive species, a proposed TCA degradation pathway is shown in Fig. 5. The chemical/plasma-chemical reactions include hydrogen abstraction by an OH radical, homolytic bond cleavage through a high energy electron, beta-scission, addition of radicals to a double bond, ejection of a lone pair electron through a high energy electron, and radical recombination with Cl, OH or H-radicals. Furthermore, the following chemical standard reactions were included: (acid catalyzed) addition of water to a double bond, and dissociation of alpha-chlorinated alcohols to acyl chlorides. The reaction scheme combines the OH radical pathways with reductive pathways including electron and atomic hydrogen reactions. The five key reaction products measured are boxed in Fig. 5 and were confirmed by standards, 1,1-dichloroethane, 1,1-dichloroethane, 1,1,1,2-tetrachloroethane, acetaldehyde, and 2,2,2-trichloroethanol. Three of the five products were also found in sonolysis experiments (1,1- dichloroethane; 1,1-dichloroethane, and 1,1,1,2-tetrachloroethane) [23]. Because sonolysis generates similar reactive species this supports the proposed reaction pathway. Acetaldehyde may be the product from preexisting contaminants in the TCA feed source or it may be the result of reductive pathways through hydrated electrons. Further work is necessary to consider these possibilities in this system since acetaldehyde has not been reported as a product of TCA [38] but electrochemical cathodic reduction can lead from carboxylic acids to aldehydes [39]. In general, this mechanism supports the hypothesis that plasma generated electrons, atomic hydrogen, and hydroxyl radicals all participate in the degradation of the TCA in the gas phase.

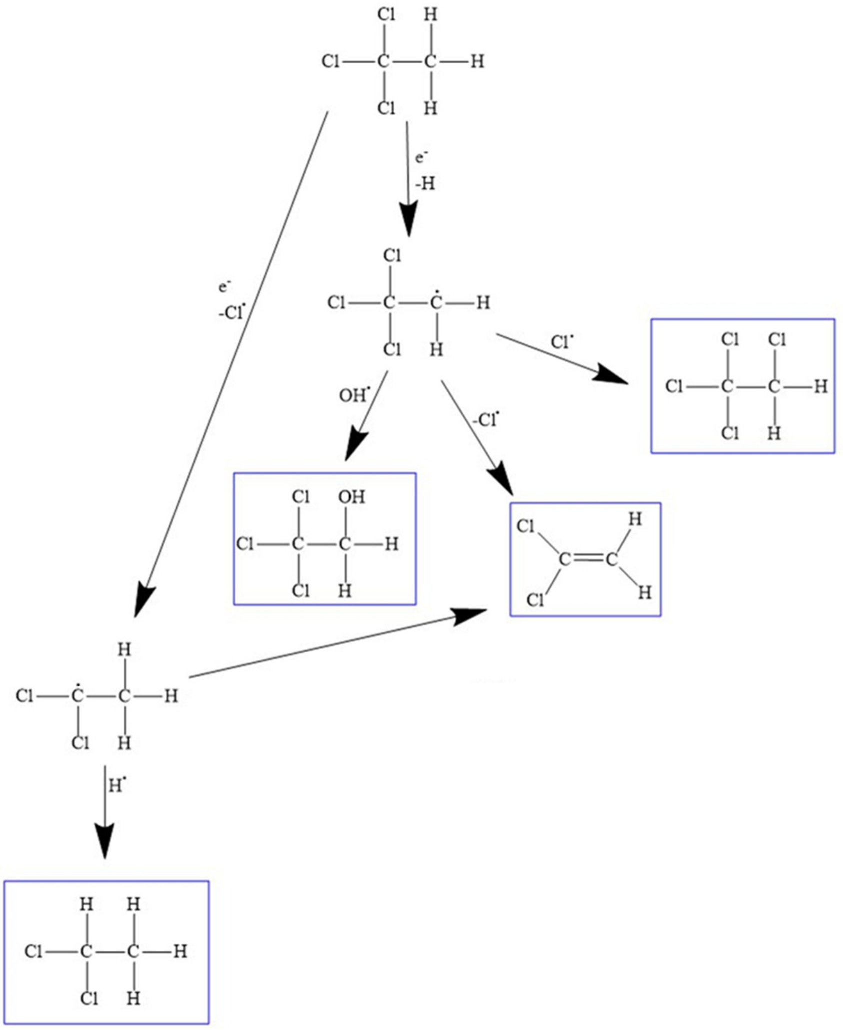

Fig. 5. Proposed TCA reaction pathway based upon observed chemical species (blue boxes) and reactions with oxidative and reductive species.

4. Conclusion

We have demonstrated the simultaneous degradation of gas and liquid phase pollutants in a gas/liquid plasma reactor. At the concentrations utilized, there were no significant interactions or interferences in degrading the pollutants simultaneously as compared to individually. The partitioning of the TCA into the gas phase while the 1,4-dioxane remains in the liquid phase is likely the cause of the independence between the two pathways. The pathway for 1-4 dioxane is likely the same as that proposed in previous work [24]. The proposed pathway for TCA suggests gas phase reactions with the plasma generated oxidizing (hydroxyl radical) and reducing (free electrons and atomic hydrogen) species.

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References

[1] Jiang B., Zheng J., Qiu S., Wu M., Zhang Q., Yan Z., and Xue Q., Review on electrical discharge plasma technology for wastewater remediation, *Chem. Eng. J.*, Vol. 236, pp. 348−368, 2014.

[2] Pasquiers S., Cormier M., and Motret O., Atmospheric pollutant removal by non-thermal plasmas: basic data needs for understanding and optimization of the process, *AIP Conference Proceedings,* Vol. 636, pp. 111−121, 2002.

[3] Sunka P., Pulse electrical discharges in water and their applications, *Phys. Plasmas*, Vol. 8, pp. 2587−2594, 2001.

[4] Malik M. A., Ghaffar A., and Malik S. A., Water purification by electrical discharges, *Plasma Sources Sci. Technol.*, Vol. 10 (1), pp. 82−91, 2001.

[5] Mededovic-Thagard S., and Locke B. R., Electrical discharge plasma for water treatment, advanced oxidation processes for water treatment: Fundamentals and Applications, M. I. Stefan, ed., London, UK: IWA Publishing, 2017.

[6] Locke B. R., Sato M., Sunka P., Hoffmann M. R., and Chang J. S., Electrohydraulic discharge and nonthermal plasma for water treatment, *Ind. Eng. Chem. Res.*, Vol. 45 (3), pp. 882−905, 2006.

[7] Kim H. H., Nonthermal plasma processing for air-pollution control: A historical review, current issues, and future prospects, *Plasma Process. Polym.*, Vol. 1 (2), pp. 91−110, 2004.

[8] Urashima K., Misaka T., Ito T., and Chang J. S., Destruction of volatile organic compounds in air by a superimposed barrier discharge plasma reactor and activated carbon filter hybrid system, *J. Adv. Oxid. Technol.*, Vol. 5 (2), pp. 135−140, 2002.

[9] Oda T., Takahashi T., and Tada K., Decomposition of dilute trichloroethylene by nonthermal plasma, *IEEE Trans. Ind. Applicat.*, Vol. 35 (2), pp. 373−379, 1999.

[10] Takeuchi N., and Yasuoka K., Review of plasma-based water treatment technologies for the decomposition of persistent organic compounds, *Jpn. J. Appl. Phys.*, Vol. 60 (SA), pp. SA0801, 2021.

[11] Zeghioud H., Phuong N.-T., Khezami L., Amrane A., and Assadi A. A., Review on discharge Plasma for water treatment: mechanism, reactor geometries, active species and combined processes, *J. Water Process Eng.*, Vol. 38, 101664, 2020.

[12] Miklos D. B., Remy C., Jekel M., Linden K. G., Drewes J. E., and Hubner U., Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review, *Water Res.*, Vol. 139, pp. 118−131, 2018.

[13] Adamson D. T., Pina E. A., Cartwright A. E., Rauch S. R., Anderson R. H., Mohr T., and Connor J. A., 1,4-Dioxane drinking water occurrence data from the third unregulated contaminant monitoring rule, *Sci. Total Environ.*, Vol. 596, pp. 236−245, 2017.

[14] Lopez J. P., Cooper W. J., Slifker R. A., Rossell L., Waite T. D., Kurucz C. N., and Nickelsen M. G., Removal of 1,1,1-trichloroethane from aqueous-solutions using the high-energy electron-beam process, *Abst. Papers Am. Chem. Soc.*, Vol. 207, pp. 90−ENVR, 1994.

[15] Li B. Z., Li L., Lin K. F., Zhang W., Lu S. G., and Luo Q. S., Removal of 1,1,1-trichloroethane from aqueous solution by a sono-activated persulfate process, *Ultrasonics Sonochem.*, Vol. 20 (3), pp. 855−863, 2013.

[16] Eberle D., Ball R., and Boving T. B., Peroxone activated persulfate treatment of 1,4-dioxane in the presence of chlorinated solvent co-contaminants, *Chemosphere*, Vol. 144, pp. 728−735, 2016.

[17] Luo Y. H., Long X. X., Wang B. Y., Zhou C., Tang Y. N., Krajmalnik-Brown R., and Rittmann B. E., A synergistic platform for continuous co-removal of 1,1,1-trichloroethane, trichloroethene, and 1,4-dioxane via catalytic dechlorination followed by biodegradation, *Environ. Sci. Technol.*, Vol. 55 (9), pp. 6363−6372, 2021.

[18] Vitale S. A., Hadidi K., Cohn D. R., and Falkos P., Electron beam generated plasma decomposition of 1,1,1-trichloroethane, *Plasma Chem. Plasma Proc.*, Vol. 16 (4), pp. 651−668, 1996.

[19] Nicoletti A., Paradisi C., and Scorrano G., Ion chemistry of chloroethanes in air at atmospheric pressure, *Rapid Commun. Mass Spectrometry*, Vol. 15 (20), pp. 1904−1911, 2001.

[20] Marotta E., Scorrano G., and Paradisi C., Ionic reactions of chlorinated volatile organic compounds in air plasma at atmospheric pressure, *Plasma Proc. Polym.*, Vol. 2 (3), pp. 209−217, 2005.

[21] Scaratti G., Basso A., Landers R., Alvarez P. J. J., Li Puma G., and Moreira R., Treatment of aqueous solutions of 1,4-dioxane by ozonation and catalytic ozonation with copper oxide (CuO), *Environ. Technol.*, Vol. 41 (11), pp. 1464−1476, 2020.

[22] Tawfik A., Degradation pathways of 1,4-dioxane in biological and advanced oxidation processes, *Desalination Water Treatment*, Vol. 178, pp. 360−386, 2020.

[23] Li B. Z., and Zhu J., Simultaneous degradation of 1,1,1-trichloroethane and solvent stabilizer 1,4-dioxane by a sono-activated persulfate process, *Chem. Eng. J.*, Vol. 284, pp. 750−763, 2016.

[24] Xiong Y., Zhang Q., Wandell R., Bresch S., Wang H., Locke B. R., and Tang Y., Synergistic 1,4-dioxane removal by non- thermal plasma followed by biodegradation, *Chem. Eng. J.*, Vol. 361, pp. 519−527, 2019.
[25] Hsieh K. C., Wandell R. J., Bresch S., and Locke B. R., Analysis of hydroxyl radical formation in a gas-liquid electrical discharge plasma reactor utilizing liquid and gaseous radical scavengers, *Plasma Proc. Polym.*, Vol. 14 (8), e1600171, 2017.
[26] Wang H., Wandell R. J., Tachibana K., Vorac J., and Locke B. R., The influence of liquid conductivity on electrical breakdown and hydrogen peroxide production in a nanosecond pulsed plasma discharge generated in a water-film plasma reactor, *J. Phys. D: Appl. Phys.*, Vol. 52 (7), 075201, 2019.
[27] Wandell R., Bresch S., Wang H., Babicky V., P. Lukes, and B. R. Locke, The effects of pulse frequency on chemical species formation in a nanosecond pulsed plasma gas-liquid film reactor, *Int. J. Plasma Environ. Sci. Technol.*, Vol. 14 (1), e01008, 2020.
[28] Bruggeman P. J., Kushner M. J., Locke B. R., Gardeniers J. G. E., Graham W. G., Graves D. B., Hofman-Caris R. C. H. M., Maric D., Reid J. P., Ceriani E., Rivas D. F., Foster J. E., Garrick S. C., Gorbanev Y., Hamaguchi S., Iza F., Jablonowski H., Klimova E., Kolb J., Krcma F., Lukes P., Machala Z., Marinov I., Mariotti D., Thagard S. M., D. Minakata, Neyts E. C., Pawlat J., Petrovic Z. L., Pflieger R., Reuter S., D. C. Schram, S. Schroter, M. Shiraiwa, Tarabova B., Tsai P. A., Verlet J. R. R., von Woedtke T., Wilson K. R., Yasui K., and Zvereva G., Plasma-liquid interactions: a review and roadmap, *Plasma Sources Sci. Technol.*, Vol. 25 (5), 053002, 2016.
[29] Thagard S. M., Takashima K., and Mizuno A., Chemistry of the positive and negative electrical discharges formed in liquid water and above a gas-liquid surface, *Plasma Chem. Plasma Proc.*, Vol. 29 (6), pp. 455−473, 2009.
[30] Rumbach P., Bartels D. M., Sankaran R. M., and Go D. B., The effect of air on solvated electron chemistry at a plasma/liquid interface, *J. Phys. D: Appl. Phys.*, Vol. 48 (42), 424001, 2015.
[31] Hsieh K., Wang H. J., and Locke B. R., Analysis of a gas-liquid film plasma reactor for organic compound oxidation, *J. Hazard. Mat.*, Vol. 317, pp. 188−197, 2016.
[32] Bulusu R. K. M., Wandell R. J., Zhang Z., Farahani M., Tang Y., and Locke B. R., Degradation of PFOA with a nanosecond-pulsed plasma gas-liquid flowing film reactor, *Plasma Process. Polym.*, Vol. 17 (8), pp. 2000074, 2020.
[33] Wandell R. J., and Locke B. R., Low-power pulsed plasma discharge in a water film reactor, *IEEE Trans. Plasma Sci.*, Vol. 42 (10), pp. 2634−2635, 2014.
[34] Wandell R. J., Wang H. H., Tachibana K., Makled B., and Locke B. R., Nanosecond pulsed plasma discharge over a flowing water film: Characterization of hydrodynamics, electrical, and plasma properties and their effect on hydrogen peroxide generation, *Plasma Process. Polym.*, Vol. 15 (6), e1800008, 2018.
[35] Wang H. H., Wandell R. J., and Locke B. R., The influence of carrier gas on plasma properties and hydrogen peroxide production in a nanosecond pulsed plasma discharge generated in a water-film plasma reactor, *J. Phys. D: Appl. Phys.*, Vol. 51 (9), 094002, 2018.
[36] Abe A., Distribution of 1,4-dioxane in relation to possible sources in the water environment, *Sci. Total Environ.*, Vol. 227 (1), pp. 41−47, 1999.
[37] Sander R., Compilation of Henry's law constants (version 4.0) for water as solvent, Atmospheric Chemistry and Physics, Vol. 15 (8), pp. 4399−4981, 2015.
[38] Gerkens R. R., and Franklin J. A., The rate of degradation of 1,1,1-trichloroethane in water by hydrolysis and dehydrochlorination, *Chemosphere*, Vol. 19 (12), pp. 1929−1937, 1989.
[39] Tafel J., and Friedrichs G., Electrolytic reduction of carbonic acids and carbonic acid-esters in a sulphuric acid solution, *Berichte Der Deutschen Chemischen Gesellschaft*, Vol. 37, pp. 3187−3191, 1904.
[40] USEPA. Toxic and Priority Pollutants under the Clean Water Act, https://www.epa.gov/eg/toxic-and-priority-pollutants-under-clean-water-act#priority, 2021.
[41] USEPA. National Primary Drinking Water Regulations, https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#one, 2021.