

Degradation of Monochloroacetic Acid by Anodic Contact Glow Discharge Electrolysis

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Abstract—Degradation of monochloroacetic acid (MCA) in water was carried out using anodic contact glow discharge electrolysis (CGDE). Accompanying the decay of MCA, the amount of total organic carbon (TOC) in the solution correspondingly decreased; meanwhile chlorine atom of MCA was released as chloride ion. It was revealed that the decay of both MCA and TOC obeyed a first-order rate law. Formate was obtained as the by-product. A reaction pathway involving successive attack of hydroxyl radical to the hydrogen atoms on the α -carbon of MCA was assumed on the basis of the observed products and kinetics.

Keywords—Monochloroacetic acid, degradation, contact glow discharge electrolysis, first-order rate law

I. INTRODUCTION

In the past decades, the water polluted with haloacetic acids (HAAs) which were discharged into drainage as a result of various human activities has caused lots of environmental problems [1]. HAAs are kind of organic pollutants, which can cause cancer [2]. monochloroacetic acid (MCA) as typical HAAs has been detected worldwide in drinking water due to the using of chlorine in conventional drinking water disinfection [3]. Recently a great deal of efforts has been devoted to treat water containing MCA. Bio-processes, including bio-film and aerobic biodegradation, for degradation MCA have been developed by researchers [4, 5]. Dechlorination of MCA by electrochemical method has also been investigated to decrease the toxicity of polluted water [6]. To exhaustive degradation of MCA, advanced oxidation processes (AOPs) have been employed to treat water containing MCA: Patrik reported that ozone could enhance the removal rate of MCA in photo processes [7].

A novel process named contact glow discharge electrolysis (CGDE) [8] for exhaustive mineralization of organic pollutants has been developed these years [9-22]. In anodic CGDE, plasma is generated locally in the vicinity of an anode contacting the surface of electrolyte. The ionic species in the plasma are accelerated by the steep potential gradient and rush into the solution. Then, in the reaction zone the energized ionic species break several water molecules into hydrogen and hydroxyl radicals [23, 24]. Hydrogen peroxide is one of the main products of anodic CGDE in the solution of inert electrolytes and it should be formed by the recombination of OH radicals [25].

Basing on a series of researches on decomposition of organic pollutants by anodic CGDE, it was assumed that hydroxyl radical would act as the most responsible key-species for the destruction of organic pollutants [9-11, 16-22]. Anodic CGDE has been proved to be one of the

hopeful AOPs to mineralize organic pollutants [9-23], thus it seems truly opportune to acquire practical knowledge of the aqueous degradation of MCA induced by anodic CGDE. In the present paper, the comprehensive degradation of MCA by means of anodic CGDE is investigated focusing on the mechanistic and kinetic aspects.

II. METHODOLOGY

The reaction apparatus for the anodic CGDE experiments is illustrated in Fig. 1. A cylindrical glass cell was employed. The anode, a platinum wire of 0.6 mm diameter sealed within a glass tube, was introduced into the cell. The cathode employed was a stainless-steel plate (35 mm \times 10 mm \times 2 mm) and placed in another glass tube, with its lower end plugged by a sintered glass disk of medium porosity, and immersed in 70 mL of an aqueous phosphate solution (8.7 mmol/L potassium dihydrogenphosphate and 30.4 mmol/L disodium hydrogenphosphate, pH = 7.4). A

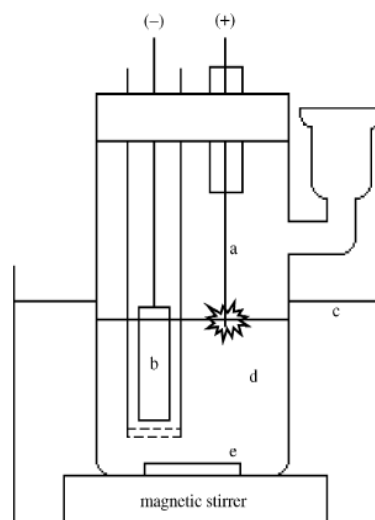


Fig. 1. Apparatus for anodic CGDE. a: anode; b: cathode; c: ice-water bath; d: electrolytic solution; e: Teflon-coated magnetic bar.

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Presented at the 9th International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy, in June 2014

voltage of 500 V from a DC power supplier was applied between the electrodes. The depth of the discharge electrode (anode) in the solution was ca. 1 mm, and adjusted so that the average current could be maintained at approximately 70 mA. The total electricity passed during anodic CGDE was measured by a digital coulomb-meter. During anodic CGDE, the solution was gently stirred with a Teflon-coated magnetic bar and the cell was placed in an ice-water bath to hold the temperature of the bulk solution at about 20°C. Reagent-grade MCA was used without further purification. Identities of the products, as well as unreacted starting material, were determined by high-performance liquid chromatography (HPLC; Shimadzu LC10A). For the quantification of MCA, a Shodex Ionpak KC-811 columns (8 I.D. \times 300 mm) connected to an ultraviolet (UV)-visible detector (Shimadzu SPD-M10A) was used; the eluent used was 50 mol/L perchloric acid. A Shodex Ionpak KC-811 column (8 \times 300 mm) with an eluent composed of 0.5 mmol/L and 15 mmol/L perchloric acid + acetonitrile (85:15 V/V) were used together with a conductivity detector (Shimadzu CDD-6A) for the analysis of formate. In addition, Shodex Ionpak IC I-524A column with the eluent of 2.5 mmol/L phthalic acid (pH 2.5, flow rate 1.5 mL/min, 40°C) was used together with a conductivity detector for the analysis of chloride ion. The amount of total organic carbon (TOC) in the solution was measured by a TOC analyser (Shimadzu TOC-VE).

III. RESULTS AND DISCUSSION

A. Degradation of MCA

When MCA (an initial concentration of 5.0 mmol/L, corresponding to 120 ppm of TOC, as shown in Fig. 2) was subjected to anodic CGDE generated in an aqueous phosphate solution, both the MCA and TOC concentrations in the solution were found to decrease smoothly over the course of the reaction. It should be noted that the decrease in TOC corresponds to the formation of inorganic carbon (IC). In addition, it was also observed that the chlorine atom of MCA was liberated as chloride ion.

The degradation of MCA by anodic CGDE is shown in Fig. 2; the variations in concentrations of MCA, TOC, and chloride ions as a function of discharge time are also described. On starting the reaction, the concentrations of both MCA and TOC decreased monotonously with reaction time. After 240 min, all of MCA disappeared and most of the TOC disappeared. This observation indicates that anodic CGDE is effective in the conversion of two carbon atoms of the carbon chain to IC.

The gap between the decay curves of MCA and TOC is indicative of the presence of organic intermediate products. However in the reaction mixture, most of them were not detected due to their lability and low concentrations in solution, only formate was detected as the main organic intermediate product and the amount of it was also worth to quantify. The variations in formate

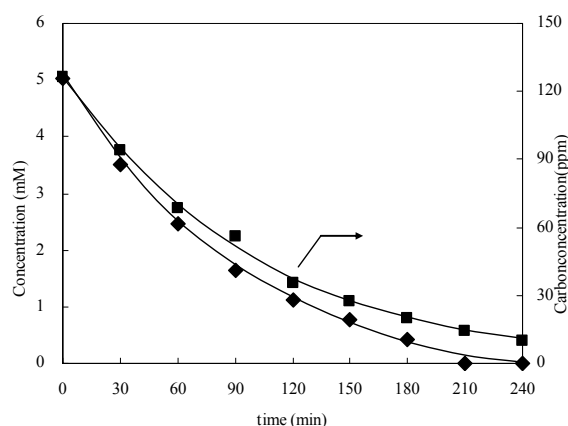


Fig. 2. Variation of concentrations with discharge time in anodic CGDE of MCA (C_0 : 5.0 mmol/L). \blacklozenge : MCA, \blacksquare : TOC.

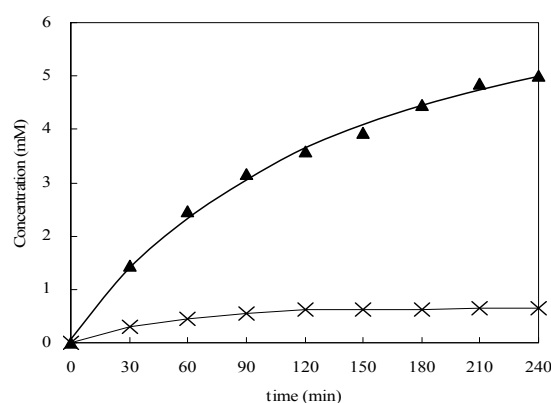


Fig. 3. Productions from anodic CGDE of MCA (C_0 : 5.0 mmol/L). \times : formate, \blacktriangle : Cl^- .

TABLE I
ELEMENTAL YIELDS OF PRODUCTS FROM ANODIC CGDE OF MCA^a

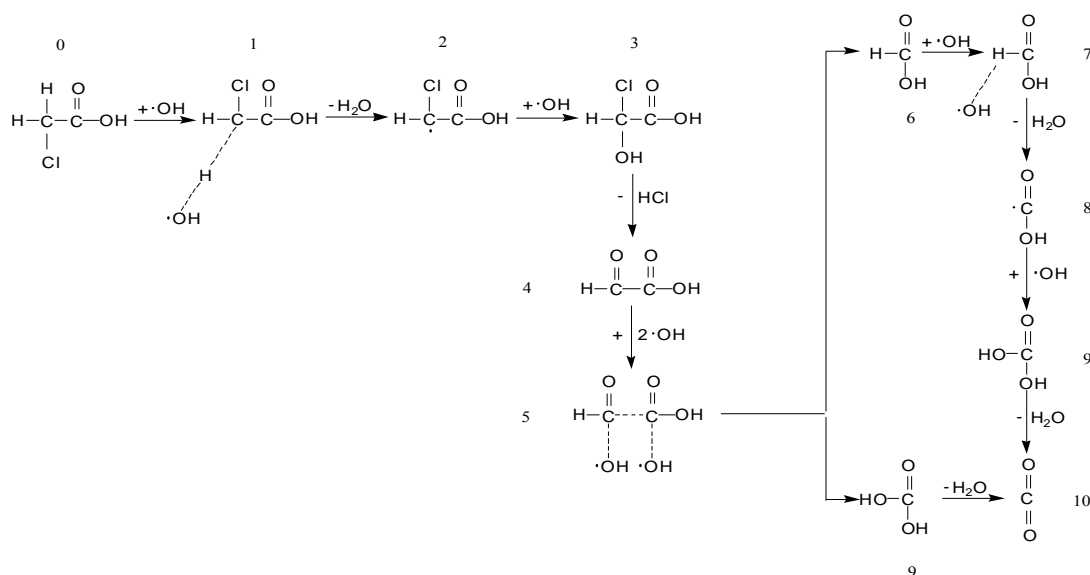
Time (min)	MCA conversion (%)	Product yield (%)				
		Chloride		Carbon		
		Cl^-	ND ^c	Formate	IC ^b	ND ^c
30	30	29	1	3	26	1
60	51	49	2	4	46	1
90	67	63	4	5	56	6
120	78	71	6	6	72	0
150	84	78	6	6	78	0
180	91	89	3	6	84	1
210	100	97	3	6	89	5
240	100	100	0	6	92	2

^a C_0 : 5.0 mmol/L.

^b Inorganic carbon.

^c Not determined.

and Cl^- concentrations as a function of discharge time are shown in Fig. 3. The formate concentration rose in the starting 120 min, and then held steady for the duration of the reaction. And no oxalate was detected in the reaction solution. The Cl^- concentration increased smoothly through the reaction. At last the chlorine atom of MCA was almost quantitatively liberated as the corresponding chloride ion (5.0 mmol/L) as another by product (in Fig. 3).



Scheme 1. A plausible pathway for the formation of formate.

The elemental yields of the aforementioned products, namely IC, formate, and Cl^- , as well as the conversion of MCA, are tabulated in Table I. The yield was defined as the percentage of moles of a certain element (C or Cl^-) in each product per initial number of moles of that element in the starting material. The yields of undetermined intermediates, specified as ND, were estimated so as to balance the sum of yields with respect to MCA conversion. Particularly in the earlier stage of run, ND of Cl^- was noticeable, but smoothly lowered as the conversion went up. While ND of C had lowest value of 0% during 120 min to 150 min. It was ascertained that ND products associated with Cl^- and C declined to 0% and 2%, respectively, at a discharge time of 240 min.

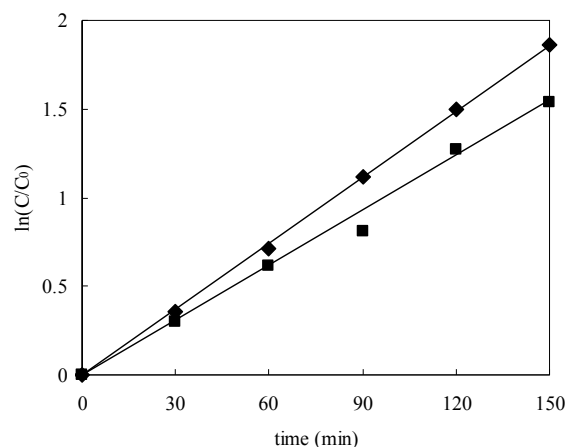
ND products associated with Cl^- and C declined to 0% and 2%, respectively, at a discharge time of 240 min.

B. Kinetics of MCA Degradation

Since the decay curves of MCA and TOC in Fig. 2 appeared to be exponential, it was attempted to apply the data to the integral rate “(1)” for the first-order reaction:

$$\ln(C_0/C) = C. \quad (1)$$

where C and C_0 denote the concentration of MCA and TOC volume at the given reaction times, k is the rate constant and t is reaction time. As a consequence, for each set of data concerning the decay of MCA or TOC, a straight line with good correlation was obtained (Fig. 4). This result indicates that both MCA and TOC were consumed according to the first-order rate law, and the slope of each straight line corresponded the apparent rate constant of the decay. And the apparent rate constants, k_{MCA} and k_{TOC} , for the decay of MCA and TOC were calculated from the slope of each line to be $1.24 \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.999$) and $1.04 \times 10^{-2} \text{ min}^{-1}$ ($R^2 = 0.997$), respectively.

Fig. 4. First-order plots with the decay of MCA and TOC in anodic CGDE of MCA (C_0 : 5.0 mmol/L). ◆: MCA, ■: TOC.

C. Degradation Path of MCA in Anodic CGDE

Basing on the analysis of production and kinetic of the degradation of MCA as above, it is suggested that hydroxyl radical, which were generated from water molecules by the action of the plasma [23, 24], was the most responsible specie for the degradation of MCA. Thus the degradation of MCA may be triggered by the attack of hydroxyl radical to the hydrogen atoms on the α -carbon of MCA, resulting in abstraction reaction of hydrogen atoms on the α -carbon to form the corresponding radical (2) as shown in Scheme 1, but never at the atoms of β -carbon. Then (2) should undergo further oxidation to form the corresponding intermediate product (3). Releasing of HCl , product (4) was generated. With the attack of two hydroxyl radicals to product (4), the oxidative chain cleavage leads to the formation of by-products: carbonic acid (9) and formate (6). Ultimately the formate (6) was mineralized to inorganic carbon (IC). Dechlorination of MCA, as seen in Schemes 1, might

proceed through the step such as: elimination of HCl from -CCl(OH)- structure to form a carbonyl group.

IV. CONCLUSION

MCA subject to anodic CGDE underwent exhaustive breakdown and eventually converted to IC. The chlorine in the MCA was liberated as chloride ion. In the initial stage, the attack of hydroxyl radical occurred to the hydrogen atom on the α -carbon of MCA, but never at those of β -carbon. The consumption of both MCA and TOC obeyed the first-order rate law. Based on the products survey and kinetic discussion, it can be assumed that degradation of aqueous MCA by anodic CGDE proceeds in a successive manner as follows: 1) the initial attack to the hydrogen atoms on the α -carbon of MCA by hydroxyl radicals, resulting in abstraction reactions of atoms on the α -carbon to form the corresponding radicals, 2) continue reaction of the corresponding radicals releasing HCl, 3) oxidative chain cleavage leading to the formation of formate and carbonic acid, and ultimately 4) mineralization to inorganic carbon (IC).

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Grant No. 51308276), Scientific Research Foundation for Doctors of Liaoning Province (Grant No. 20141123) and the Youth Science Foundation of University of Science and Technology Liaoning (Grant No. 2012QN02). Special thanks go to Professor Meguru Tezuka for his comments and support of this work.

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