Determination of Overall Kinetic Constants for Mediated Electrochemical Oxidation of Phenol from CO_2 Measurements[1]

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Abstract—Mediated electrochemical oxidation is the latest achievement in environmental electrochemistry for the complete oxidation of organic pollutants. Transition or inner transition elements in an acid medium are usually employed as the mediator–electrolyte combination. The organic pollutants upon oxidation are completely converted to carbon dioxide and water. Since the oxidizing ability of the medium is so vigorous, the changes in the reactant concentrations or intermediates formed are usually difficult to analyze, but the product formed (CO_2) can be measured and quantified in most of the cases. Therefore, in MEO reactions the kinetics can be followed either by monitoring the oxidant concentration changes or by measuring the product concentrations. In real applications the oxidant is regenerated continuously in situ and, hence, the oxidant concentration is maintained throughout the system. Therefore, in continuous organic feeding reactions, the product CO_2 could be monitored and kinetics could be followed. We report in this paper a simple procedure for the calculation of the overall kinetic constants for the destruction of phenol from CO_2 measurements. The procedure is based on the summation of the difference between the total amounts of organic added to the system and reacted to obtain CO_2 evolution patterns. The CO_2 patterns were then fitted with the experimental results to obtain the overall kinetic constants. Thermodynamic parameters have been obtained for phenol destruction from the overall kinetic constants.

INTRODUCTION

Mediated electrochemical oxidation (MEO) has been identified by the United Nations Environmental Program [1] as one of the advanced and sustainable processes for the complete oxidation of solid, liquid, and gas phase organic pollutants [2–7]. The MEO process was initially developed for the dissolution of radioactive materials in nuclear waste processing units but later turned out to be an excellent method for the complete oxidation of organic pollutants [8–11]. In this process transition or inner transition metals are used as mediator ions in an acid medium. The mediator couples exhibit a high redox potential. Among the various mediators, cerium and silver have been studied extensively. It was found that in the MEO reactions the organics are completely mineralized to CO_2 and water in a short amount of time. However the analyses of the reaction intermediates and their mechanistic pathway of destruction were not clearly established due to the presence of a powerful metal ion oxidant and the very fast degradation of intermediate species. Therefore, in most of the MEO reactions the product, i.e., CO_2, was quantitatively estimated rather than the reactant concentrations to follow the kinetics of the reaction [12, 13].

It has been reported that in the oxidations involving a metal ion like Ag(II) or Ce(IV) with organic substrates the reaction follows first order kinetics in each of the two reactants, i.e., the metal ion concentration and substrate concentration and second order overall [8, 14, 15].

In this study we have used cerium in a nitric acid medium for the complete oxidation of phenol chosen as the model organic pollutant. The Ce(IV) oxidant in nitric acid was electrochemically produced from its reduced precursor using an electrochemical cell and used for the complete oxidation of phenol which was continuously fed to the reactor with simultaneous Ce(IV) regeneration. The overall rate of the conversion of phenol to CO_2 was determined using a new method proposed in this paper. The kinetics of MEO of phenol from continuous CO_2 measurements has not been reported in the literature.

EXPERIMENTAL

Materials

Cerium(III) nitrate hexahydrate (99%) was purchased from Sigma-Aldrich; phenol, ferrous sulfate (extra pure), and nitric acid (60%) were obtained from Daejung Chemicals and Metals Co., Ltd., Korea. All the chemicals were used as received. The water used

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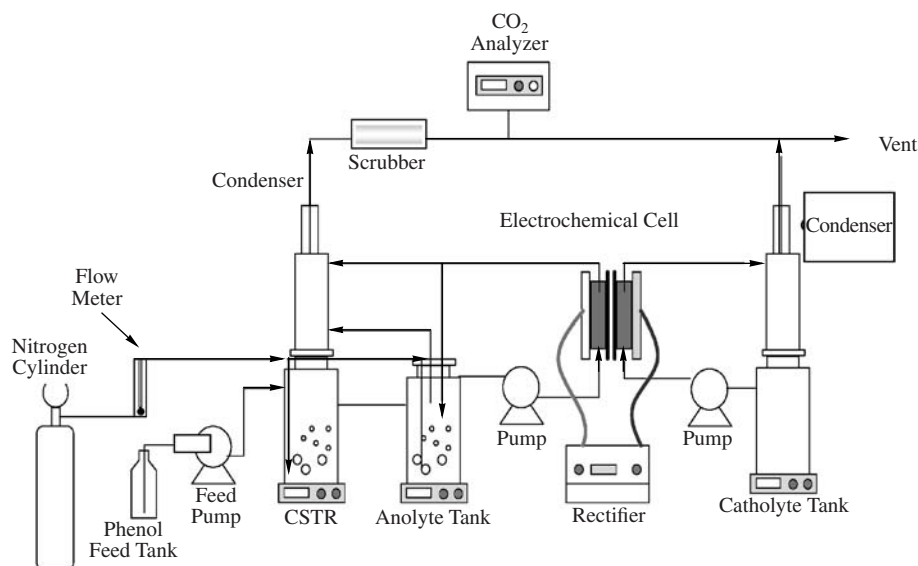[1] The text was submitted by the authors in English.

Fig. 1. Schematic diagram of the MEO experimental set up.

was purified by reverse osmosis (Human Power III plus, Korea).

Methods

The overall schematic diagram of the MEO system is shown in Fig. 1. The electrochemical cell [16] was fabricated in our laboratory, with the mesh type DSA anode (IrO_2/Ti; 140 cm^2) and cathode (Ti; 140 cm^2) separated by a Nafion® 324 membrane. The oxidation of Ce(III) in nitric acid was carried out at a constant cell current of 10 A. The concentration of the Ce(IV) was estimated at various time intervals by potentiometric titration with ferrous sulfate [17].

The continuous organic feeding experiments were carried out in a continuously stirred tank reactor as shown in Fig. 1. In these studies the Ce(IV) oxidant solution was first prepared using the electrochemical cell and, after the required concentration of Ce(IV) was reached, phenol solution was injected continuously for 30 min. The carbon dioxide produced during organic destruction was purged by the carrier gas stream (nitrogen; 2.0 L min^{-1}) and taken to the infrared-CO_2 analyzer (Environmental Instruments, Anagas CD 98). The organic in the feed was totally mineralized to CO_2 and water, and therefore, the net result observed was the dilution of oxidant solution. This dilution was balanced by capturing the water vapor from the anolyte tank. Since the concentration of nitric acid is well below its azeotropic point, the vapor condensed was richer in water with very little nitric acid content. The loss of acidity was found to be less and was compensated before the start of each experiment.

RESULTS AND DISCUSSION

The oxidation of phenol was carried out by injecting a phenol solution of known concentration to the oxidant solution comprising 0.8 M Ce(IV) in 3 M nitric acid at 353 K. The real time evolution of CO_2 in a continuous process is presented in Fig. 2.

From the shape of the CO_2 evolution curve, the experimental procedure can be understood. During the first 30 min, the CO_2 evolution increased due to continuous phenol injection, and after addition was stopped, the remaining organic undergoes oxidation and produces CO_2. This decreasing part of the curve is similar to batch phenol oxidation [4].

In a continuous organic addition reaction, the remaining organic present in the system could be calculated using stoichiometry by knowing the amount added and reacted. A general and simple mathematical relationship was arrived at based on the quantity of organic added and remaining in the system using arbitrary CO_2 formation rate constant (k) values as described in the next section. The k values were adjusted, and several CO_2 curves were drawn. These curves were then matched to the experimental curves. The k value, which gives a smooth fitting to the experimental curves, was chosen as the overall rate constant for that reaction. Thus, a single CO_2 formation rate constant was calculated for the continuous process.

As can be seen in the table, at the step $N = 0$ some quantity of organic is added which is assumed to be not reacting in that moment, and its concentration becomes ΔC. In the step $N = 1$, a new portion of organic is added, and now, this is present in the system (ΔC) with the previously added and partly unreacted organic ($\Delta C \exp(-kt)$). The concentration of the remaining organic is shown in the fourth column. These expres-
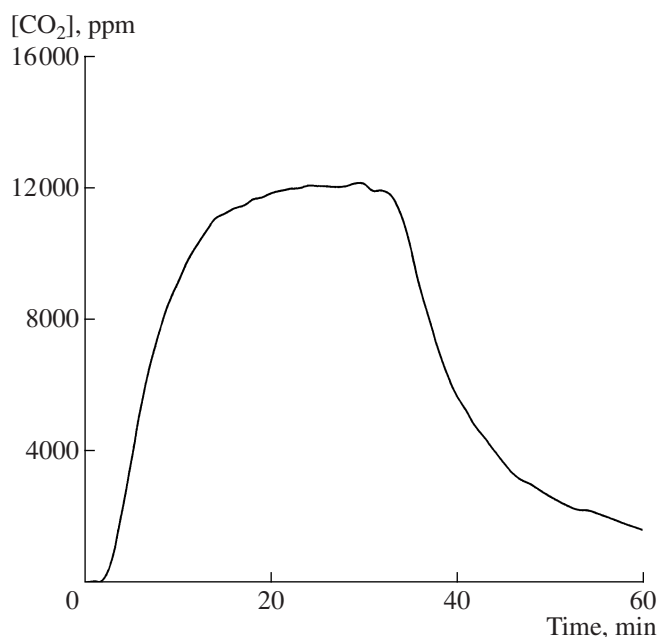
Fig. 2. Real time CO_2 evolution pattern (ppm by volume) for phenol oxidation in continuous feeding mode ([Phenol]: 9.6 mM; [Ce(IV)]: 0.8 M; [HNO$_3$]: 3 M; Temp.: 353 K).
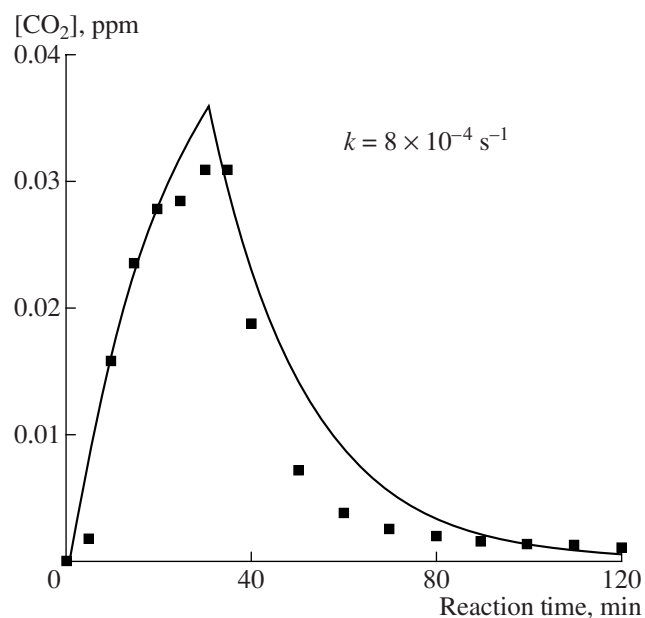

$k = 8 \times 10^{-4} \text{ s}^{-1}$

Fig. 3. Profiles of CO_2 formation vs. time for the prediction based on the proposed procedure (solid line) and experimental values (points) for phenol oxidation in continuous addition mode for the conditions shown in Fig. 2.

sions are further simplified using a geometrical progression and given in the fifth column.

The table presents the results of calculations of the unreacted organic in the system only during the addition. If the organic addition is stopped, however, the calculation for concentration changes may be obtained according to the first order kinetics. The only unknown parameter was the k value. Setting k values in the expected range, numerical calculations were made. Figure 3 shows the comparison of the predicted CO_2 evolution pattern and experimental data. From arbitrarily chosen k values, several modeling curves were drawn and the sum of the squares of the difference between the experimental and modeling data was calculated for each of them according to the least squares method. The k value with the minimum difference was chosen as the closest one to the experiment (Fig. 4).

Modeling terms for organic concentration calculations for continuous process of organic destruction

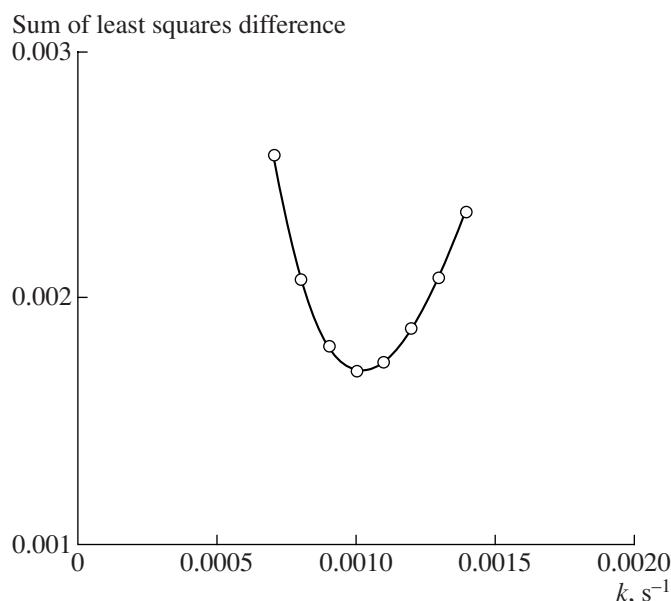| Time	Differential time	Amount of organic compound		
		amount of organic added	unreacted organic at the given time	summation of GP
0	0	0	0	0
1	Δt	ΔC	ΔC	ΔC
2	$2\Delta t$	$2\Delta C$	$\Delta C + \Delta C\exp(-k\Delta t)$	$\Delta C[1 - \exp(-k2\Delta t)]/[1 - \exp(-k\Delta t)]$
3	$3\Delta t$	$3\Delta C$	$\Delta C + \Delta C\exp(-k\Delta t) + \Delta C\exp(-k2\Delta t)$	$\Delta C[1 - \exp(-k3\Delta t)]/[1 - \exp(-k\Delta t)]$
4	$4\Delta t$	$4\Delta C$	$\Delta C + \Delta C\exp(-k\Delta t) + \Delta C\exp(-k2\Delta t) + \Delta C\exp(-k3\Delta t)$	$\Delta C[1 - \exp(-k4\Delta t)]/[1 - \exp(-k\Delta t)]$
……	……	……	……	……
m	$m\Delta t$	$m\Delta C$	$\Delta C + \Delta C\exp(-k\Delta t) + \Delta C\exp(-k2\Delta t) + \Delta C\exp(-k3\Delta t) + ... + \Delta C\exp(-km\Delta t)$	$\Delta C[1 - \exp(-km\Delta t)]/[1 - \exp(-k\Delta t)]$
……	……	……	……	……
n	t	C	$\Delta C + \Delta C\exp(-k\Delta t) + \Delta C\exp(-k2\Delta t) + \Delta C\exp(-k3\Delta t) + ... + \Delta C\exp[-k(n + 1)\Delta t]$	$\Delta C\{1 - \exp[-k(n + 1)\Delta t]\}/[1 - \exp(-k\Delta t)]$

Sum of least squares difference

Fig. 4. Eyring plot for the oxidation of phenol.

$\ln(k/T)$ [s^{-1} K^{-1}]

$$y = -3.1368x - 3.8454$$
$$R^2 = 0.9792$$

$(1/T) \times 10^3$, K^{-1}

Fig. 5. Plot of sum of the least squares differences vs. overall rate constants.

This procedure was adopted to obtain the overall CO_2 formation rate constants for different experimental conditions in the continuous organic feeding mode, and the values were found to be in good agreement between different experimental data sets.

A good enough agreement is observed between the experimental data and predicted curves (Fig. 3). However, the curve is closer to the modeling during the organic addition. After stopping the organic addition, some discrepancy is seen between the two, and the experimental points change more sharply and the modeling curve is smoother. The values of CO_2 formation rate constants ranged from 4.0×10^{-4} to 1.1×10^{-3} s^{-1} for the overall process condition changes including the temperature dependence in the interval 343–368 K.

The k values at different temperatures were used to calculate the activation parameters. Figure 5 shows the plot between $\ln k$ versus $1/T$ for continuous phenol feeding. The activation energy was found to be 29 kJ mol^{-1}. The comparison between batch and continuous feeding CO_2 formation rate constants and activation energies revealed that though some differences exist in the formation rate constants, the activation energies calculated in each mode of destruction were in a narrow range suggesting a similar course of destruction. The activation energy for the destruction of urea in the silver MEO process studied using cyclic voltammetry was reported to be 44 kJ mol^{-1} [18]. This is comparable to the one reported in this work and suggests the possibility of obtaining thermodynamic parameters from the overall CO_2 formation rate constants in the MEO process. Also, it should be stated that a single step kinetic model may not be sufficient to describe the organic destruction completely and the CO_2 formation rate constant repre-
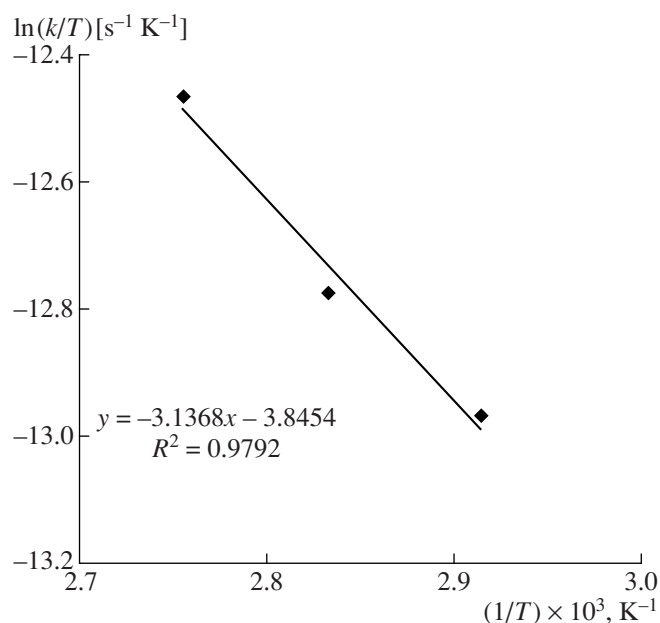
sents only the sum of the rates of all reactions leading to the final product CO_2. Nevertheless the calculation of CO_2 formation rate constants during organic destruction by the MEO process provides a simple means of following the reaction and arriving at the thermodynamic parameters in an otherwise powerful oxidant medium with a number of short living intermediates and the kinetics are difficult to obtain by the usual methods due to the complexity of many reactions.

CONCLUSIONS

The complete oxidation of phenol was carried out by mediated electrochemical oxidation in the continuous feeding mode. The extent of complete oxidation was estimated by measuring the amount of CO_2 evolved. A simple mathematical procedure was proposed to calculate the overall rate constant from the remaining organic present in the solution based on an arbitrarily chosen k value. From the amounts of organic added and the remaining quantities, the CO_2 evolution patterns are simulated for different assumed k values. The evolved CO_2 pattern was then matched with the experimental pattern. The k value was chosen based on the LSD fit. The CO_2 formation rate constants at different temperatures were used for the calculation of activation energies and presented.

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