Electrochemical Reduction of Halobenzenes in the Presence of Carbon Dioxide

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The electrochemical reduction of halobenzenes in the presence of CO_2 on a Hg cathode was investigated. The reduction of iodobenzene and bromobenzene under CO_2 yielded benzoic acid as a fixation product of CO_2. However, the reduction of CO_2 in the presence of chlorobenzene produced no benzoic acid. It is confirmed that the reduction of halobenzenes is important to fixate CO_2 on phenyl group and the reaction of $CO_2^{\cdot-}$ with halobenzenes is slow. In the present electrolysis, the phenylmercury radical is considered as an intermediate for the formation of benzoic acid.

1 Introduction

Carbon dioxide (CO_2) is the final, stable compound obtained in the oxidation of carbon compounds and is boundless resources in the carbon cycles. In order to use the carbon resources effectively, the electrochemical fixation of CO_2 to organic compounds has been markedly developed. The electroreduction of *n*-butyl bromide in the presence of CO_2 on a Hg cathode in dimethylformamide (DMF) produces dibutylmercury, dibutyl oxalate, and butyl valerate[1];

$$n\text{-BuBr} \xrightarrow[\substack{CO_2\\ \text{Hg cathode}}]{\text{reduction}} Bu_2Hg + (CO_2Bu)_2 + BuCO_2Bu \quad (1)$$

In this reaction the formation of the anion radical of CO_2 ($CO_2^{\cdot-}$) is essential to fixate CO_2 on the butyl group; electrolysis at a potential, where only butyl bromide is reduced (and CO_2 not reduced), yields no estersn or acids.

We report herein the electrochemical reduction of aromatic halides (iodobenzene, bromobenzene, chlorobenzene) with a Hg cathode under CO_2. The reduction of iodobenzene produced benzoic acid as a fixated product of CO_2 on the phenyl group at a potential where only iodobenzene is reduced (whereas CO_2 not reduced). It appears that the reduction mechanism for the present electrolysis of halobenzenes is somewhat different from that for the electrochemical reduction of alkyl halides under CO_2.

2 Experimental

DMF was dried over Na_2SO_4 or Na_2CO_3 for several days and distilled at a reduced pressure prior to use. Tetraethylammonium perchlorate (TEAP) was synthesized and purified by the reported method[2]. Halobenzenes were purchased commercially and were distilled before use.

Cyclic voltammetry was carried out using conventional instruments with hanging mercury drop electrode (HMDE) or a Hg coated Pt wire electrode as the working electrode and a Pt wire counter electrode in DMF solution containing 0.1 M (mol dm^{-3}) TEAP. The potentials were referenced to a saturated calomel electrode (SCE) with multi-junction to prevent contamination from water or KCl.

All macro-electrolyses were performed with a Yanaco VE-8 controlled potential electrolyzer. The cell was a divided H-type with a Hg pool cathode (area *ca.* 6 cm^2), a Pt gauze anode and an SCE with the multi-junction. The catholyte consisted of 20 cm^3 DMF solution containing halobenzenes and 0.1 M TEAP, continuously bubbled with CO_2 or N_2 gas.

After the electrolysis the catholyte was acidified with diluted HCl, extracted with ether, and then concentrated for gas chromatography. Gas chromatographic analyses were carried out with a Shimadzu GC-6A machine equipped with a hydrogen flame ionization detector; columns used for the analyses were a 2 m×3 mmϕ SUS packed with Carbowax 20 M on Chromosorb W and a 1.5 m×3 mmϕ SUS packed with DEGS (+5% H_3PO_4) on Diasolid M. Nitrogen was used as the carrier gas. The determination of benzene, benzoic acid, and the unreacted halobenzenes were performed from the gas chromatographic data by comparison with calibration

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lines of authentic samples. Diphenylmercury was detected by TLC (hexane : ethyl acetate = 10 : 1).

3 Results and Discussion

3.1 Controlled potential macro-electrolysis

The controlled potential macro-electrolyses of iodobenzene were carried out with a Hg pool cathode at −1.8 V *vs.* SCE. At the potential only iodobenzene is reduced (whereas CO_2 not reduced). The results are summarized in Table 1. Under CO_2 benzoic acid was obtained as a main product. In all cases, benzene, small amounts of diphenylmercury, and some other unidentified products were detected. The yield of benzoic acid (based on the amount of the consumed iodobenzene) is almost independent of the initial concentration of iodobenzene. The formation of diphenylmercury may suggest the participation of the Hg cathode as a reactant in the reduction. In the present electrolyses, phenyl benzoate, phenol, or biphenyl could not be detected. The addition of phenol as a proton source resulted in an increase of the yield of benzene.

The electroreduction of bromobenzene under CO_2 also produced benzoic acid, small amounts of diphenylmercury, and some other unidentified products (Table 2). In this case, the cathode potential was set at −2.3 V *vs.* SCE where both bromobenzene and CO_2 are reduced. The current efficiencies for the formation of benzoic acid in this case were quite low compared with those in the electroreduction of iodobenzene. This indicates that most of charge was consumed by the reduction of CO_2 to $CO_2^{\cdot-}$ and the reactivity of $CO_2^{\cdot-}$ with bromobenzene may be low.

Table 2 Macro-electrolysis of bromobenzene under CO_2

Run	Conv. /%	Passed charge $\times10^{-5}$/C mol^{-1}	Yield/%		C.E. /%
			PhH	PhCOOH	
1	26	0.9		36	20
2	50	2.2	9	37	16
3	63	3.0	13	38	15
4	88	6.0	21	39	11

Initial concentration of bromobenzene: 46 mM, Solvent: 0.1 M TEAP/DMF, Cathode: Hg pool (area *ca.* 6 cm^2), Cathode potential: −2.3 V *vs.* SCE

The electroreduction of CO_2 in the presence of chlorobenzene was also carried out at −2.3 V *vs.* SCE where only CO_2 is reduced (whereas chlorobenzene not reduced). In this case, no benzoic acid was detected.

$$\mathrm{PhCl} \xrightarrow[\substack{-2.3\ \mathrm{V}\ vs.\ \mathrm{SCE}\\ 2.5\times10^5\ \mathrm{C\ mol^{-1}}\\ \mathrm{Hg\ cathode}}]{\mathrm{CO_2}} \text{no benzoic acid} \qquad (2)$$

Therefore the following is deduced; the reduction of halobenzenes is important for the fixation of CO_2 to the phenyl group and the reactivity of $CO_2^{\cdot-}$ with halobenzenes, if any, is low. The above is contrast well with the electroreduction of alkyl halides on a Hg cathode under CO_2, in which the formation of $CO_2^{\cdot-}$ is essential to fixate CO_2 on the alkyl group[1].

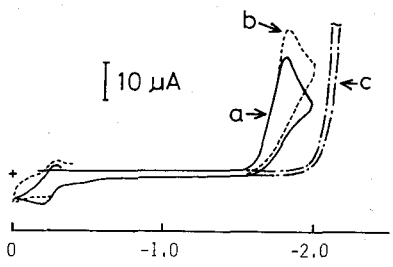
3.2 Cyclic voltammetry

Figure 1 depicts the cyclic voltammograms of 1.0 mM iodobenzene under N_2 and under saturated CO_2, together with that of CO_2, on an HMDE in DMF solution. Iodobenzene shows

Table 1 Macro-electrolysis of iodobenzene under CO_2

Run	Conc. of PhI/mM	Conv.[a]/%	Passed charge $\times10^{-5}$/C mol^{-1}	Yield[b]/%		C.E.[c]/%
				PhH	PhCOOH	
1	10	87	1.3	12	33	43
2	20	53	1.0	2	35	36
3	50	77	1.1	7	40	54
4[d]	50	49	1.0	30	0	

a) Conversion of iodobenzene, b) Based on the amount of consumed iodobenzene, c) Current efficiency for the formation of benzoic acid, d) Under N_2 in the presence of *ca.* 0.1 M phenol Solvent: 0.1 M TEAP/DMF, Cathode: Hg pool (area *ca.* 6 cm^2), Cathode potential: −1.8 V *vs.* SCE

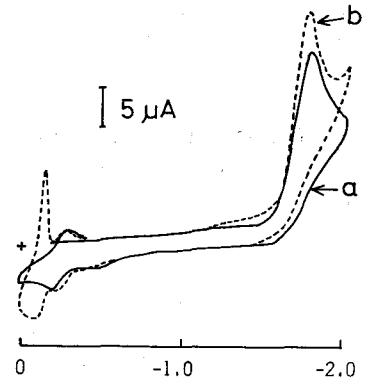


E/V *vs.* SCE

Fig. 1 Cyclic voltammograms of 1.0 mM iodobenzene under N_2 (a) and under saturated CO_2 (b). Curve (c) represents the cyclic voltammogram of CO_2
Electrolyte: 0.1 M TEAP/DMF, Electrode: HMDE, Scan rate: 80 mV s^{-1}

an irreversible reduction peak at −1.80 V *vs.* SCE and reversible peak at *ca.* −0.3 V *vs.* SCE which is originated from the redox reaction of Hg/Hg_2I_2; the iodide ion is splitted off from the parent compound in the course of the reduction. The onset potential for the reduction of CO_2 appears at *ca.* −2.0 V *vs.* SCE; therefore, CO_2 is more difficult to be reduced than iodobenzene. The peak current analysis suggests that the reduction of iodobenzene is not two-electron process. The saturation of the electrolyte solution with CO_2 resulted in *ca.* 1.2 fold increase in the peak current. The same increase was also observed by the addition of phenol as a proton source under N_2 (Fig. 2). These phenomena may indicate that the reduction process approaches two-electron uptake by the addition of CO_2 or proton and that CO_2 molecule influences the reduction in a same way as proton.

On the Hg electrode the reduction peak potential of iodobenzene is observed to be exceptionally positive compared with those on the other types of electrodes. For instance, on a plate electrode of Pt, glassy carbon or SnO_2, the reduction peak appeared at more negative potentials than −2.0 V *vs.* SCE, indicating the participation of the Hg electrode as a reactant in the course of the reduction. This is reinforced by the result of macro-electrolysis in which a small amount of diphenylmercury was detected in the reaction products. The participation of a Hg electrode as a reactant has been frequently observed in the electroreduction of organic halides[3]



E/V *vs.* SCE

Fig. 2 Cyclic voltammograms of 1.0 mM iodobenzene in the absence (a) and presence (b) of *ca.* 10 mM phenol under N_2
Electrolyte: 0.1 M TEAP/DMF, Electrode: HMDE, Scan rate: 82 mV s^{-1}

or organometallic compounds[4]. The electrochemical reduction of some alkyl halides on a Hg electrode yields organomercury compounds almost quantitatively[5]. The participation of Hg has also been observed in the electroreduction of iodobenzene even in an aqueous media[6]. Therefore, in aprotic solvent, *e.g.*, DMF, the Hg electrode may influence the reduction of halobenzenes more significantly. In the reduction of tetraphenylstibonium ion on a Hg cathode in an aqueous solution, the phenylmercury radical ($PhHg^{\cdot}$) has been considered as an intermediate for the formation of benzene[7].

$$Ph_4Sb^+ + Hg + e \longrightarrow Ph_3Sb + PhHg^{\cdot} \quad (3)$$

$$PhHg^{\cdot} \longrightarrow 1/2\ Ph_2Hg + 1/2\ Hg \quad (4)$$

$$PhHg^{\cdot} + H^+ + e \longrightarrow PhH + Hg \quad (5)$$

The radical would also be the intermediate in the present electrolysis. Therefore, the following mechanism is deduced for the present electrolysis.

$$PhX + Hg + e \longrightarrow PhHg^{\cdot} + X^- \quad (6)$$

$$PhHg^{\cdot} \longrightarrow 1/2\ Ph_2Hg + 1/2\ Hg \quad (4)$$

$$PhHg^{\cdot} + CO_2 + e \longrightarrow PhCO_2^{\cdot -} + Hg \quad (7)$$

$$PhHg^{\cdot} + \begin{cases} SH \\ H_2O(\text{residual}) + e \longrightarrow \\ Et_3N^+CH_2CH_3 \end{cases}$$

$$PhH + \begin{cases} S^- \\ OH^- \\ Et_3N + CH_3{=}CH_2 \end{cases} + Hg \quad (8)$$

SH = DMF; X = I, Br

The solvent, the supporting electrolyte, or the residual water acts as a hydrogen source for the benzene formation[5,8]. The reduction of bromobenzene under CO_2 would proceed *via* the same mechanism as that of iodobenzene, although the effect of CO_2 on the reduction could not be demonstrated since the reduction peak potential of bromobenzene (−2.35 V *vs.* SCE) is more negative than that of CO_2 as shown in Fig. 3.

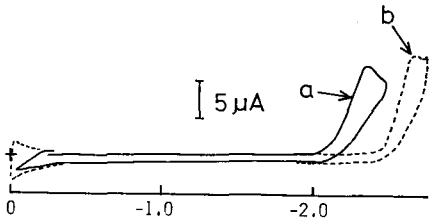


Fig. 3 Cyclic voltammograms of 1.0 mM bromobenzene (a) and 1.0 mM chlorobenzene (b) under N_2
Electrolyte: 0.1 M TEAP/DMF, Electrode: Hg coated Pt wire, Scan rate: 100 mV s^{-1}

The same argument may also be applicable to the reduction of chlorobenzene. It is also notable that the reaction of $CO_2^{\cdot-}$ with bromobenzene and chlorobenzene, if any, is slow, which is deduced from the results of macro-electrolyses.

$$CO_2^{\cdot-} + PhX \longrightarrow \text{no or slow reaction} \quad (9)$$
$$X = Br, Cl$$

However, the detailed mechanism for the present reaction is still unclear; further investigations about the reduction is now underway.

4 Conclusion

The electroreduction of iodobenzene and bromobenzene under CO_2 yielded benzoic acid as a fixation product of CO_2 to the phenyl group. However, the reduction of CO_2 in the presence of chlorobenzene produced no benzoic acid. Therefore, it is deduced that the reduction of halobenzene is important to fixate CO_2 to the phenyl group and the reactivity of $CO_2^{\cdot-}$ with halobenzenes is low. In the present reaction, the phenylmercury radical is considered as an intermediate for the formation of benzoic acid.

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