

## Reaction of Br<sub>2</sub> with Adsorbed CO on Pt, Studied by the Surface Interrogation Mode of Scanning Electrochemical Microscopy

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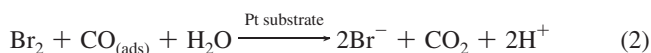
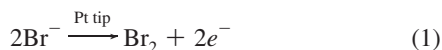
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We studied the reaction of bromine (Br<sub>2</sub>) with adsorbed carbon monoxide (CO<sub>(ads)</sub>) on polycrystalline platinum in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub>, to yield CO<sub>2</sub> and Br<sup>-</sup>, by the recently introduced surface interrogation<sup>1</sup> mode of scanning electrochemical microscopy (SI-SECM).<sup>2,3</sup> In this technique, a “titrant” is electrogenerated at a tip in close proximity to the surface under investigation, thus allowing the *in situ* detection and quantification of adsorbed intermediates at the solid–liquid interface. In the present Communication, we demonstrate its utility for the evaluation of a new reaction, where Pt acts not only as a support for CO<sub>(ads)</sub> but also as a heterogeneous catalyst that promotes the oxidation process.

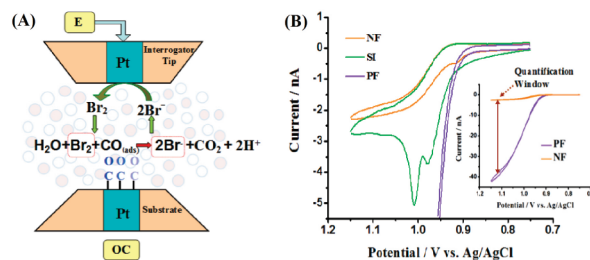
The adsorption and electrochemical oxidation of CO on Pt, on both single-crystal and polycrystalline surfaces, have been widely studied<sup>4</sup> by electrochemical techniques<sup>5–8</sup> and their combination with Raman and IR spectroscopy.<sup>9–11</sup> Part of the interest in these studies is driven by the identification of CO<sub>(ads)</sub> as an important blocking intermediate (i.e., a *poison*) in the oxidation of short-chain alcohols and organic acids<sup>12</sup> for their use in fuel cells.<sup>3,13</sup> Studies of the electrochemical oxidation of CO<sub>(ads)</sub> on Pt have traditionally been carried out by scanning or stepping an electrode into the oxidizing potential regime, where the formed OH<sup>\*</sup><sub>(ads)</sub> radical is proposed to transform CO<sub>(ads)</sub> into CO<sub>2</sub>.<sup>5,9,14</sup> With the SI-SECM technique at hand, we sought to find a tip-generated reactive substance that could achieve this transformation, in the hope of providing new strategies for quantification of CO<sub>(ads)</sub> in catalytic systems and perhaps for the removal of this strongly adsorbed intermediate. The reactive Br<sup>\*</sup> radical is of particular interest since its precursor, Br<sub>2</sub>, can be electrogenerated at a SECM setup<sup>15,16</sup> and its oxidizing properties are comparable to those of OH<sup>\*</sup><sub>(ads)</sub>.<sup>17</sup>

Figure 1A shows schematically the SI-SECM mode for the production of Br<sub>2</sub> from bromide (Br<sup>-</sup>, initially present in solution) and its reaction with CO<sub>(ads)</sub> at the Pt substrate. Here two ultramicroelectrodes (UMEs), one acting as an interrogator tip and the other as a substrate, were concentrically aligned and separated by a gap of *ca.* 1–2 μm. The substrate was first dosed with CO and maintained afterward at open circuit. The solution was then changed to 1 mM KBr in 0.5 M H<sub>2</sub>SO<sub>4</sub> (without disturbing the aligned electrodes). As shown in Figure 1A, after stripping any CO<sub>(ads)</sub> on the interrogator tip (*E*<sub>rest</sub> = 0.75 V vs Ag/AgCl), the tip was scanned across an appropriate potential range (0.75–1.156 V vs Ag/AgCl) to produce Br<sub>2</sub>, as shown in eq 1; we assume the overall reaction of Br<sub>2</sub> with CO<sub>(ads)</sub> at the Pt surface proceeds according to eq 2.



Reaction 2 regenerates the initial bromide anion, which produces a transient positive feedback loop<sup>18</sup> at the interrogator

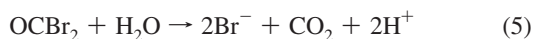
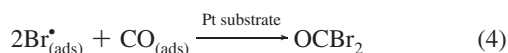
tip as long as there is CO<sub>(ads)</sub> with which to react.<sup>1</sup> This transient positive feedback loop produces an increase in the current at the interrogator tip due to an enhanced flux of Br<sup>-</sup> because of the proximity of the Pt substrate to the tip.<sup>2</sup> Figure 1B shows a SI result in the cyclic voltammetry (CV) mode and its comparison to the negative feedback (NF) mode, i.e., a blank experiment with the Pt substrate at open circuit, and to the electrochemical positive feedback (PF) mode, i.e., a blank experiment with the Pt substrate set at a potential where it can reduce Br<sub>2</sub>. The theory of the SI mode<sup>1</sup> shows that, during chemical reaction at the substrate, the current of the interrogator electrode is within the electrochemical window shown in the inset of Figure 1B. Consumption of the adsorbate causes the response of the



**Figure 1.** SI-SECM detection of CO<sub>(ads)</sub> on a Pt UME substrate. (A) Production of reactive Br<sub>2</sub> from electrochemical oxidation of Br<sup>-</sup> (initially present in solution) at the interrogator tip. Br<sub>2</sub> diffuses and reacts with CO<sub>(ads)</sub> at the Pt substrate, which is kept at open circuit, to yield CO<sub>2</sub> and regenerate Br<sup>-</sup>, which is recycled to the interrogator tip, giving a transient positive feedback. (B) Comparison of negative feedback (NF), positive feedback (PF), and SI; all scans *v* = 20 mV/s, all solutions 0.5 M H<sub>2</sub>SO<sub>4</sub> with 1 mM KBr, Ar-purged, and kept under an Ar blanket. Interrogator tip held for 20 s at 0.75 V and then scanned from 0.75 to 1.15 V vs Ag/AgCl in all runs. Pt substrate conditions: SI, held at open circuit and pre-dosed with CO (5 min at 0.1 V vs Ag/AgCl); NF, held at open circuit, no pre-dosing; PF, held at 0.75 V vs Ag/AgCl, no pre-dosing. Inset shows comparison of NF and PF.

interrogator tip to decay to NF. The SI scans (Figure 1B) revealed a response that consisted of two peaks, often merging into a single peak with a shoulder (e.g., see Figure S1, Supporting Information). Independent of shape, the quantification of the amount of adsorbate was consistent in all runs. This was done by integration of the SI scans to yield the reacted charge of the adsorbate, which we compared to the charge for the underpotential deposition of hydrogen on Pt<sup>19</sup> for a series of experiments, as shown in Table S1 (Supporting Information). We found the CO coverage on polycrystalline Pt,  $\theta_{\text{CO}}$ , to be  $\sim 0.5$ , which is lower than the result recently reported for Pt (111) ( $\sim 0.68$ ).<sup>6</sup>

A possible route for the oxidation of CO<sub>(ads)</sub> by Br<sub>2</sub> is shown in eqs 3–5:



In fact, the product of reaction 4,  $\text{OCBr}_2$  or “bromophosgene” (an analogue of phosgene), has been reported (but also debated)<sup>20</sup> to be the product of a photosensitized low-yield reaction of  $\text{Br}_2$  and CO in the gas phase in the absence of catalyst, where the radical-forming reaction 3 proceeds through photochemical excitation. In our experiment, the Pt substrate provides a catalytic surface where reaction 3 happens more readily. The hydrolysis process in reaction 5 is thermodynamically allowed<sup>21</sup> and provides the  $\text{Br}^-$  necessary for the transient positive feedback as well as a source of oxygen for the production of  $\text{CO}_2$ . If CO is not supported on Pt and only dissolved in solution,  $\text{Br}_2$  is unable to oxidize it, as shown by CV on a macroelectrode (Figure S2, Supporting Information).

A second SI experiment involved the co-adsorption of CO and cyanide ( $\text{CN}^-$ ) on the Pt UME surface.<sup>22</sup> A cyanide-covered Pt UME was used to limit the amount of  $\text{CO}_{(\text{ads})}$  at Pt in order to verify its reaction with  $\text{Br}_2$ , as shown in Figure S3 (Supporting Information). The SI-SECM results show that, with  $\text{CN}^-$ , the adsorption of CO is blocked and furthermore that, despite the isoelectronic nature of  $\text{CN}^-$  and CO, their reactivity toward  $\text{Br}_2$  is different. This suggests that the formation of  $\text{OCBr}_2$  is an important step in the reaction scheme or that  $\text{CN}^-$  blocks sites for the dissociation of  $\text{Br}_2$ .

Finally, a bulk experiment was carried out to identify  $\text{CO}_2$  as the end product of the reaction. A beaker with 10 mmol of  $\text{Br}_2$  in 100 mL of 0.5 M  $\text{H}_2\text{SO}_4$  was bubbled with CO through an inlet where Ar was also continuously passed; Pt black was added as a catalyst. The outlet of the beaker was connected to a container with 100 mL of a saturated and Ar-purged solution of  $\text{Ba}(\text{OH})_2$  (transparent). A control experiment, in which no Pt black was added, showed only cloudiness in the  $\text{Ba}(\text{OH})_2$  solution after 5 min of CO bubbling. This is attributed to small impurities of  $\text{CO}_2$  in the CO feed. When Pt black was added to the reaction mixture, an abundant precipitate of  $\text{BaCO}_3$  was observed in the  $\text{Ba}(\text{OH})_2$  solution. The precipitate was identified as the carbonate through the “carbonate-acid test”. The addition of  $\text{AgClO}_4$  solution to the residue of the reaction mixture showed the precipitation of whitish-yellow  $\text{AgBr}$ , which also supports  $\text{Br}^-$  as an end product. This experiment confirms that CO can be oxidized to  $\text{CO}_2$  by  $\text{Br}_2$  through the catalytic action of Pt.<sup>23</sup>

In conclusion, the SI-SECM technique allowed the production of  $\text{Br}_2$  on an interrogator tip, which reported transient positive feedback (due to  $\text{Br}^-$  regeneration) as an indication of the reactivity of this halogen with  $\text{CO}_{(\text{ads})}$  on a Pt substrate.  $\text{CO}_{(\text{ads})}$  under saturation conditions was reproducibly quantified at the polycrystalline Pt surface with  $\theta_{\text{CO}} \approx 0.5$ . The reaction is shown to be blocked by the action of pre-adsorbed cyanide, which demonstrates the surface character of the process. The formation of  $\text{CO}_2$  as an end product was further tested in a bulk experiment. The use of SI-SECM provided access to the study of a reaction that has not been previously reported to be catalyzed by Pt, a finding that would

otherwise be difficult to prove with conventional electrochemistry on a single electrode.

**Acknowledgment.** Q.W. is on leave from Chemistry Department, School of Science, Beijing Institute of Technology, Beijing, China, and thanks the National Scholarship Fund of the China Scholarship Council for support and research advisor Dr. Huibo Shao from the Beijing Institute of Technology. Helpful discussions with Fu-Ren F. Fan and Cheng-Lan Lin are also gratefully acknowledged. J.R.-L. thanks the William S. Livingston Endowment Fund for a research fellowship and the complementary scholarship support provided by Secretaría de Educación Pública de México and the Mexican Government. We acknowledge support from the Robert A. Welch Foundation (F-0021) and the National Science Foundation (CHE-0808927).

**Supporting Information Available:** Additional experimental details, surface interrogation scan, and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Caution!** Because of the possibility of forming bromophosgene (eq 4), these experiments were performed in a hood at all times, and extensive Ar purging of the reaction products was done after the conclusion.  $\text{OCBr}_2$  is unstable in basic solution, so the  $\text{Ba}(\text{OH})_2$  traps it in addition to the  $\text{CO}_2$ .

JA907626T