

Bromide oxidation on a polycrystalline platinum rotating disk electrode in aqueous solutions

Jing Xu and Daniel Scherson

Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106

In situ reflection absorption UV-visible spectroscopy was used to detect solution phase products generated during the oxidation of bromide on the surface of a polycrystalline platinum rotating disk electrode, Pt(poly) RDE, as a function of the applied potential and rotation rate, ω , in aqueous acidic solutions.

The set up employed for these measurements was similar to that described by Shi et al.¹ involving in this case a Cary 60 spectrophotometer and a different set of reflection optics to be specified in detail elsewhere.

Shown in Fig. 1 is a polarization curve recorded with a Pt(poly) RDE in an aqueous 0.01 M KBr solution in 0.1M HClO₄ at $\omega = 1300$ rpm. As clearly shown, the current reached a fairly well defined plateau, I_{lim} , at potentials $E > 1.4$ V. A plot of I_{lim} vs $\sqrt{\omega}$ at $E = 1.45$ V vs RHE, yielded a straight line with a close to zero intercept characteristic of a diffusion limited process.

A series of UV visible reflection absorption spectra were then acquired in the same solution at various ω values in the range $400 < \omega < 2500$ rpm with the Pt RDE polarized at 1.45 V (see Fig. 2), yielding in each case a very prominent peak at 266 nm, characteristic of tribromide in aqueous solutions.² Unlike the results obtained for iron hexacyanoferrate reported in our previous study using a similar RDE spectroscopy system,¹ the optical signal for the present system was found to increase monotonically with the rotation rate. One possible explanation for this behavior may be found in the much higher molar absorptivity of tribromide (4.09×10^7 cm²/mol) compared to that of the iron complex (1.75×10^5 cm²/mol) at their corresponding absorption maxima, i.e. 266 and 390 nm, respectively. Some evidence in support of this view was provided by monitoring the absorbance at the limiting current as a function of time which as shown in Fig. 3 increased rather markedly for all rotating rates examined, where the lack of linearity is in all likelihood related to the evaporation of bromine from the solution. Efforts are currently underway to monitor the reflectance of the surface at near normal incidence at a fixed wavelength away from the absorption bands of the electrolyte while the bromide is being oxidized on the surface of the Pt RDE. The results of these dual beam experiments will be reported in due course.

REFERENCES

1. Shi, P.; Scherson, D. A., *Anal. Chem.* **2004**, *76*, 2398.
2. Liu, Q.; Margerum, D.W. *Environ. Sci. Technol.* **2001**, *35*, 1127.

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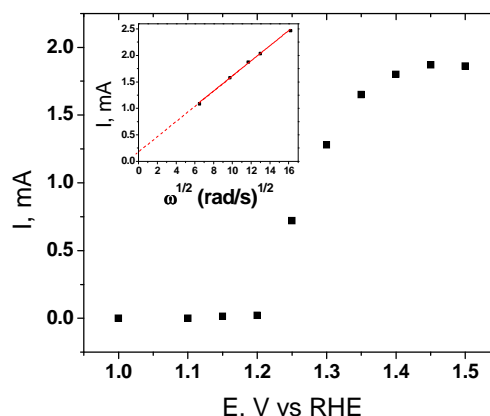


Fig. 1. Polarization curve for a Pt(poly) RDE in an aqueous 0.01 M KBr solution in 0.1M HClO₄ recorded at $\omega = 1300$ rpm. **Insert.** Plot of I_{lim} for a PtRDE electrode for bromide oxidation, as a function of $\sqrt{\omega}$ based on the disk data, in 0.1M HClO₄ + 0.01M KBr by holding disk potential $E = 1.45$ V vs RHE.

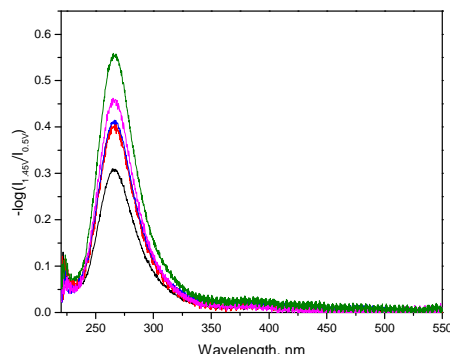


Fig. 2. UV visible reflection absorption potential difference spectra recorded with a Pt RDE in 0.1M HClO₄ + 0.01M KBr solution while holding the disk potential at 1.45 V vs. RHE using the spectrum recorded at $E = 0.5$ V (no tribromide in solution) as a reference, for $\omega = 400$ (black), 900 (red), 1300 (blue), 1600 (magenta), 2500 rpm (olive).

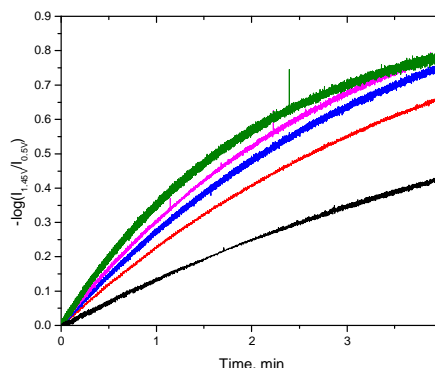


Fig. 3. Plots of $-\log(I_{1.45V}/I_{0.5V})$ vs. time recorded at $\lambda = 266$ nm under the same conditions as those specified in the caption Fig. 1, for $\omega = 400$ (black), 900 (red), 1300 (blue), 1600 (magenta) and 2500 rpm (olive).