

Investigation of the Electrocatalytic Reduction of Peroxydisulfate Using Scanning Electrochemical Microscopy

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Abstract: The elementary steps of the electrocatalytic reduction of $\text{S}_2\text{O}_8^{2-}$ using the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox couple were investigated using scanning electrochemical microscopy (SECM) and steady-state voltammetry (SSV). SECM investigations were carried out in a 0.1 M KCl solution using a 3.5- μm radius carbon ultramicroelectrode (UME) as the SECM tip and a 25- μm radius platinum UME as the substrate electrode. Approach curves were recorded in the positive feedback mode of SECM by reducing $\text{Ru}(\text{NH}_3)_6^{3+}$ at the tip electrode and oxidizing $\text{Ru}(\text{NH}_3)_6^{2+}$ at the substrate electrode, as a function of the tip-substrate separation and $\text{S}_2\text{O}_8^{2-}$ concentration. The one-electron reaction between electrogenerated $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ yields the unstable $\text{S}_2\text{O}_8^{3*-}$, which rapidly dissociates to produce highly oxidizing $\text{SO}_4^{\bullet-}$. Because $\text{SO}_4^{\bullet-}$ is such a strongly oxidizing species, it can be further reduced at *both* the tip or the substrate, or it can react with $\text{Ru}(\text{NH}_3)_6^{2+}$ to regenerate $\text{Ru}(\text{NH}_3)_6^{3+}$. SECM approach curves display a complex dependence on the tip-substrate distance, d , due to redox mediation reactions at both the tip and the substrate. Finite element method (FEM) simulations of both SECM approach curves and SSV confirm a previously proposed mechanism for the mediated reduction of $\text{S}_2\text{O}_8^{2-}$ using $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox couple. Our results provide a lower limit for dissociation rate constant of $\text{S}_2\text{O}_8^{3*-}$ ($\sim 1 \times 10^6 \text{ s}^{-1}$), as well as the

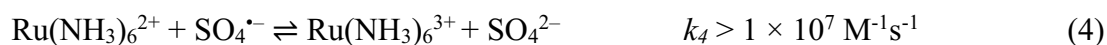
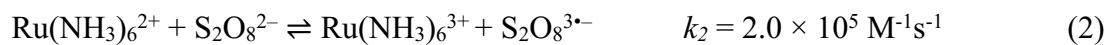
rate constants for electron transfer between $\text{SO}_4^{\bullet-}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ ($\sim 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and between $\text{S}_2\text{O}_8^{2-}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ ($\sim 7 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$).

Introduction

Peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$) is an oxidizing reagent widely used in industrial processes, such as in the etching of printed circuit boards¹ and water remediation,² due to its oxidizing properties, low cost, and ease of handling. Cleavage of the peroxo bond at elevated temperatures or using light, also referred to as $\text{S}_2\text{O}_8^{2-}$ activation,^{3,4} results in the formation of the sulfate radical anion ($\text{SO}_4^{\bullet-}$), which has a standard reduction potential (E^θ) of $\sim 2.2 \text{ V}$ vs. Ag/AgCl .⁵ The resulting $\text{SO}_4^{\bullet-}$ is capable of abstracting an electron or a hydrogen atom from molecules to form SO_4^{2-} or HSO_4^- , respectively.² The ability of $\text{SO}_4^{\bullet-}$ to abstract a hydrogen atom is leveraged frequently in organic synthesis for C-H activation.⁶⁻⁸ For instance, McMillan and coworkers carried out α -arylation of ethers using photochemical reduction of $\text{S}_2\text{O}_8^{2-}$.⁹

Recently, we reported the selective oxidation of alcohols to the corresponding aldehydes/ketones ($\text{pH} < 7$) and carboxylic acids ($\text{pH} > 7$) via the electrocatalytic reduction of $\text{S}_2\text{O}_8^{2-}$ to $\text{S}_2\text{O}_8^{3\bullet-}$ using electrogenerated $\text{Ru}(\text{NH}_3)_6^{2+}$.¹⁰ Our prior studies suggested an eight-step mechanism for the overall alcohol oxidation, with the first five steps, shown below as eqs. 1-5, involving the generation of $\text{SO}_4^{\bullet-}$ (eqs. 1-3) followed by its reaction either with $\text{Ru}(\text{NH}_3)_6^{2+}$ (eq. 4) or by direct reduction at the electrode (eq. 5).¹⁰ Eqs. 4 and 5 represent *quenching* reactions, preventing $\text{SO}_4^{\bullet-}$ from participating in the intended oxidation of the alcohol substrate. Cyclic voltammetry (CV) studies performed using glassy carbon macroelectrodes, along with finite-difference simulations, were employed to estimate the rate constants of eq. 2 as $\sim 2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ and provided lower limits for eq. 3 ($> 1 \times 10^6 \text{ s}^{-1}$), and eq. 4 ($> 1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$).¹⁰ Density functional

theory (DFT) and molecular dynamics computational analysis, however, suggest that $\text{S}_2\text{O}_8^{3-}$ fragmentation occurs on time scales of $\sim 10^{-12}$ s.¹⁰ Similarly, the free energy change for the homogeneous reduction of $\text{SO}_4^{\bullet-}$ by $\text{Ru}(\text{NH}_3)_6^{2+}$, based on E^0 values of eqs. 1 and 5, $\Delta G \sim -2.4$ eV, would suggest that this single electron-transfer reaction should occur at a diffusion-controlled rate. Thus, the rate constants of eqs. 3 and 4 should be significantly higher than the lower limits previously reported based on CV analysis.

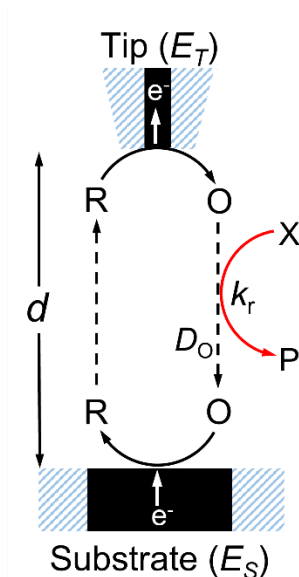


Reactions of thermally or photochemically generated $\text{SO}_4^{\bullet-}$ with other species are generally very rapid and have been traditionally investigated using spectroscopic methods.^{11,12} The kinetics of rapid homogeneous reactions that follow an initial electron-transfer step, e.g., the oxidation of $\text{Ru}(\text{NH}_3)_6^{2+}$ by $\text{S}_2\text{O}_8^{2-}$ (eq. 2), can be investigated using a variety of electrochemical methods, such as fast-scan CV (FSCV)¹³ and scanning electrochemical microscopy (SECM).¹⁴ Analysis of data obtained from time-dependent methods, e.g. FSCV, is complicated due to large contributions to the current from capacitive charging and adsorbed species. As a result, SECM analysis, which is generally based on steady-state current-potential (i - E) measurements, has been increasingly employed to measure the kinetics of fast electrochemical reactions.¹⁵⁻¹⁷ For instance, Bard and coworkers investigated the rate constants of elementary steps involved in the electrooxidation of

oxalate and measured the lifetime of transient species $\text{CO}_2^{\bullet-}$ (10 ns) and $\text{C}_2\text{O}_4^{\bullet-}$ (1.3 μs) in *N,N*-dimethylformamide.^{18,19} In a more recent study, Rodríguez-López, et al. employed SECM in tandem with electrogenerated chemiluminescence to accurately measure ion annihilation rate constant (k_{ann}) in reaction consist of Rubrene and $[\text{Ru}(\text{bpy})_3]^{2+}$ as $k_{\text{an}} > 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.²⁰

The principles of SECM instrumentation and the electrochemical measurements necessary for kinetic investigations are described in detail elsewhere.²¹ Briefly, SECM comprises two electrodes, oriented with their active surfaces parallel to each other. Frequently, a disk-shaped metal tip (radius $< 10 \mu\text{m}$), referred to as an ultramicroelectrode (UME), is used in conjunction with a larger substrate electrode. The electrode potentials of the tip and the substrate are independently controlled, while the distance between the two electrodes (d) is actively controlled using piezoelectric positioners, and can be varied from large distances, where the electrodes are non-interacting, to very small separations, where interactions occur by diffusion and reactions of redox molecules electrogenerated at the two electrodes. The resulting tip current (i_t) vs. d plot is referred to as an approach curve and can provide direct experimental insights into the mechanism and kinetics of chemical reactions coupled to an electrode reaction.

Scheme 1 shows a simple conceptual example of using SECM to measure the rate of a bimolecular reaction involving species generated at the tip. Here, the electrochemical oxidation of species R , present in the bulk solution, at the tip electrode yields species O , which undergoes either a second-order reaction, $O + X \rightarrow P$, to form an electro-inactive species P , or diffuses across the tip-substrate gap to be reduced back to R at the substrate.



Scheme 1. Simple example of using SECM in positive feedback mode to measure the rate of a bimolecular reaction, $O + X \rightarrow P$. For small values of k_r , the redox species R and O undergo electrochemical oxidation and reduction at the tip and substrate electrodes, respectively, resulting in positive feedback and an increased tip current as the tip-substrate distance, d , is decreased. For large k_r values, O is consumed by the homogeneous reaction, resulting in decreased feedback. Approach curves (i_t vs. d) are analyzed to determine k_r .

In the absence of the chemical reaction, the reduction of O at the substrate electrode, held at a potential negative of formal potential, $E^{0'}$, of the O/R couple, results in a positive feedback cycle, corresponding to R diffusing back to the tip electrode where it is oxidized back to O , resulting in an increased tip current. In this limiting case of no homogeneous chemical reaction, the tip current increases from a steady-state constant value at large d (corresponding to no feedback between the tip and substrate) to a much larger value at smaller values of d (corresponding to strong feedback). Conversely, if O is consumed by the chemical reaction before it reaches the substrate to be reduced, the amount of positive feedback is reduced when the tip approaches the substrate.

These basic concepts can be made more quantitative by considering the half-life of O associated with its conversion to P (τ_r), and the timescale of diffusion of O from the tip to the substrate (τ_d), as expressed by eqs. 6 and 7, respectively.

$$\tau_r = 1/k_r C_O \quad (6)$$

$$\tau_d = d^2/2D_O \quad (7)$$

In eqs. 6 and 7, D_O and C_O are the diffusion coefficient (D) and concentration of O , respectively, and k_r is the second-order rate constant for $O + X \rightarrow P$. The expression for τ_r , eq. 6, is approximate and assumes that the initial bulk concentrations of R and X are equal (a condition that is generally not true). A negligible amount of O arrives at the substrate electrode when $\tau_d \gg \tau_r$ (*i.e.*, large d and/or large k_r). With decreasing d or k_r , τ_d can be comparable to or less than τ_r , *i.e.*, $\tau_d \leq \tau_r$. Under these conditions, a larger fraction of O survives the crossing of the tip-substrate gap without reaction, resulting in its reduction at the substrate electrode, and subsequent diffusion of R back to the UME tip resulting in positive feedback. Therefore, the substrate electrode approach curve and the collection efficiency (*i.e.*, the ratio of the substrate electrode current to the tip electrode current) as a function of d provides quantitative information about k_r . Analyses of SECM approach curves to verify a proposed mechanism or to determine reaction rate constants are generally performed by comparing computer simulations based on diffusion and reaction rate expressions to the experimental data. Detailed discussions of using SECM to analyze many different reaction mechanisms can be found in the literature.²²⁻²⁵

When combined, eqs. 6 and 7 suggest that the measurement of very fast kinetics requires very small values of d . For instance, a reaction with $k_r = 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $C_O \sim C_X \sim 1 \text{ mM}$ requires tip-substrate separation on the order of $d \sim 10\text{-}100 \text{ nm}$ in order to observe the effect of the chemical reaction on the feedback current, assuming a typical value of $\sim 10^{-5} \text{ cm}^2/\text{s}$ for D_O . This experimental requirement of very small d values is very challenging due to the necessity of fabricating nanotip electrodes that allow the positioning of the tip very close to the substrate.

Herein, we report the use of steady-state voltammetry (SSV) at UMEs and SECM for investigating the mechanism and rates of $\text{S}_2\text{O}_8^{2-}$ reduction using the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ electrocatalyst system. As discussed above, prior cyclic voltammetry investigations allowed only estimates of the lower limits of the rate constants for $\text{S}_2\text{O}_8^{3+-}$ dissociation (eq. 3) and the bimolecular electron-transfer reaction between $\text{SO}_4^{\bullet-}$ with $\text{Ru}(\text{NH}_3)_6^{2+}$ (eq. 4). We show that SECM approach curves, obtained using a relatively large tip ($3.5\text{-}\mu\text{m}$ radius), can be used to measure the electron-transfer rate constant for the reaction between $\text{SO}_4^{\bullet-}$ with $\text{Ru}(\text{NH}_3)_6^{2+}$, which approaches a diffusion-limited value ($\sim 10^9 \text{ M}^{-1}\text{s}^{-1}$), corresponding to one of the fastest bimolecular reactions ever measured using SECM. The ability to measure such fast reactions with a large tip is a somewhat counter-intuitive finding and, as shown below, results from spatial localization of homogeneous electron-transfer reactions near both the tip and substrate electrodes. Finally, we present a straightforward approach to fabricate carbon ultramicroelectrodes (UME) with moderately small insulator-to-electrode radius ratios (referred to as the RG ratio in SECM analysis).

Materials and Methods

Reagents.

The following reagents were used as received: Ag ink (Sigma Aldrich), W rod (diameter = 0.0254 mm, Goodfellow), platinum wire (radius = 25 μm , Goodfellow), carbon fiber (radius = 3.5 μm , Goodfellow), hexaammineruthenium(III) chloride (Sigma Aldrich, 98%), sodium peroxydisulfate (Fisher Scientific, 98%), potassium chloride (Fisher Scientific, 99%). The capillary glass was purchased from King Precision Glass Inc. (ID = 0.4267 ± 0.0500 , OD = 1.00 ± 0.05 , and L = 75 ± 3.0 mm) and treated as outlined previously.²⁶ Aqueous solutions were prepared using Millipore water. An adhesive epoxy (LOCTITE® EA 9340), 3M aluminum oxide Microfinishing/lapping film, and Microcut S polishing cloth (Buehler) were used in C-UME preparation.

Electrochemical Instrumentation.

Voltammetric studies were performed using a Biologics Dual Channel SP300 Potentiostat, equipped with a low current amplifier. The SECM measurements were performed using a homebuilt bipotentiostat comprised of a Dagan Chem-Clamp with a preamplifier head-stage (Dagan Corporation, U.S.A).²⁷ University of Warwick electrochemical scanning probe microscopy software was used to record current–time and current–distance curves.²⁸ Acquired data were processed with OriginPro 2022 software.

Fabrication of UME

The C-UMEs used for the SECM experiments were prepared with the four-step process as depicted in Figure S1, adapted in part from the report by Mauzeroll and coworkers.²⁶ A detailed description of the procedure for preparation of C-UME is presented in the Supporting Information. In summary, the C fiber was inserted into the glass capillary. Next, the C fiber and the glass

capillary were pulled together using a P-2000 Sutter laser puller. Finally, the tapered glass with the enclosed C fiber were subjected to thermal treatment and the follow-up precision polishing to make a flat disk with RG ratio (glass-to-C radius ratio). As shown in Figure 1, this fabrication procedure yields C-UMEs of $RG \sim 5$ with RG values varied slightly for different electrodes.

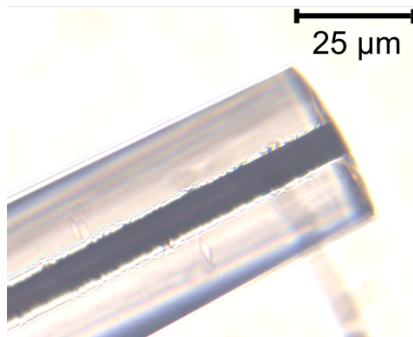


Figure 1. Side view of a homemade C-UME obtained with an optical microscope. The RG ratio of the C-UME was estimated as ~ 5 .

Detailed procedures to make C- and Pt-UMEs with large RG ratios (*i.e.*, > 20) for the SSV and SECM measurements are presented in the Supporting Information. Briefly, a ~ 5 mm piece of C or Pt wire was connected to a stiff W rod via Ag ink. Next, the W rod with the electrode material on the leading end was inserted into the glass capillary, one end of which had been previously sealed in an oxyhydrogen torch. Once the electrode material touched the sealed end of the capillary, the assembly was heated in the oxyhydrogen torch to incorporate the electrode material into the glass. Finally, the electrode was polished to expose the electrode material and obtain a flat surface.

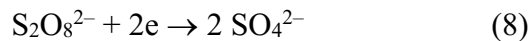
Finite Element (FEM) Simulations.

The SSV and SECM simulations were performed using COMSOL Multiphysics® v5.4 software. The Supporting Information provides: a full Comsol simulation report; a simplified representation of the 2-D axisymmetric simulation model; a summary of reaction parameter values; diffusion-reaction equations; initial and boundary conditions; and equations for the currents at the tip and the substrate.

Results and Discussions

SSV Analysis

Figure 2 shows SSVs recorded using a 3.5- μm radius C-UME in an O_2 -free aqueous solution containing 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and 0.1 M KCl. In the absence of $\text{S}_2\text{O}_8^{2-}$, the voltammogram reaches a steady-state diffusion-limited current of ~ -1.1 nA at potentials more negative than -0.30 V vs. Ag/AgCl. With the addition of increasing amounts of $\text{S}_2\text{O}_8^{2-}$ (corresponding to $\text{S}_2\text{O}_8^{2-}$ concentrations between 0.60 to 2.4 mM), the voltammetric current increases steadily, a consequence of the electrocatalytic homogeneous reduction of $\text{S}_2\text{O}_8^{2-}$ by $\text{Ru}(\text{NH}_3)_6^{2+}$ (eq. 2), which regenerates $\text{Ru}(\text{NH}_3)_6^{3+}$. Additionally, the dissociation of $\text{S}_2\text{O}_8^{3-}$ yields $\text{SO}_4^{\bullet-}$, which is also either directly reduced to SO_4^{2-} at the electrode (eq. 5) or reduced through its homogeneous reaction with $\text{Ru}(\text{NH}_3)_6^{2+}$ to yield $\text{Ru}(\text{NH}_3)_6^{3+}$ (eq. 4) that is then reduced at the electrode (eq. 1). Thus, the combination of eqs. 1 and 4 (mediated reduction of $\text{SO}_4^{\bullet-}$ pathway) is equivalent to eq. 5 (direct reduction of $\text{SO}_4^{\bullet-}$ pathway), both resulting in a second electron transferred from the electrode to yield SO_4^{2-} . The overall reaction for the mediated reduction of $\text{S}_2\text{O}_8^{2-}$, eq. (8), is obtained by combining eqs. 1, 2, 3, and 5 (direct reduction of $\text{SO}_4^{\bullet-}$ pathway) or by combining eqs. 1 (twice), 2, 3, and 4 (indirect reduction of $\text{SO}_4^{\bullet-}$ pathway).



The SSVs in the presence of $\text{S}_2\text{O}_8^{2-}$, Figure 2, show several non-ideal behaviors: (i) a pre-wave at the foot of the main wave, (ii) a small hysteresis between the forward and reverse scan, and (iii) a sloping limiting current that becomes more apparent at high $\text{S}_2\text{O}_8^{2-}$ concentrations. We believe that at least a partial explanation for these non-idealities is either the adsorption of $\text{S}_2\text{O}_8^{2-}$, the onset of direct $\text{S}_2\text{O}_8^{2-}$ reduction at the C-UME electrode, and/or ion-pairing between $\text{Ru}(\text{NH}_3)_6^{3+}$ (and/or $\text{Ru}(\text{NH}_3)_6^{2+}$) with $\text{S}_2\text{O}_8^{2-}$. While we have not systematically investigated any of these possibilities, we note previous reports of ion-pairing of $\text{Ru}(\text{NH}_3)_6^{3+}$ with SO_4^{2-} in aqueous solutions,²⁹ and ion-pairing of $\text{Ru}(\text{bpy})_3^{2+}$ with $\text{S}_2\text{O}_8^{2-}$ (where bpy = 2,2'-bipyridine) in mixed H_2O /acetonitrile solutions.³⁰ Additionally, the SSV response for the direct reduction of $\text{S}_2\text{O}_8^{2-}$ at the C-UME, shown in the Supporting Information, indicates that $\text{S}_2\text{O}_8^{2-}$ reduction, which is kinetically slow at C, commences at about -0.45 V vs Ag/AgCl . While these non-ideal behaviors limit our analysis of the SSV response, the increase in current upon addition of $\text{S}_2\text{O}_8^{2-}$ to the solution is clearly dominated by the electrocatalytic reduction of $\text{S}_2\text{O}_8^{2-}$ by $\text{Ru}(\text{NH}_3)_6^{3+}$, as discussed above.

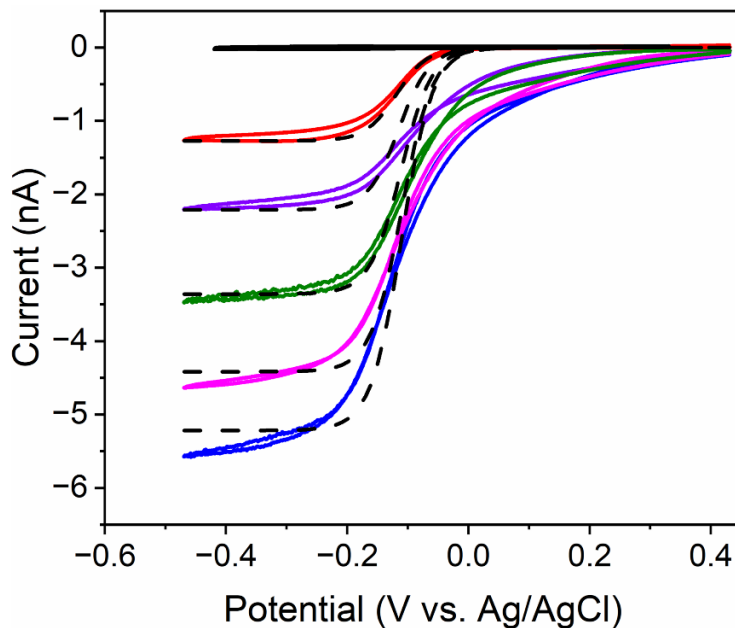


Figure 2. Experimental (solid lines) and simulated (dashed lines) voltammograms for aqueous solutions containing 0.1 M KCl (black), 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and 0.1 M KCl (red), and 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ with 0.1 M KCl and $\text{S}_2\text{O}_8^{2-}$ at 0.60 (purple), 1.2 (green), 1.8 (magenta), and 2.4 mM (blue). All voltammograms were recorded at $\nu = 5$ mV/s with 3.5- μm radius C-UME working electrode in an O_2 -free aqueous solution. The potential of the working electrode was swept from 0.4 V to -0.5 V and back to 0.4 V.

The SSV responses of the C-UME in the absence and presence of $\text{S}_2\text{O}_8^{2-}$ were simulated with the FEM method. Details of FEM simulations including major assumptions, diffusion coefficient of various species (D), heterogeneous electron transfer rate constants, and standard reduction potentials (E^0) are reported in the Supporting Information. Moreover, Table S1 and S2 provides a complete list of thermodynamic and kinetic parameters used in the simulation.

Best fits of simulations to the experimental SSVs using the above-mentioned parameters were obtained by adjusting the rate constant, k_2 , for the homogeneous electron transfer between $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{S}_2\text{O}_8^{2-}$, eq. 2. The dissociation rate constant of $\text{S}_2\text{O}_8^{3-}$, k_3 , was assumed to be $1 \times 10^{10} \text{ s}^{-1}$, consistent with theoretical estimates. The homogeneous reaction between $\text{SO}_4^{\cdot-}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ (eq. 4) was assumed to be diffusion-controlled; hence a rate constant of $1 \times 10^{10} \text{ M}^{-1}$

$^1\text{s}^{-1}$ was used for k_4 . Our simulations only approximated the observed SSV response due to the non-idealities in the experimental curves, as discussed above. Additionally, we found that the set of voltammograms in Figure 2 acquired at different $\text{S}_2\text{O}_8^{2-}$ concentrations (0.60 to 2.4 mM) could not be fit by a unique value of k_2 (see Table S2). Rather, the best fits over this concentration range required varying k_2 from 1.5×10^5 to $6.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ with increasing $\text{S}_2\text{O}_8^{2-}$ concentration.

In a previous report, we showed that the simulations of the cyclic voltammetric (CV) response for the same system, but using a large glassy carbon electrode (radius = 1.49 mm), were in near-perfect agreement with experimental CVs obtained in solutions containing 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$, 0.1 M Na_2SO_4 , and $\text{S}_2\text{O}_8^{2-}$ (2 to 8 mM).¹⁰ In addition to the electrode material and size, the only difference between the present and prior experiments is the choice of supporting electrolyte, KCl vs. Na_2SO_4 , respectively. A single value of $k_2 = 2.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for the reaction between $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{S}_2\text{O}_8^{2-}$ (eq. 2) was found to yield good fits to the prior CV results, independent of $\text{S}_2\text{O}_8^{2-}$ concentration, in reasonable agreement with values listed in Table S2. However, we do not have an explanation for why k_2 in the SSV experiments appears to increase as a function of $\text{S}_2\text{O}_8^{2-}$ concentration. As shown below, with increasing concentration of $\text{S}_2\text{O}_8^{2-}$, a slightly larger k_2 value is also needed to simulate SECM approach curves obtained in 0.1 M KCl solutions containing 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$, consistent with the SSV findings.

SECM Analysis

In order to provide an initial validation of the SECM methodology, approach curves were obtained in an O_2 -free solution containing 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and 0.1 M KCl. The potential of the C tip and Pt substrate electrodes were set at -0.4 and 0.4 V vs Ag/AgCl, respectively, to reduce $\text{Ru}(\text{NH}_3)_6^{3+}$ and oxidize $\text{Ru}(\text{NH}_3)_6^{2+}$ at their diffusion-controlled rates. In SECM analysis,

approach curves showing the dependencies of the tip and substrate currents (i_t and i_s) on the distance between the tip and substrate, d , are generally plotted in terms of a normalized distance, $L = d/a$, where a is the tip radius. Figure 3 shows typical i_t - L and i_s - L curves (black) recorded in the absence of $S_2O_8^{2-}$. These curves correspond to the classical positive feedback mechanism between the two electrodes, as depicted in Scheme 2A. At large values of L , i_t approaches the value of the diffusion-limited current observed in SSV (*i.e.*, ~ -1 nA, Figure 2), while i_s falls to zero. Conversely, as the tip approaches the substrate ($L < 2.5$), both i_t and i_s rapidly increase indicating the onset of strong positive feedback. FEM simulations of the approach curves presented in the Supporting Information are in good agreement with experimental curves for this simple experiment, and demonstrate that, as expected, essentially 100 % of the $Ru(NH_3)_6^{2+}$ generated at the C tip is oxidized at the Pt substrate when $L < 2.5$ (*i.e.*, $d < 9$ μm).

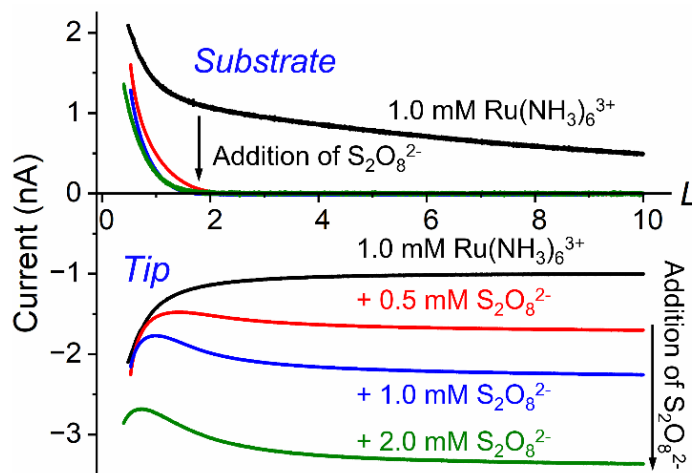


Figure 3. Experimental approach curve for 1.0 mM $Ru(NH_3)_6^{3+}$ in the absence of $S_2O_8^{2-}$ (black) and the presence of 0.50 (red), 1.0 (blue), and 2.0 mM $S_2O_8^{2-}$ (green). Approach curves were recorded using a 3.5- μm radius C-UME tip electrode ($RG \sim 5$) and a 25- μm radius Pt-UME substrate electrode ($RG = 20$). All measurements were made in an O_2 -free aqueous solution containing 0.1 M KCl at pH = 6.50. Positive current at the substrate (i_s) corresponds to a net oxidation; negative currents, i_t , at the tip correspond to a net reduction.

SECM approach curves obtained in solutions containing $\text{Ru}(\text{NH}_3)_6^{3+}$, $\text{S}_2\text{O}_8^{2-}$, and KCl are significantly more complex than in solutions containing only $\text{Ru}(\text{NH}_3)_6^{3+}$ and KCl, due to reactions involved in the electrocatalytic reduction of $\text{S}_2\text{O}_8^{2-}$. Scheme 2B depicts what we believe are the important heterogeneous and homogeneous reactions occurring between the tip and substrate electrodes, following the initial reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ at the tip electrode. As before, the tip and substrate electrodes are held at potentials corresponding, respectively, to the diffusion-limited reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ (-0.4 V) and oxidation of $\text{Ru}(\text{NH}_3)_6^{2+}$ (0.4 V). In addition to these reactions, $\text{SO}_4^{\bullet-}$ can be reduced at either the tip or the substrate, since the reduction potential for the $\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}$ couple, 2.21 V, is very positive of either tip or substrate electrode potential. Thus, upon formation and dissociation of $\text{S}_2\text{O}_8^{3\bullet-}$ to yield $\text{SO}_4^{\bullet-}$, both $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{SO}_4^{\bullet-}$ are reduced at the C tip. At the Pt substrate, $\text{Ru}(\text{NH}_3)_6^{2+}$ is oxidized while $\text{SO}_4^{\bullet-}$ is also reduced. As noted above in the discussion of the SSV data, $\text{Ru}(\text{NH}_3)_6^{2+}$ is homogeneously oxidized back to $\text{Ru}(\text{NH}_3)_6^{3+}$ through its reaction with either $\text{S}_2\text{O}_8^{2-}$ or $\text{SO}_4^{\bullet-}$. A key objective of the SECM measurement is the determination of the rate constant for the reaction of $\text{Ru}(\text{NH}_3)_6^{2+}$ with $\text{SO}_4^{\bullet-}$ (i.e., eq. 4). As before, the dimerization of $\text{SO}_4^{\bullet-}$ to yield $\text{S}_2\text{O}_8^{2-}$ was not included in the simulation analysis due to its negligible concentration in the gap region (see Supporting Information).

The approach curves shown in Figure 3 for solutions containing both $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{S}_2\text{O}_8^{2-}$ can be summarized as follows:

Substrate:

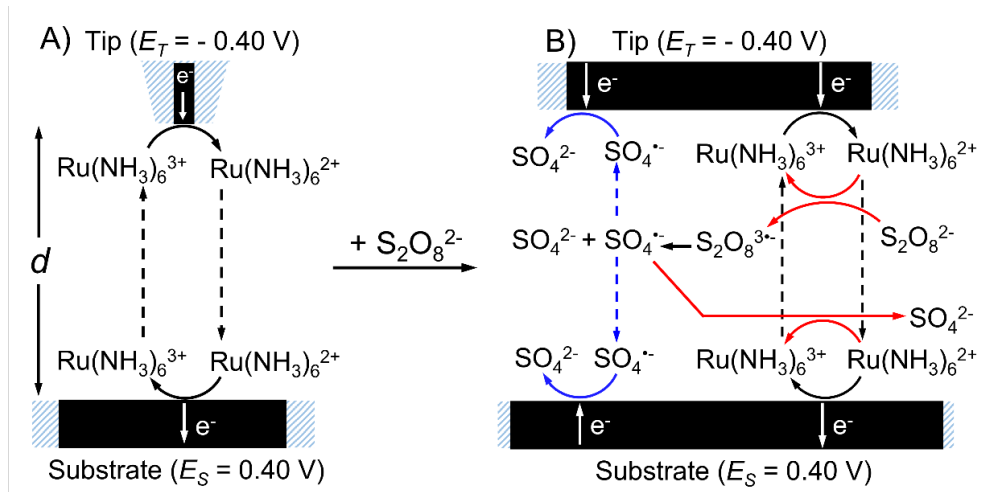
- At large gap separations, $2 < L < 10$ ($7.0 \mu\text{m} < d < 35 \mu\text{m}$), i_s decreases to the baseline, indicating that all $\text{Ru}(\text{NH}_3)_6^{2+}$ generated at the tip electrode reacts with $\text{S}_2\text{O}_8^{2-}$ or $\text{SO}_4^{\bullet-}$

before it reaches the substrate electrode, and/or that the anodic current due to oxidation of $\text{Ru}(\text{NH}_3)_6^{2+}$ is precisely canceled out by the cathodic current due to reduction of $\text{SO}_4^{\bullet-}$.

- At small gap separations, $L < 2$ ($d < 7.0 \text{ } \mu\text{m}$), i_s increases rapidly with decreasing L as $\text{Ru}(\text{NH}_3)_6^{2+}$ starts to arrive at the substrate electrode resulting in positive feedback.
- As shown in Figure 3, the i_s - L curves are essentially independent of $\text{S}_2\text{O}_8^{2-}$ concentration.

Tip:

- At large gap separations, $3 < L < 10$ (i.e., $10.5 \text{ } \mu\text{m} < d < 35 \text{ } \mu\text{m}$), i_t remains essentially constant, confirming that the substrate electrode has no influence on the rate of $\text{Ru}(\text{NH}_3)_6^{3+}$ reduction and the following homogeneous chemical reactions. The magnitude of i_t increases with increasing $\text{S}_2\text{O}_8^{2-}$ due to the electrocatalytic reduction of $\text{S}_2\text{O}_8^{2-}$, analogous to the mechanism offered for the SSV response.
- At intermediate gap separations, $1.5 < L < 3$ ($5.25 \text{ } \mu\text{m} < d < 10.5 \text{ } \mu\text{m}$), i_t decreases with decreasing L , due to the reduction of mass transport of $\text{S}_2\text{O}_8^{2-}$ from the bulk solution into the gap region.
- At small gap separations, $L < 1.5$ ($d < 5.25 \text{ } \mu\text{m}$), i_t increases rapidly with decreasing L as $\text{Ru}(\text{NH}_3)_6^{2+}$ starts to arrive at the substrate electrode resulting in positive feedback to the tip.



Scheme 2. Electrochemical and chemical reactions occurring in the gap region between the tip and the substrate electrode in the (A) absence and (B) presence of the $S_2O_8^{2-}$. The dashed lines represent diffusion.

The enhancement of i_t with increasing $S_2O_8^{2-}$ concentration for $2 < L < 10$ (*i.e.*, red, blue, and green trace in Figure 3) is attributed to the increasingly rapid regeneration of $Ru(NH_3)_6^{3+}$ by the reaction of $Ru(NH_3)_6^{2+}$ with $S_2O_8^{2-}$ and $SO_4^{\bullet-}$ (*i.e.*, eqs. 2 and 4). FEM simulations were used to determine the value of k_2 from the tip and substrate approach curves. In these simulations, the dissociation of $S_2O_8^{3\bullet-}$ yielding $SO_4^{\bullet-}$ was assumed to be very fast ($k_3 = 10^{10} \text{ s}^{-1}$). Also, the homogeneous electron-transfer reaction between $SO_4^{\bullet-}$ and $Ru(NH_3)_6^{2+}$ was assumed to be diffusion-controlled ($k_4 = 10^{10} \text{ M}^{-1}\text{s}^{-1}$). Small variations of these values had no effect on the simulated results. As shown in Figure 4, k_2 was determined as $\sim 1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for a solution containing 2.0 mM $S_2O_8^{2-}$ and 1.0 mM $Ru(NH_3)_6^{3+}$. Similarly, values for k_2 in solutions containing 0.50 mM $S_2O_8^{2-}$ and 1.0 mM $S_2O_8^{2-}$ were determined to be $\sim 5 \times 10^5$ and $\sim 6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, respectively (Supporting Information). In conclusion, k_2 determined by SECM increased by approximately a factor of 2x for $S_2O_8^{2-}$ concentrations between 0.5 and 2 mM, with an average value of $7.0 (\pm 2.4) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, in reasonable agreement with values determined by SSV (Table S2), but somewhat higher than previously obtained using CV ($\sim 2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$).¹⁰

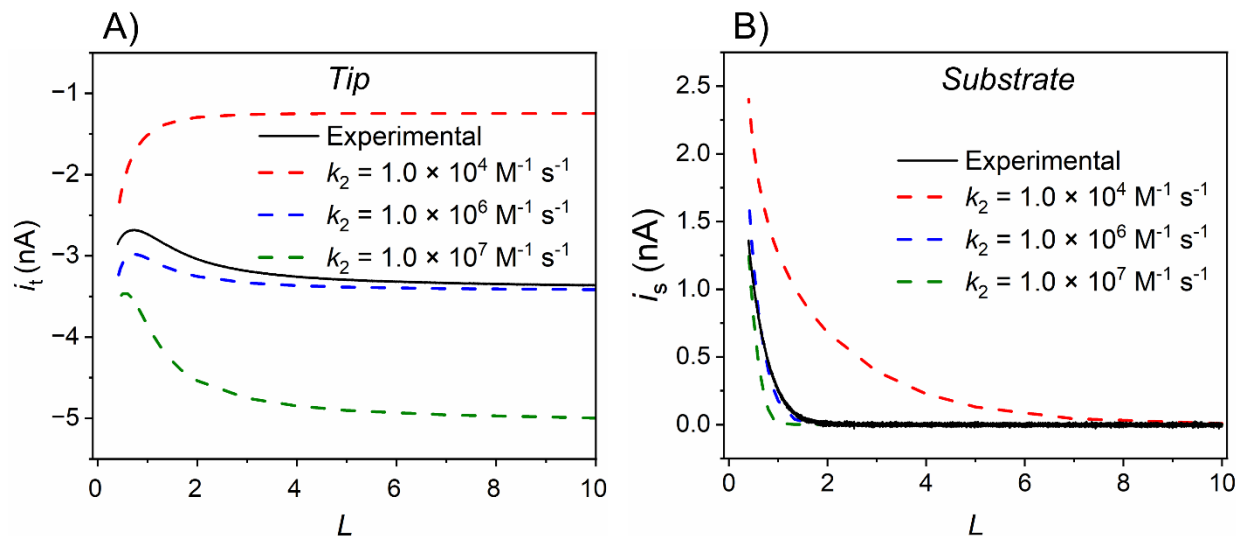


Figure 4. Effect of k_2 on the (A) tip and the (B) substrate current. Solid black lines show the experimental approach curves for 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and 2.0 mM $\text{S}_2\text{O}_8^{2-}$, and dashed colored lines represent the FEM simulations using k_2 values of $1.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (red), $1.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (blue), and $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (green). Approach curves were recorded using a 3.5- μm radius C-UME tip electrode ($\text{RG} \sim 5$) and a 25- μm radius ($\text{RG} = 20$) Pt-UME substrate electrode in an O_2 -free aqueous solution containing 0.1 M KCl (pH = 6.50). All simulations were carried out using $k_3 = 1.0 \times 10^{10} \text{ s}^{-1}$, $k_4 = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

The decrease of i_t between $1.5 < L < 3$, Figure 4A, is the result of hindered mass transport of $\text{S}_2\text{O}_8^{2-}$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ into the gap region caused by the proximity of the substrate electrode to the tip. This argument is supported by FEM simulations, discussed in detail in the Supporting Information. Finally, further decreasing L below 1.5 causes i_t to increase, a consequence of simple redox cycling of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ between the tip and the substrate electrode, Figure 4A.

As indicated in Scheme 2B, i_s is the sum of the current due to oxidation of $\text{Ru}(\text{NH}_3)_6^{2+}$ and the reduction of $\text{SO}_4^{\bullet-}$. As shown in 4B, i_s decreases to the zero current baseline level for $L > 2$ in the presence of $\text{S}_2\text{O}_8^{2-}$. Two possible explanations for this decrease are: i) generation of equal currents at the substrate with opposite polarity arising from eq. 5 and eq. 1, or ii) reaction of $\text{SO}_4^{\bullet-}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ (eq. 4) in the gap region, resulting in negligible amounts of $\text{SO}_4^{\bullet-}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ being transported to the substrate electrode. Simulated concentration profiles of $\text{Ru}(\text{NH}_3)_6^{3+}$,

$\text{Ru}(\text{NH}_3)_6^{2+}$, $\text{S}_2\text{O}_8^{2-}$, and $\text{SO}_4^{\bullet-}$ are shown in Figure 5 for $L = 10$, 1.5 , and 0.35 . At large and moderate values of L , the simulations indicate that $\text{SO}_4^{\bullet-}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ react within the gap, before reaching the substrate electrode. The concentrations of both species are negligibly small in the proximity of the substrate, resulting in zero current. Conversely, for $L < 2$ (Figure 5), the decreased flux of $\text{S}_2\text{O}_8^{2-}$ into the gap reduces the amount of $\text{SO}_4^{\bullet-}$ generated by homogeneous reactions, allowing $\text{Ru}(\text{NH}_3)_6^{2+}$ to reach the substrate, resulting in a significant anodic i_s , and the corresponding feedback to the tip. Inspection of the concentration gradients of $\text{Ru}(\text{NH}_3)_6^{2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+}$ in Part E of Figure 5, corresponding to $L = 0.35$, shows that the flux of $\text{Ru}(\text{NH}_3)_6^{2+}$ at the substrate is just slightly lower than that of $\text{Ru}(\text{NH}_3)_6^{3+}$ at the tip.

The concentration profiles for $\text{SO}_4^{\bullet-}$ are shown for $L = 10$, 1.5 , and 0.35 on an expanded scale in parts B, D, and F in Figure 5. Noting the change in the concentration scale (μM instead of mM), it is clear that the concentration of $\text{SO}_4^{\bullet-}$ is vanishingly small at all gap distances. This appears to be a consequence of the heterogeneous reduction of $\text{SO}_4^{\bullet-}$ at both electrodes, as well as its reduction by $\text{Ru}(\text{NH}_3)_6^{2+}$ in the solution between the tip and gap. The low concentration of $\text{SO}_4^{\bullet-}$ for all values of L clearly justifies ignoring the second-order dimerization of $\text{SO}_4^{\bullet-}$ to $\text{S}_2\text{O}_8^{2-}$, as previously noted.

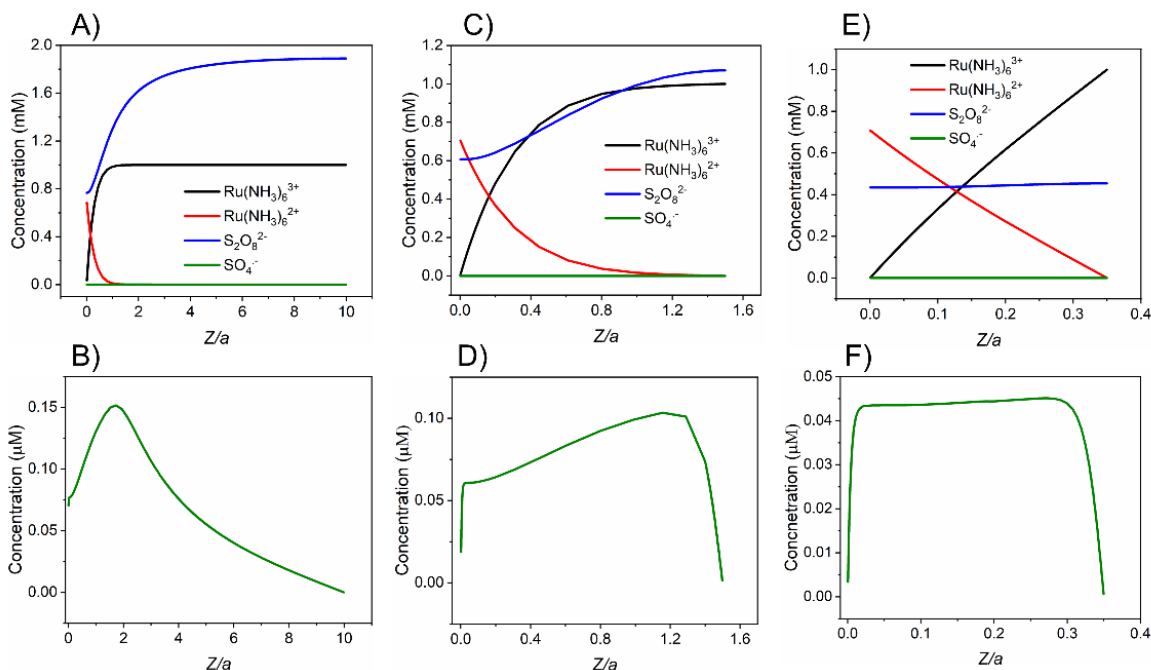


Figure 5. Concentration profiles of Ru(NH₃)₆³⁺ (black), Ru(NH₃)₆²⁺ (red), S₂O₈²⁻ (blue), and SO₄⁻ (green) for $L = 10$ (A, B), 1.5 (C, D) and 0.35 (E, F). Concentration profiles were extracted from FEM simulations for an aqueous solution containing $1.0 \text{ mM Ru(NH}_3)_6^{3+}$ and $2.0 \text{ mM S}_2\text{O}_8^{2-}$ with $k_2 = 1.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, $k_3 = 1.0 \times 10^{10} \text{ s}^{-1}$, and $k_4 = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ with a $3.5\text{-}\mu\text{m}$ radius ($\text{RG} = 5$) C-UME tip electrode and $25\text{-}\mu\text{m}$ radius ($\text{RG} = 20$) Pt-UME substrate electrode.

FEM simulations were also used to determine the rate, k_4 , for the electron-transfer reaction between Ru(NH₃)₆²⁺ and SO₄⁻. Figure 6 shows simulated approach curves with various k_4 values, while the k_2 and k_3 were held constant at $1.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $1.0 \times 10^{10} \text{ s}^{-1}$, respectively. The simulated approach curves for i_t and i_s converged to the experimental data with increasing k_4 values and remained sensitive to k_4 for values approaching up to $1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, which is two orders of magnitude higher than our previous lower limit determined by CV using a glassy carbon macroelectrode. We conclude from the SECM data that k_4 is greater than or equal to $\sim 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.

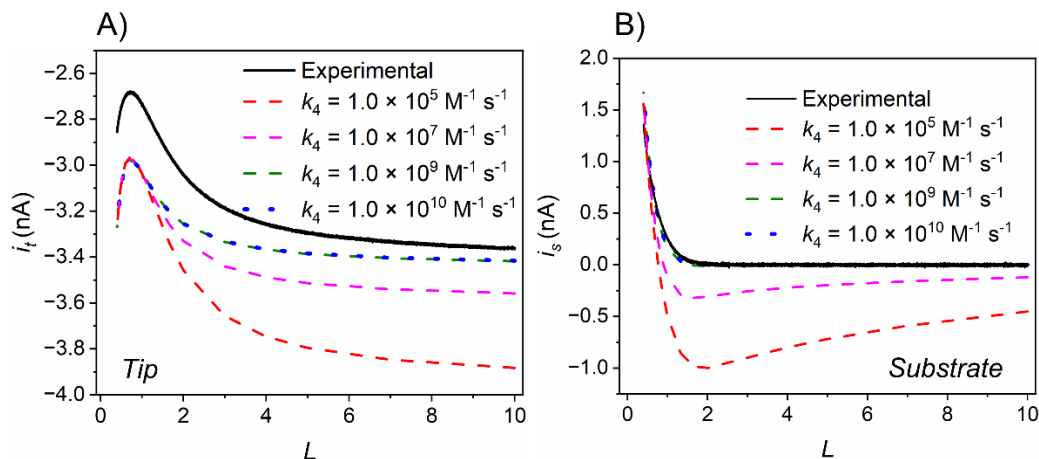


Figure 6. Effect of the k_4 on the (A) tip and (B) substrate current. The solid black line shows the experimental approach curve for 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and 2.0 mM $\text{S}_2\text{O}_8^{2-}$, and colored lines represent FEM simulation with k_4 values of $1.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (dashed red), $1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ (dashed magenta), $1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (dashed green), and $1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (dotted blue). Approach curves were recorded using a 3.5- μm radius C-UME tip electrode ($\text{RG} \sim 5$) and a 25- μm radius Pt-UME substrate electrode ($\text{RG} = 20$) in an O_2 -free aqueous solution containing 0.1 M KCl ($\text{pH} = 6.50$). All simulations were carried out using $k_2 = 1.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ and $k_3 = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$.

Finally, the approach curves of both the tip and the substrate electrode were simulated via FEM simulations using the rate constants determined by the above SECM measurements and compared to the experimental curves for 1.0 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{S}_2\text{O}_8^{2-}$ concentrations of 0.50, 1.0, and 2.0 mM. It is clear from the results shown in Figure 7A-C that the simulated approach curves for i_t and i_s are in reasonably good agreement with the experimental curves, supporting the accuracy of the values of k_2 , k_3 and k_4 determined by SECM.

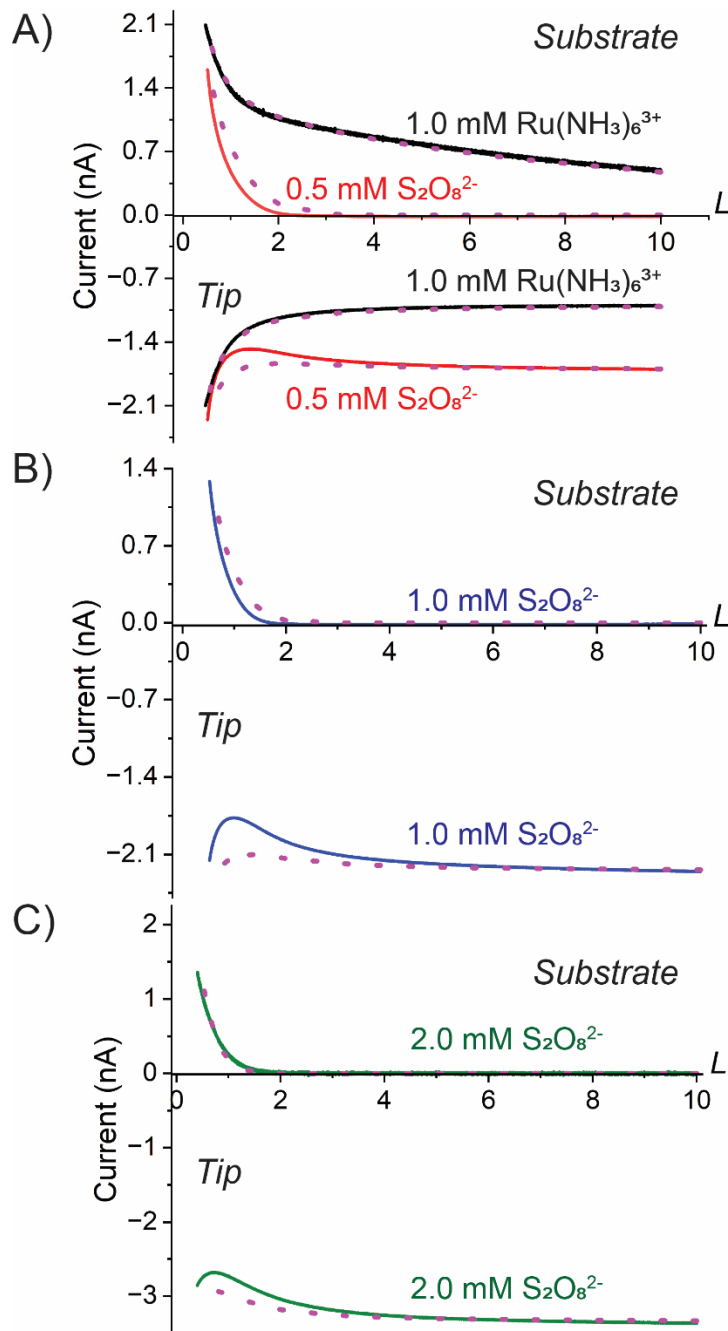


Figure 7. Experimental approach curves for A) 1.0 mM Ru(NH₃)₆³⁺ (black) and 1.0 mM Ru(NH₃)₆³⁺ with 0.50 mM S₂O₈²⁻ (red), B) 1.0 mM Ru(NH₃)₆³⁺ with 1.0 mM S₂O₈²⁻ (blue), and C) 1.0 mM Ru(NH₃)₆³⁺ with 2.0 mM S₂O₈²⁻ (green). Dotted magenta lines represent FEM simulation with $k_3 = 1.0 \times 10^6 \text{ s}^{-1}$, and $k_4 = 1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. k_2 values of $5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, $6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, and $1 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ were employed for simulating approach curves at 0.50 mM, 1.0 mM, and 2.0 mM S₂O₈²⁻, respectively. Approach curves were recorded using a 3.5- μm radius C-UME tip electrode (RG ~ 5) and a 25- μm radius (RG = 20) Pt-UME substrate electrode in an O₂-free aqueous solution containing 0.1 M KCl (pH = 6.50).

Conclusion

In the present work, we used SECM to investigate the kinetics of the elementary steps involved in the homogeneous reduction of $\text{S}_2\text{O}_8^{2-}$. The electrocatalytic reduction of $\text{S}_2\text{O}_8^{2-}$ via $\text{Ru}(\text{NH}_3)_6^{3+}$ includes five elementary steps in an aqueous solution. The average rate constant for the homogeneous reduction of $\text{S}_2\text{O}_8^{2-}$ via electrogenerated $\text{Ru}(\text{NH}_3)_6^{2+}$ was measured to be $\sim 5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ from SSV and $\sim 7 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ from SECM measurements. Both values are slightly higher than previous findings based on CV ($2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$).¹⁰ Our SECM analysis is insensitive to values greater than $1 \times 10^6 \text{ s}^{-1}$ for the rate of $\text{S}_2\text{O}_8^{3+}$ decomposition (i.e., eq. 3), which is also consistent with previous findings. Finally, a lower limit for the rate constant of the reaction between $\text{SO}_4^{\bullet-}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ was determined as $\sim 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ using SECM measurements. This value is two orders of magnitude larger than previously reported and is consistent with values suggested by computations methods.¹⁰

Associated Content

Supporting Information is available free of charge at:

Details of steady-state voltammetry studies and parameters used for digital simulation of SSV, details of parameters used for simulation of SECM approach curves, and details of COMSOL model employed for simulation of steady-state voltammograms and approach curves.

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Notes

The authors declare no competing financial interest.

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