

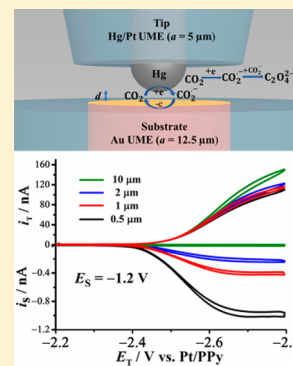
Detection of $\text{CO}_2^{\bullet-}$ in the Electrochemical Reduction of Carbon Dioxide in *N,N*-Dimethylformamide by Scanning Electrochemical Microscopy

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Supporting Information

ABSTRACT: The electrocatalytic reduction of CO_2 has been studied extensively and produces a number of products. The initial reaction in the CO_2 reduction is often taken to be the 1e formation of the radical anion, $\text{CO}_2^{\bullet-}$. However, the electrochemical detection and characterization of $\text{CO}_2^{\bullet-}$ is challenging because of the short lifetime of $\text{CO}_2^{\bullet-}$, which can dimerize and react with proton donors and even mild oxidants. Here, we report the generation and quantitative determination of $\text{CO}_2^{\bullet-}$ in *N,N*-dimethylformamide (DMF) with the tip generation/substrate collection (TG/SC) mode of scanning electrochemical microscopy (SECM). CO_2 was reduced at a hemisphere-shaped Hg/Pt ultramicroelectrode (UME) or a Hg/Au film UME, which were utilized as the SECM tips. The $\text{CO}_2^{\bullet-}$ produced can either dimerize to form oxalate within the nanogap between SECM tip and substrate or collected at SECM substrate (e.g., an Au UME). The collection efficiency (CE) for $\text{CO}_2^{\bullet-}$ depends on the distance (d) between the tip and substrate. The dimerization rate ($6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and half-life (10 ns) of $\text{CO}_2^{\bullet-}$ can be evaluated by fitting the collection efficiency vs distance curve. The dimerized species of $\text{CO}_2^{\bullet-}$, oxalate, can also be determined quantitatively. Furthermore, the formal potential ($E^{0'}$) and heterogeneous rate constant (k_0) for CO_2 reduction were determined with different quaternary ammonium electrolytes. The significant difference in k_0 is due to a tunneling effect caused by the adsorption of the electrolytes on the electrode surface at negative potentials.



INTRODUCTION

A recent upsurge in interest in the direct and catalyzed electrochemical reduction of CO_2 stems from the possibility of converting CO_2 into fuel for energy storage and conversion.^{1–3} Although extensive experimental and theoretical studies of the heterogeneous electrocatalytic (inner sphere) reactions^{1,4} have been reported, the reaction mechanisms are still not clear. A generally proposed first step is the initial production of $\text{CO}_2^{\bullet-}$, through a one electron-transfer reduction at the electrode surface. The generated $\text{CO}_2^{\bullet-}$ can then be protonated, dimerize, or be further reduced to the species of interest depending on the electrode material and solution composition (reactions 1–3).^{4,5}



Although $\text{CO}_2^{\bullet-}$ was proposed decades ago as the initial product for CO_2 reduction, this species has rarely been observed experimentally, due to its extremely short lifetime in either aqueous or nonaqueous solutions. Since a reliable and quantitative method for its measurement has been absent, the reaction mechanism cannot be elucidated. A fair amount of effort has been spent on exploring spectroscopic methods, such as Raman⁶ and Fourier transform infrared (FTIR)⁷ spectroscopy,

in aqueous and aprotic solutions for the detection of $\text{CO}_2^{\bullet-}$ adsorbed on the metal electrode surface. Unfortunately, quantitative information and direct electrochemical behavior of this species has not been obtained. Fast-scan cyclic voltammetry (FSCV) was used by Savéant, Amatore, and co-workers to study CO_2 reduction in anhydrous DMF.⁸ The standard potential (E^0) for $\text{CO}_2/\text{CO}_2^{\bullet-}$ was evaluated to be -2.21 V vs SCE at a scan rate of 4400 V s^{-1} . The dimerization rate constant was initially calculated to be $10^7 \text{ M}^{-1} \text{ s}^{-1}$, but this value was subsequently corrected to be $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in their later work.⁹ However, the intrinsic disadvantages of FSCV, even with ultramicroelectrodes (UMEs), such as interference by large contributions from double layer capacitance charging and adsorbed species affect the precision of the measurements, as seen in earlier experiments and make study of short-lived species difficult at high scan rates.¹⁰ The above-mentioned problems can be circumvented by using SECM to evaluate electrochemically generated $\text{CO}_2^{\bullet-}$. Since the measurements of SECM are conducted at steady state, it has the advantage over transient electrochemical techniques in that it is not perturbed by capacitive effects and electroactive adsorbed species.¹⁰ As a result, it is a powerful tool for the detection of extremely unstable radical species and the study of reaction mechanisms.¹⁰ Acrylonitrile,¹¹ guanosine,¹² and *N,N*-dimethylani-

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line¹³ radicals in aprotic solution and Sn(III)¹⁴ and superoxide¹⁵ intermediate in aqueous solution were studied using SECM by taking advantage of the micro- or nanogap between SECM tip and substrate. Moreover, the effect of tunneling on the electron transfer rates of Ru(bpy)₃²⁺ oxidation and reduction¹⁶ and the kinetics and mechanism of radical ion annihilation mode of electrogenerated chemiluminescence (ECL)¹⁷ were also investigated within the nanogap. Here, we propose a method to detect CO₂^{•-} using the TG/SC mode of SECM in DMF. Taking advantage of the nanogap and micrometer-sized electrode, we can prove the existence of CO₂^{•-} electrochemically at steady state. Importantly, by fitting the collection efficiency of CO₂^{•-} at different distances, the half-life of CO₂^{•-} and kinetic parameters for dimerization can be obtained. The high energetic barrier associated with a large structural change, from a linear to a V-shape as shown, for example, by DFT calculation, explains the relatively small rate of the reduction reaction. Moreover, the significant difference in the heterogeneous rate constant (*k*⁰) for CO₂ reduction in the presence of different tetra-alkylammonium electrolytes was observed and was attributed to the effect of tunneling, through a layer of the adsorbed electrolyte at the electrode surface at relatively negative potentials. In addition, SECM can show the distribution of the products of CO₂ reduction in real-time without the need for additional analytical instruments. The obtained results indicate the possibility of utilizing SECM as an efficient tool to study the mechanism of CO₂ reduction in the presence of different homogeneous and heterogeneous catalysts.

EXPERIMENTAL SECTION

Chemicals and Materials. Mercurous nitrate (Hg₂(NO₃)₂; ≥ 97%), potassium nitrate (KNO₃; trace metal basis, 99%), nitric acid (HNO₃; trace metal basis), acetonitrile (CH₃CN; 99.9%), decamethylferrocene (DMFc; 99%), anhydrous *N,N*-dimethylformamide (DMF; 99.9%) were purchased from Fisher Scientific (Pittsburgh, PA). Tetrabutylammonium hexafluorophosphate (TBAPF₆; ≥99%), tetrapropylammonium hexafluorophosphate (TPAPF₆; ≥98%), tetraethylammonium hexafluorophosphate (TEAPF₆; ≥99%), tetraheptylammonium tetraphenylborate (THeATPB; selectophore), tetraoctylammonium bromide (TOABr; ≥98%), and pyrrole (99%) were acquired from Sigma-Aldrich (St. Louis, MO). All reagents were used without further purification. All aqueous solutions were prepared with ultrapure water with the resistivity of 18.3 MΩ/cm from a Milli-Q Integral system (EDM Millipore, Billerica, MA). Argon (5.0 UHP) and carbon dioxide (10%, balance nitrogen, 4.0 UHP) gas were obtained from Praxair.

Electrode Fabrication. The process for the fabrication of disk UMEs with different radius (*a*) has been well described elsewhere.^{10,18} In this study, we use hemisphere-shaped Hg/Pt UMEs^{19,20} fabricated by electrochemical reduction of mercurous ions on a Pt UME (*a* = 5 μm) with RG (ratio of the radius of the electrode to that of the Pt wire) of 5. Briefly, the electrode potential was held at -100 mV vs Ag/AgCl for ~40 s in a chronoamperometric step using an aqueous solution containing 10 mM Hg₂(NO₃)₂, 0.1 M KNO₃, and 0.5% HNO₃. The amount of mercury (19.0 ± 2.0 pmol) deposited on the platinum surface was deduced by integrating the chronoamperometric current, which is the total charge under the reduction peak (Figure S1). This value agrees well with the calculation (17.6 pmol) for a hemisphere. Since Pt does not dissolve appreciably in Hg, this electrode contains rather pure Hg with a very flat surface. However, the Hg/Pt UME is sensitive to vibrations and shape changes with potential at very negative values. A similar method was utilized for the fabrication of Hg/Au film UMEs.²¹ In this case, a thin Hg film and essentially disk-shaped electrode is obtained, but the Hg contains appreciable Au levels. To prevent contamination from metal ions (e.g.,

Ag⁺) and water during SECM experiments, a Pt/PPy reference electrode was fabricated by electrochemical deposition of a polypyrrole (PPy) film onto a Pt wire in CH₃CN containing 0.1 M TBAPF₆ and 0.01 M pyrrole as described earlier.²² The obtained reference electrode was placed into a glass tube filled with DMF containing 0.1 M TBAPF₆ with a frit at one end. Good potential stability of Pt/PPy reference electrode was observed, and the potential of Pt/PPy was calibrated to be -0.19 V vs aqueous saturated calomel electrode (SCE).

Instrumentation. The electrochemical measurements were carried out with a CHI 660C potentiostat (CH Instruments, Austin, TX). A CHI 920C SECM workstation (CH Instruments, Austin, TX) for SECM measurements was placed inside an argon atmosphere drybox to avoid contamination of solution from water and oxygen. Carbon dioxide (10%) was introduced to the SECM cell directly through bubbling DMF solution for about 5 min before the experiments. The concentration of CO₂ was estimated to be 20 mM in DMF based on an earlier report.^{23,24} The electrodes and cell configuration are shown in Figure 1. CO₂ was reduced on a hemisphere-shaped Hg/Pt UME (*a*

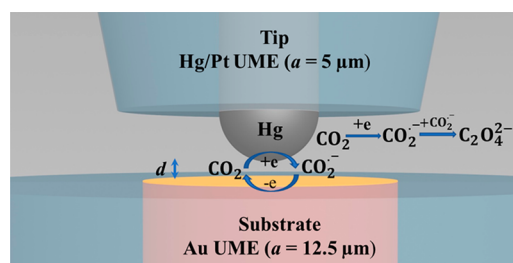


Figure 1. Schematic depiction of the collection of the CO₂^{•-} radical in TG/SC mode of SECM.

= 5 μm), which was utilized as the SECM tip. The predominant species, oxalate, was generated by CO₂^{•-} dimerization at the upper portion of the hemisphere, whereas at lower portion of the hemisphere, CO₂^{•-} was captured by the SECM substrate (e.g., a = 12.5 μm Au UME). A Pt/PPy electrode and a Pt wire served as the reference and counter electrodes, respectively. An accurate alignment of the SECM tip and substrate was required before the SECM experiments. The tip and substrate were initially aligned with two digital microscopes (Park, Santa Clara, CA), and then a more accurate alignment was accomplished through a *x* and *y*-axis probe scanning curve, combined with the substrate generation/tip collection (SG-TC) mode of SECM.¹³ DMFc was utilized as the redox-mediator to monitor the tip position when it was in close proximity to the substrate and to determine the gap spacing (*d*). As indicated in Figure S2A, well-defined steady-state currents of 1 mM DMFc were obtained in anhydrous DMF containing 0.1 M TBAPF₆ for a *a* = 5 μm Hg/Pt UME and a *a* = 12.5 μm Au UME (Figure S2A), respectively. The steady-state current obtained agreed well with the theoretical calculation. An experimental approach curve (Figure S2B, red curve) is presented together with the theoretical COMSOL simulation (Multiphysics v4.2 software, COMSOL, Inc., Burlington, MA) within the same parameters (Figure S2B, black dotted curve). The experimental results are well in line with the simulated result, which also indicates the accurate alignment of the tip and substrate.

DFT Simulation. The spin-polarized density functional theory (DFT) calculations were performed using the projector-augmented wave (PAW) method²⁵ as implemented in the Vienna ab initio simulation package (VASP).²⁶ An energy cutoff of 600 eV for the plane wave basis set was used to expand the Kohn–Sham orbitals. The hybrid density functional theory proposed by Heyd, Scuseria, and Ernzerhof (HSE06)²⁷ was used to approximate the electronic exchange and correlation. Solvation effects, which are prominent in stabilizing ionic species, were taken into account by using an implicit solvation model implemented into VASP by Mathew and Hennig.²⁸ The background dielectric constant of DMF was set to 36.7.

RESULTS AND DISCUSSION

CV of CO₂ Reduction. Cyclic voltammogram (CV) of 20 mM CO₂ at a Hg/Pt UME ($a = 5 \mu\text{m}$) in DMF containing 0.1 M TBAPF₆ is shown in Figure 2. Well-defined reduction waves

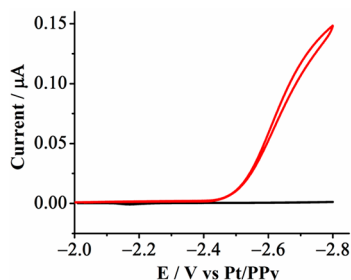


Figure 2. CVs of a Hg/Pt UME ($a = 5 \mu\text{m}$) in DMF containing 0.1 M TBAPF₆ in the absence (black curve) and presence of 20 mM CO₂ (red curve) at a scan rate of 100 mV s⁻¹.

(red curve) were observed with the half-wave potential ($E_{1/2}$) of -2.63 V . The steady-state current (i_{ss}), $0.15 \mu\text{A}$, was obtained. The number of the electrons transferred ($n = 0.92$) was deduced using eq 4

$$i_{ss} = 2\pi nFDca \quad (4)$$

where F is the Faraday constant ($96\,500 \text{ C mol}^{-1}$), D is the diffusion coefficient ($2.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$),⁹ c is the concentration of CO₂ (20 mM), and a is the radius of the UME ($5 \mu\text{m}$). The background current was negligible in the absence of CO₂ (black curve). Pt can be easily wet by Hg and yet has a low solubility in it, and the identical CO₂ reduction waves were obtained repeatedly at the Hg/Pt UMEs. No adsorption of CO₂ and/or of its reduction intermediates (e.g., CO₂^{•-}) was apparent, thus Hg can be considered as a suitable electrochemical material for CO₂ reduction.^{5,9} Although the results indicate that the reduction process at the Hg/Pt surface consumes one electron per mole of CO₂, the lack of a current plateau was observed and was mainly attributed to the instability of the Hg/Pt UME at the very negative potentials.

CO₂ Reduction by TG/SC Mode of SECM. TG/SC mode of SECM was employed for the studies of CO₂ reduction. Since the CO₂^{•-} does not adsorb on the Hg/Pt surface, once it is generated at the SECM tip ($a = 5 \mu\text{m}$ Hg/Pt UME), it diffuses away and is collected by an SECM substrate (e.g., $a = 12.5 \mu\text{m}$ Au UME). To accomplish that, a small d (distance between tip and substrate) is required, so that CO₂^{•-} can diffuse across the gap before further reactions take place. In order to assess the redox behavior of CO₂^{•-}, the tip potential (E_T) was held constant at -2.8 V to generate CO₂^{•-} continuously (Figure 3A, red curve), whereas the substrate potential (E_S) was scanned from -2.1 V to -0.9 V to collect the generated CO₂^{•-}. The collection of CO₂^{•-} (Figure 3A, black curve) is shown by the increase of substrate current (i_S) at d of $1 \mu\text{m}$. The tip current (i_T) increased under this condition because some CO₂^{•-} was oxidized back to CO₂ at the substrate and fed back to the tip. Since i_T reached a plateau at around -1.2 V , E_S was held at -1.2 V in Figure 3B to collect the generated CO₂^{•-} at different d to evaluate the variation of i_S with d . The reduction of 20 mM CO₂ at the SECM tip was conducted (Figure 3B, top) by sweeping E_T from -2.2 V to -2.8 V , while E_S was held constant at -1.2 V to oxidize CO₂^{•-} back to CO₂ (Figure 3B, bottom). As d decreased from $10 \mu\text{m}$

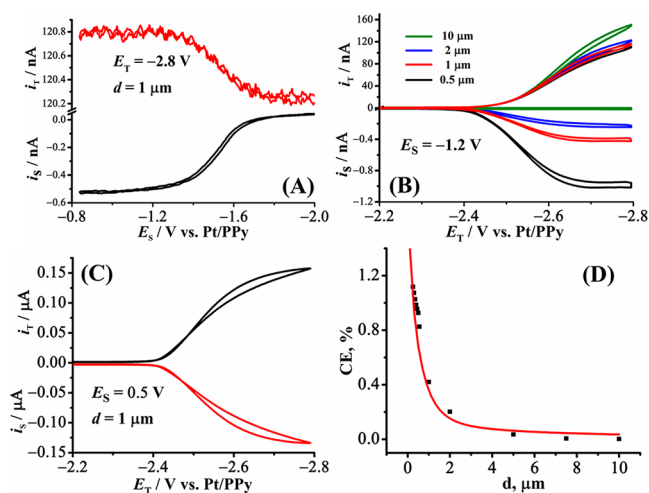


Figure 3. (A) CO₂^{•-} (black curve) collected at a SECM substrate ($a = 12.5 \mu\text{m}$ Au UME) in DMF containing 0.1 M TBAPF₆ by holding E_T at -2.8 V , while scanning E_S from -2.1 V to -0.9 V ($d = 1 \mu\text{m}$). i_T is shown in the red curve. (B) CVs of 20 mM CO₂ reduction (top) acquired at a SECM tip ($a = 5 \mu\text{m}$ Hg/Pt UME) and corresponding i_S of CO₂^{•-} (bottom) at the d of 10 (green), 2 (blue), 1 (red), and $0.5 \mu\text{m}$ (black curve), respectively. The E_S was held at -1.2 V while scanning E_T from -2.2 V to -2.8 V . Part C is the same as part B except the E_S was held at 0.5 V to collect oxalate (red curve) at d of $1 \mu\text{m}$. (D) Experimental CE (black dotted) of CO₂^{•-} and the best fit of the results (red curve) with the EC model of simulation. The scan rates for parts A–C were 100 mV/s.

to 200 nm , i_T decreased because of the hindered diffusion. Meanwhile, i_S was only observable when the tip was close to the substrate ($d \leq 2 \mu\text{m}$) and increased with smaller d . The dimerized species of CO₂^{•-}, oxalate, can also be captured at the substrate by holding E_S at a more positive potential, 0.5 V (Figure 3C, red curve), while sweeping the E_T from -2.2 V to -2.8 V (Figure 3C, black curve). For the determination of oxalate, the solution in SECM needed to be replaced by fresh electrolyte without DMFc to prevent interference by its oxidation. The high CE ($\sim 90\%$, $d = 1 \mu\text{m}$) for oxalate indicates that it is the predominant species during the CO₂ reduction at Hg/Pt UMEs. Although CO₂^{•-} can react with CO₂ or trace amounts of water based on the previous report,⁵ the dimerization clearly predominates over other reactions under our experimental conditions. This observation is consistent with another report by Savéant and co-workers.⁹ The CE for CO₂^{•-} is small, even at small d , as shown in Figure 3D (black dotted curve). As d decreased from $10 \mu\text{m}$ to 200 nm , the CE increased to 1.1% . The relatively low CE was primarily due to the extremely fast dimerization rate of CO₂^{•-}; the hemispherical shape of the SECM tip (Figure 1) also contributes. We calculated the dimerization rate of CO₂^{•-} using COMSOL Multiphysics v4.2 software as described in Figure S3. The best fit of the CE curve as a function of d , with the EC model for a given rate constant (k_c) for the dimerization reaction, is shown in Figure 3D (red curve). Comparing the simulated and experimental data indicated that k_c is about $6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The half-life of CO₂^{•-}, $t_{1/2}$, is about 10 ns using the equation of $t_{1/2} = 1/(k_c c)$. These values represent the fastest homogeneous coupling reaction and shortest half-life measured electrochemically to date.

To alleviate possible problems with a hemispherical Hg/Pt UME, experiments were also carried out with a Hg/Au

electrode with a thin Hg film on an Au UME. Results for this electrode for CO₂ reduction are shown in Figure 4. In general,

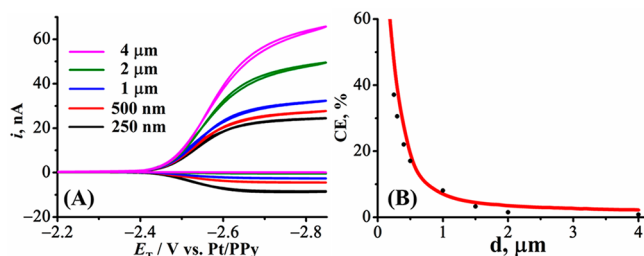


Figure 4. (A) 20 mM CO₂ reduction (top) at a SECM tip ($a = 5 \mu\text{m}$ Hg/Au UME) and corresponding collection currents of CO₂^{•-} (bottom) at a SECM substrate ($a = 12.5 \mu\text{m}$ Au UME) in DMF containing 0.1 M TBAPF₆ at different d values (4, 2, 1, 0.5, and 0.25 μm). The E_s was held at -1.2 V while scanning E_r from -2.2 V to -2.85 V. (B) Experimental CE (black dotted) and the best fit of the experimental data (red curve) for CO₂^{•-} with the EC model of simulation.

the results are similar to those with the Hg/Pt UME, but higher collection efficiencies (~37%) and more resolved limiting currents were found. UMEs with other metals (Pt and Au) were also tried as tips for the reduction of CO₂ in DMF. However, satisfactory and repeatable CVs could not be obtained.

The electrochemical behavior of CO₂^{•-} was also evaluated with different SECM substrate collectors (Pt and Hg/Au) using a Hg/Pt UME as the tip (Figure S4). A shift of CO₂^{•-} oxidation in the positive direction at a Pt substrate was observed (Figure S4, red curve). This might be caused by the passivation of the Pt surface by trace amounts of CO in the solution.²⁹

Heterogeneous Electron Transfer (ET) Rate of CO₂ Reduction. In general, the rates of simple 1e transfer are quite large. Under these conditions, the radical ion produced can be detected^{11–13} using the TG/SC mode of SECM by holding E_s close to the onset potential of the reduction at the tip. However, for the CO₂ reduction, a large separation of potential for reduction ($E_{1/2} = -2.63$ V, Figure 2) and product oxidation ($E_{1/2} = -1.51$ V, Figure 3) is found, indicating a slower ET reaction. This can be attributed to the large reorganization energy, i.e., the Marcus λ , because of a large structural change on ET. It is well-known that CO₂ undergoes a large structural change, from a linear to a V-shape on reduction. To address this, DFT calculations were employed to estimate the magnitude of the inner and outer reorganization energy of the reaction. After the structure of CO₂ and CO₂^{•-} was optimized, we obtained the potential energy curves (PECs) for CO₂ + e (Figure SSA, blue curve) and CO₂^{•-} (Figure SSA, red curve), which were evaluated as a function of reaction coordinate (bent angle 180–135° and C–O bond length 1.162–1.234 Å) under implicit solvent (DMF) with a dielectric constant of 36.7. The energy surface for CO₂ follows a parabolic shape. CO₂^{•-} remains stable when the molecule is bent. In the absence of solvent and electrolyte, once CO₂^{•-} is halfway from the bent to the linear structure, CO₂^{•-} is no longer stable due to the facile detachment of an electron from the CO₂^{•-} molecule. Note that the loss of an electron from CO₂^{•-} could be an artifact due to the missing cation in our simulation. At the predicted equilibrium potential ($E_{\text{eq}} = -2.4$ V vs SHE), the Gibbs activation energy (ΔG^*) for CO₂

reduction is calculated to be 0.5 eV (Figure SSB). On the basis of the simulation, k^0 is estimated to be $2.2 \times 10^{-4} \text{ cm s}^{-1}$ using eq 5^{18,30}

$$k^0 = K_p \nu_n \kappa \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (5)$$

where κ is the electronic transmission coefficient, which is taken initially as unity, assuming that CO₂ reduction at the Hg/Pt surface is a purely adiabatic reaction (Figure 2); K_p is the precursor equilibrium constant (~60 pm);³⁰ and ν_n is the nuclear frequency factor ($1.1 \times 10^{12} \text{ s}^{-1}$), which was determined by eq 6³⁰

$$\nu_n = \tau_L^{-1} \left(\frac{\Delta G^*}{4\pi RT}\right)^{1/2} \quad (6)$$

where τ_L is the longitudinal solvent relaxation time (1.1 ps for DMF).³¹ The estimated k^0 represents an upper limit of the reaction rate. The uncertainty of the theoretically estimated k^0 largely relies on the uncertainty of the value of κ , which is determined by the adiabaticity of the reaction.

Effect of Tunneling on the ET Rate. There has been recent interest in the effects of tunneling on electrode reactions.^{32–36} Since κ exponentially depends on the distance between the electrode and reactant, we carried out CV experiments with electrolytes of different sizes, so that the nature of the reaction can be determined from the behavior of k^0 as a function of electrolyte size. The CVs of CO₂ reduction on a Hg/Pt UME ($a = 5 \mu\text{m}$) containing different electrolytes are shown in Figure 5. The $E_{1/2}$ shifted the negative direction

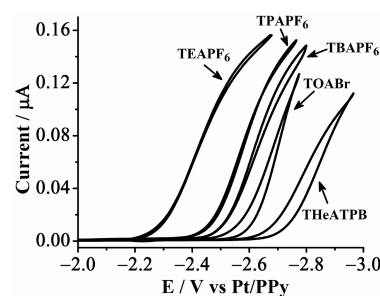


Figure 5. CVs of 20 mM CO₂ reduction collected at a Hg/Pt UME ($a = 5 \mu\text{m}$) in DMF solution containing 0.1 M TEAPF₆, TPAPF₆, TBAPF₆, THeATPB, and TOABr, respectively.

from -2.38 V (TEAPF₆) to -2.67 V (TOABr) with the increase of cation size, except for THeATPB, which shows the most negative reduction potential ($E_{1/2} = -2.83$ V). Fawcett³⁷ and Evans³⁸ and co-workers attributed this phenomenon to a tunneling effect which occurs for reduction at relatively negative potential with respect to the potential of zero charge (PZC). The negatively charged electrode adsorbs a large amount of cations, which subsequently form a dense layer on the electrode, preventing the close approach of CO₂ to the electrode surface and further slows the electron transfer. On the basis of our results, the size of the anion of the supporting electrolyte may also contribute to the thickness of the tunneling layer. Capacitance measurements in the presence of different electrolytes at relatively negative potentials were conducted and the total double layer capacitance was calculated, as shown in Table S1. The double layer capacitance decreases as the size of the electrolytes increase, indicating the existence of an adsorbed electrolyte species on the electrode surface.³⁷

Table 1. Potentials and Kinetic Parameters^a for 20 mM CO₂ Reduction from Steady-State Voltammograms Using 0.1 M TEAPF₆ and TBAPF₆, Respectively

	electrolyte	$E_{1/2}^c$ (V)	$E_{1/2}^a$ (V)	$E^{0'}$ (V)	$D,^b$ cm ² /s	α	$k_c, M^{-1} s^{-1}$	$k^0, cm/s$
Hg/Pt UME	0.1 M TEAPF ₆	-2.57	-1.91	-2.24	2.3×10^{-5}	0.42	6.0×10^8	1.5×10^{-4}
Hg/Pt UME	0.1 M TBAPF ₆	-2.82	-1.70	-2.26	2.3×10^{-5}	0.45	6.0×10^8	2.4×10^{-6}
Hg/Au UME	0.1 M TBAPF ₆			-2.26	2.3×10^{-5}	0.56	6.0×10^8	1.0×10^{-6}

^aThe potential was converted to values vs aqueous SCE. ^b D was corrected to be 2.3×10^{-5} cm²/s for the best fit.

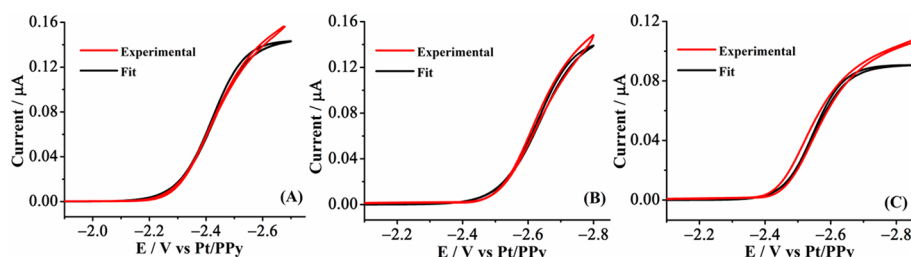


Figure 6. Experimental (red) and simulated CVs (black curves) for 20 mM CO₂ reduction at a Hg/Pt UME ($a = 5 \mu\text{m}$, A and B) and a Hg/Au UME ($a = 5 \mu\text{m}$, C) in the presence of 0.1 M TEAPF₆ (A) and 0.1 M TBAPF₆ (B and C), respectively. The parameters are shown in Table 1.

An alternative explanation of supporting electrolyte effects involves ion pairing of the cation with CO₂^{•-}. We can test this by examining whether the formal potential for CO₂ reduction ($E^{0'}$), estimated as the average of the cathodic and anodic $E_{1/2}$ values, e.g., for TEAPF₆ and TBAPF₆, are the same. Significant ion pairing should assist in the formation of CO₂^{•-} and cause a positive shift in potential. In order to assess that, the voltammetric behavior of CO₂^{•-} at a Hg/Au UME ($a = 12.5 \mu\text{m}$) was obtained in Figure S6. As shown in Table 1, $E^{0'}$ for the TEA⁺ and TBA⁺ salts are -2.24 and -2.26 V, respectively, suggesting lack of ion pairing.

We obtained k^0 for 20 mM CO₂ reduction at a $a = 5 \mu\text{m}$ Hg/Pt UME by simulating the experimental voltammograms with 0.1 M TEAPF₆ (Figure 6A) and 0.1 M TBAPF₆ solution (Figure 6B), respectively, using Digielch software (Gamry Inc., Warminster, PA). The simulation included the effect of the dimerization reaction. The results are shown in Table 1. The larger k^0 of the TEAPF₆ solution is also consistent with the tunneling model. The simulation of the experimental voltammogram of 20 mM CO₂ reduction at a $a = 5 \mu\text{m}$ Hg/Au UME with 0.1 M TBAPF₆ was also conducted, as shown in Figure 6C. The value of k^0 (1.0×10^{-6} cm/s) was comparable with the one obtained at the Hg/Pt UME in 0.1 M TBAPF₆ (3.0×10^{-6} cm/s). However, the changes in the shape of the Hg hemisphere and side reactions at steady-state region affect the accurate measurements of k^0 . This part will be improved and kinetics studies of the side reactions will also be conducted in planned new studies.

CONCLUSIONS

SECM was utilized to study the mechanism of CO₂ reduction. The initial product, an unstable intermediate, CO₂^{•-}, was captured for the first time using the TG/SC mode of SECM. We were able to accurately assess the dimerization rate ($6.0 \times 10^8 M^{-1} s^{-1}$) and half-life (10 ns) of CO₂^{•-} by fitting the experimental data with the theoretical simulation. This represents the fastest homogeneous coupling reaction and shortest half-life that has been measured electrochemically. Our experimental data and DFT calculation both verified the irreversibility of the reaction. Formal potential ($E^{0'}$) and heterogeneous rate constant (k^0) for CO₂ reduction were calculated with TEAPF₆ and TBAPF₆ as electrolytes,

respectively. The significant difference in k^0 is due to the “tunneling effect” caused by the adsorption of the electrolyte on the electrode surface at negative potential with respect to PZC. Moreover, the capability of quantitative and real-time detection of stable products (e.g., oxalate) during CO₂ reduction also facilitates the analysis of the product distribution of CO₂ reduction. To the best of our knowledge, this is the first report to present a way to quantitatively measure CO₂^{•-} in aprotic solution without the interference of capacitive charging. As CO₂^{•-} is a critical species during CO₂ reduction, the ability to quantitatively measure this intermediate within the nanogap provides the possibility of utilizing SECM as a tool to conduct mechanism studies for CO₂ reduction with heterogeneous and homogeneous catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08702.

Chronoamperogram of mercury deposition at a Pt UME; CV and approach curve of UMEs, COMSOL simulation parameters, CV of CO₂^{•-} at different substrates, DFT calculation, capacities calculation, and collection of CO₂^{•-} with TEAPF₆ as an electrolyte (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Hori, Y. Electrochemical CO₂ reduction on metal electrodes. In *Modern Aspects of Electrochemistry*; Vayenas, C., White, R., Gamboa-Aldeco, M., Eds.; Springer: New York, 2008; Vol. 42, p 89.
- (2) Kim, D.; Sakimoto, K. K.; Hong, D. C.; Yang, P. D. *Angew. Chem., Int. Ed.* **2015**, *54*, 3259.
- (3) Olah, G. A.; Prakash, G. S.; Goepfert, A. *J. Am. Chem. Soc.* **2011**, *133*, 12881.
- (4) Costentin, C.; Robert, M.; Saveant, J. M. *Chem. Soc. Rev.* **2013**, *42*, 2423.
- (5) Amatore, C.; Saveant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 5021.
- (6) Mcquillan, A. J.; Hendra, P. J.; Fleischmann, M. J. *Electroanal. Chem. Interfacial Electrochem.* **1975**, *65*, 933.
- (7) Chandrasekaran, K.; Bockris, J. O. *Surf. Sci.* **1987**, *185*, 495.
- (8) Lamy, E.; Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *78*, 403.
- (9) Gennaro, A.; Isse, A. A.; Severin, M. G.; Vianello, E.; Bhugun, I.; Saveant, J. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3963.
- (10) Bard, A. J.; Mirkin, M. V. *Scanning Electrochemical Microscopy*, 2nd ed.; CRC Press: Boca Raton, FL, 2012.
- (11) Zhou, F. M.; Bard, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 393.
- (12) Bi, S. P.; Liu, B.; Fan, F. R. F.; Bard, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 3690.
- (13) Cao, F. H.; Kim, J.; Bard, A. J. *J. Am. Chem. Soc.* **2014**, *136*, 18163.
- (14) Chang, J. H.; Bard, A. J. *J. Am. Chem. Soc.* **2014**, *136*, 311.
- (15) Zhou, M.; Yu, Y.; Hu, K. K.; Mirkin, M. V. *J. Am. Chem. Soc.* **2015**, *137*, 6517.
- (16) Shen, M.; Bard, A. J. *J. Am. Chem. Soc.* **2011**, *133*, 15737.
- (17) Rodríguez-López, J.; Shen, M.; Nepomnyashchii, A. B.; Bard, A. J. *J. Am. Chem. Soc.* **2012**, *134*, 9240.
- (18) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, 2001.
- (19) Mauzeroll, J.; Hueske, E. A.; Bard, A. J. *Anal. Chem.* **2003**, *75*, 3880.
- (20) Wehmeyer, K. R.; Wightman, R. M. *Anal. Chem.* **1985**, *57*, 1989.
- (21) Jung, C. H.; Sanchez-Sanchez, C. M.; Lin, C. L.; Rodriguez-Lopez, J.; Bard, A. J. *Anal. Chem.* **2009**, *81*, 7003.
- (22) Ghilane, J.; Hapiot, P.; Bard, A. J. *Anal. Chem.* **2006**, *78*, 6868.
- (23) Gennaro, A.; Isse, A. A.; Vianello, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1990**, *289*, 203.
- (24) Wadhawan, J. D.; Welford, P. J.; McPeak, H. B.; Hahn, C. E. W.; Compton, R. G. *Sens. Actuators, B* **2003**, *88*, 40.
- (25) Kresse, G.; Hafner, J. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *47*, 558.
- (26) Kresse, G.; Joubert, D. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758.
- (27) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, *118*, 8207.
- (28) Fishman, M.; Zhuang, H. L.; Mathew, K.; Dirschka, W.; Hennig, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, 245402.
- (29) Dhar, K.; Cavallotti, C. *J. Phys. Chem. A* **2014**, *118*, 8676.
- (30) Fawcett, W. R.; Opallo, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2131.
- (31) Fawcett, W. R.; Foss, C. A. *Electrochim. Acta* **1991**, *36*, 1767.
- (32) Barfidokht, A.; Ciampi, S.; Luais, E.; Darwish, N.; Gooding, J. J. *Anal. Chem.* **2013**, *85*, 1073.
- (33) Chazalviel, J. N.; Allongue, P. *J. Am. Chem. Soc.* **2011**, *133*, 762.
- (34) Gosavi, S.; Marcus, R. A. *J. Phys. Chem. B* **2000**, *104*, 2067.
- (35) Hill, C. M.; Kim, J.; Bard, A. J. *J. Am. Chem. Soc.* **2015**, *137*, 11321.
- (36) Hill, C. M.; Kim, J.; Bodappa, N.; Bard, A. J. *J. Am. Chem. Soc.* **2017**, *139*, 6114.
- (37) Fawcett, W. R.; Fedurco, M.; Opallo, M. *J. Phys. Chem.* **1992**, *96*, 9959.
- (38) Evans, D. H. *Chem. Rev.* **2008**, *108*, 2113.