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Electrocatalytic Dealkylation of Amines Mediated by Ferrocene

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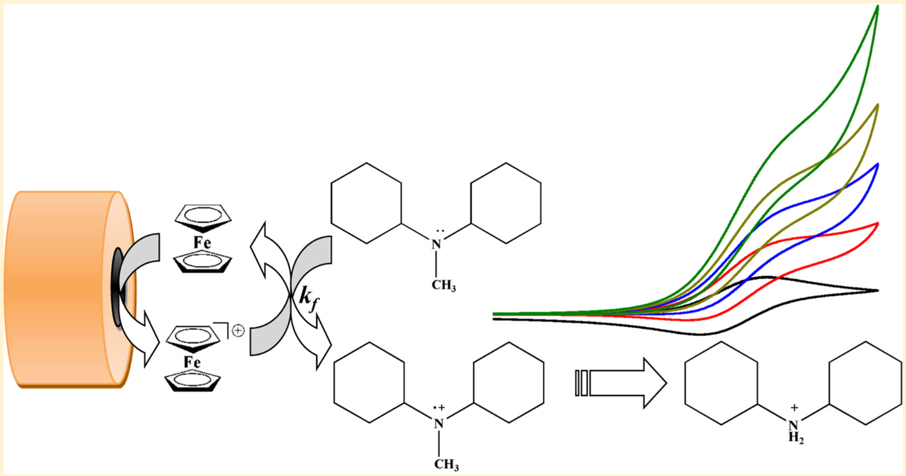
Supporting Information



ABSTRACT: The homogeneous catalytic oxidation of dicyclohexylamine (DCHA), *N*,*N*-dimethylcyclohexylamine (DMCHA) and *N*,*N*-dicyclohexylmethylamine (DCHMA) has been investigated in the presence of electrochemically generated ferrocenium ions as the catalyst. Mechanistic details for this electrocatalytic process have been scrutinized with the use of cyclic voltammetry, bulk electrolysis, and digital simulations techniques. A one-electron catalytic process between ferrocene and the respective amines was observed. The products obtained from bulk electrolysis were isolated and identified by FTIR, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. Both DCHMA and DMCHA proceed to yield a secondary amine product by the elimination of one methyl group. In the absence of this group, as in the case of DCHA, the cycloalkyl group is then eliminated. The catalytic efficiency and the second-order rate constants were estimated and found to follow the order DCHA ≪ DMCHA < DCHMA. The results presented in this work should open up a new avenue to achieve simple, low-cost, and efficient amine oxidation, which could be useful in several areas of chemistry.

■ INTRODUCTION

Amines are a family of chemical compounds that share as a common feature the presence of at least one sp^3-hybridized nitrogen atom forming three covalent bonds to other atoms. It also contains a lone pair of electrons in the remaining unbounded hybrid orbital. This last set of electrons is responsible for the chemical and electrochemical reactivity observed. Amines participate in many important biological and chemical reactions and hence are of interest in the food, corrosion, agrochemicals, pharmaceutical, and other industries.[1,2]

The direct electrochemical oxidation of aromatic amines has been extensively investigated, as the generated intermediate in these reactions has a tendency to polymerize to yield useful conductive polymers as the final product.[3] Nonetheless, the electrochemical oxidation also may produce dimers as the final product in the great majority of the cases through the formation of C−C bonds (benzidines), C−N bonds (phenylamines), or N−N bonds (hydrazines).[1,4−7]

Electrochemical oxidation of aliphatic amines at conventional electrodes, such as glassy carbon (GC) and platinum, produces more unusable intermediates than in the case of aromatic amines due to the lack of delocalization of the radical cation charge generated on the nitrogen atom. Moreover, the study of these processes is complicated due to the surface fouling of the working electrode by oxidation products generally observed (most commonly with oxidation products of primary amines).[8,9] The need to apply very positive potentials also represents a problem. The potential for oxidation is dependent on the structure of the aliphatic amine, with primary amines (1.4−2.0 V vs NHE) being more difficult to oxidize than secondary or tertiary (1.0−1.3 V vs NHE) ones.[10−12]

The catalytic and electrocatalytic oxidation of aliphatic amines with reversible redox couple acting as a mediator has been much less investigated.[13−15] However, it has the

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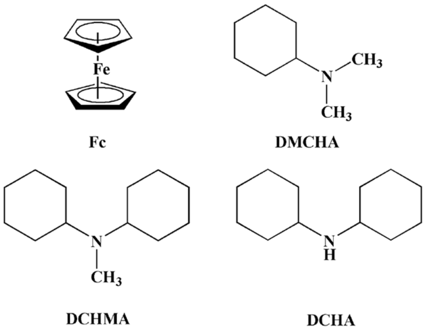
advantage to decrease the overpotential needed for the oxidation of amines, as well as to minimize the surface fouling effect on the working electrodes.[15] This correspondingly increases the sensitivity and enhances the reliability and reproducibility of the obtained data. As discussed by Torriero et al., an ideal catalyst (or mediator) needs to have a standard reversible potential which is less positive than the oxidation potential of the substrate, exhibits fast electron-transfer kinetics, and is stable in both the oxidized and reduced form toward the species present in the reaction media.[15,16] Effective mediators who meet these requirements are based on ruthenium complexes, quinone, and ferrocene (Fc) and their derivatives, either homogeneously dispersed in the solution or immobilized in a monolayer or multilayer configuration onto the electrode surface.[12,13,15,17−19] Although it is generally understood that the oxidation products depend on the type of oxidant, the reaction medium and the nature of the aliphatic group attached to the nitrogen atom, little is known about the products obtained from the catalytic oxidation of aliphatic amines. Generally, primary amines and symmetric secondaries and tertiary aliphatic amines have been studied.[15,20] However, only the work of Torriero et al. provides a comprehensive electrocatalytic analysis for the oxidation of propylamine, diethylamine, pyrrolidine, and triethylamine using the electrochemically generated ferrocenium (Fc^+) ion as the catalyst.[15]

Scheme 1. Structure of the Redox Catalyst and Amines under Investigation



In the present work, mechanistic details of the homogeneous catalytic oxidation of dicyclohexylamine (DCHA), *N*,*N*-dimethylcyclohexylamine (DMCHA), and *N*,*N*-dicyclohexylmethylamine (DCHMA, Scheme 1) in acetonitrile and dichloromethane containing 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte have been investigated by voltammetric and related techniques when the electrochemically generated ferrocenium ion is used as the catalyst. The catalytic oxidation rate constant, k_f, the catalytic efficiency, and the influences of the experimental conditions on the catalytic oxidation current are discussed. The catalytic oxidation mechanisms for the different amines are also discussed in detail.

■ RESULTS AND DISCUSSION

Curves *a* in Figure 1A−C represent the cyclic voltammograms (CVs) of ferrocene (Fc) in acetonitrile solution containing 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte. The voltammetric properties in this and dichloromethane solvent systems are consistent with a reversible one-electron redox process to form ferrocenium ion (Fc^+), as previously described.[15,16] A similar redox behavior can also be observed in a very large number of solvent systems.[16] The Fc midpoint potentials (E_m) calculated from the average of the oxidation (E_p^{ox}) and reduction (E_p^{red}) peak potentials ($E_m = 1/2(E_p^{ox} + E_p^{red})$), are 0.509 and 0.548 V vs $DmFc^{0/+}$ redox couple in acetonitrile and dichloromethane containing 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte, respectively.[15]

The CVs for the direct oxidation of DCHMA (Figure 1A, curve *b*), DMCHA (Figure 1B, curve *b*), and DCHA (Figure 1C, curve *b*) on a glassy carbon electrode were also recorded in acetonitrile solution containing 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte. An oxidation peak at respectively around 0.734, 0.871, and 1.175 V vs $DmFc^{0/+}$ for DCHMA, DMCHA, and DCHA (Table 1) were observed when the potential is scanned in the positive direction. When the potential scan direction is reversed, no complementary reduction peak is observed over the potential window and at the different scan rates studied (from 0.02 to 2 V s^{-1}). These voltammograms are typical for charge transfer processes coupled with fast irreversible chemical reactions.[21] The direct electrochemical oxidation of related secondary and tertiary amines has been reported by Ross and Mann et al. to proceed via a one-electron oxidation process.[22,23] The reaction mechanism will be discussed later.

The oxidation of Fc to the corresponding Fc^+, in the presence of the different cyclohexylamines, was also studied. Figure 1 provides examples of catalytic voltammograms observed upon addition of 15 mM DCHMA (Figure 1A, curve c), 110 mM DMCHA (Figure 1B, curve c) and 400 mM DCHA (Figure 1C, curve c). It is observed that the Fc oxidation current intensity was substantially increased, while its reversible behavior changed to a chemically irreversible one. Given that the irreversible peak potentials for the direct oxidation of these amines at the GC electrode surface are more anodic respect to the Fc oxidation potential (Figures 1, curve *b* and Table 1), the increase in the anodic current on CVs *c* is attributed to the regeneration of ferrocene resulting from the reaction of Fc^+ with the respective amines, following a classical electrochemical catalytic (EC′) mechanism.[15,24] Consequently, the current detected, *I*, is the sum of two contributions: (i) the diffusion-controlled current (I_d) of Fc in the absence of amine-containing compound and (ii) the catalytic current (I_L).[15]

Figure 2A shows an example of CVs of 0.75 mM Fc in CH_3CN (0.1 M $[Bu_4N][PF_6]$) in the absence and presence of increasing concentrations of DMCHA (see Figure S1 for DCHMA and DCHA behavior). The addition of amines triggers an increase in the catalytic current. Figure 2B shows the variations of the respective limiting current as a function of the concentration of the amine. The catalytic current is normalized toward I_d. It is observed that at a given scan rate, I_L/I_d increases linearly as a consequence of increasing the concentration of the amine up to 15, 70, and 120 mM for DCHMA, DMCHA and DCHA, respectively, deviating from the linearity at higher concentrations. Simultaneously, the voltammograms change from a peak-shape to sigmoidal-shaped curves, where the half-wave potential, $E_{1/2}$, for the sigmoidal curve coincides with the E_m value for the $Fc^{0/+}$ couple. Due to DCHA solubility limitations, this change was only observed at scan rates lower than 20 mV s^{-1} (Figure S1). Meanwhile, the shape of the Fc voltammograms loses its S-shape at high DCHMA concentrations at the expense of a current slope that appears at high potential values. The origin of this slope on raising the DCHMA concentration is related to the direct oxidation of the amine. Thereby, the observed current at high amine concentrations (≥10 mM DCHMA) is a summary of

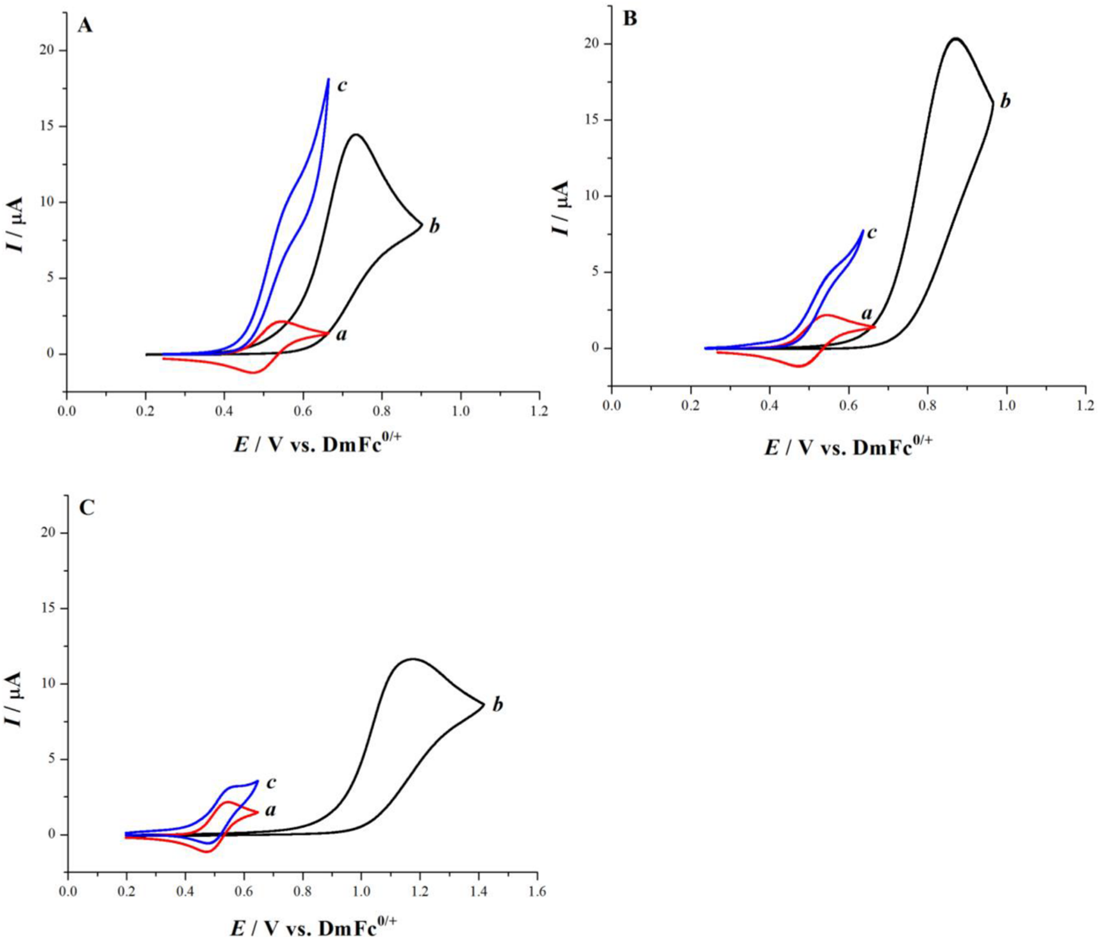


Figure 1. CVs obtained with a scan rate of 0.1 V s^{-1} at a glassy carbon electrode (1.0 mm diameter) for the oxidation of 0.75 mM Fc (A, B, and C, *a*), 4.3 mM DCHMA (A, *b*), 8.3 mM DMCHA (B, *b*), 5.2 mM DCHA (C, *b*), and 0.75 mM Fc in the presence of 15 mM DCHMA (A, *c*), 110 mM DMCHA (B, *c*), and 400 mM DCHA (C, *c*) in 0.1 M $[Bu_4N][PF_6]$ acetonitrile. T = 21 ± 1 °C.

Table 1

amine[a]	ΔE (V vs DmFc$^{0/+}$)[b]	$I_L/\gamma I_d$	k_f (M^{-1} s^{-1})[c]
DCHMA	0.734	1.023	460
DMCHA	0.871	0.048	55
DCHA	1.175	0.004	1.6

[a] DCHMA = *N,N*-dicyclohexylmethylamine, DMCHA = *N,N*-dimethylcyclohexylamine, DCHA = dicyclohexylamine. [b] Difference between the DmFc midpoint potential and the irreversible oxidation peak potential for the designated amine compounds. [c] Values obtained by comparison of digital simulations of CVs and experimental data over a wide range of scan rates, Fc concentrations, and amine concentrations.

both the previously mentioned catalytic process and the direct DCHMA oxidation. It is hypothesized that electrode fouling products of the direct oxidation of DCHMA could be responsible for the limiting behavior observed (Figure 2B).

Figure 2C presents the voltammograms of Fc in the presence of an excess of DMCHA at different scan rates. As previously discussed, a pure catalytic behavior with voltammograms close to S-shapes and limiting current independent of scan rates, mainly in the range of 0.01−0.1 V s^{-1}, can only be observed when the substrate is in large excess respect to the catalyst and the catalysis is not very fast so that an amine concentration gradient across the reaction layer is not being created.[15] From Figure 2A, it is possible to see that the excess factor, $\gamma = c_A^*/c_{Fc}^*$, increases from 1 to 147 (c_A^* and c_{Fc}^* are the concentrations of amine and ferrocene, respectively). When the γ values are large enough for the consumption of amine to be negligible, the classical sigmoidal-shaped catalytic response is observed with I_L following the relationship

$$I_L = FAc_{Fc}^{*}\sqrt{D_{Fc}k_f c_A^{*}}$$

where A, F, k_f, and D_{Fc} are the electrode area, Faraday constant, rate constant for the forward reaction, and diffusion coefficient of Fc, respectively. Thus, a purely kinetically controlled condition is achieved when the homogeneous kinetics is the rate-limiting step. Conversely, for small values of γ or large values of k_f, the consumption of amine is faster than its diffusion from the bulk solution to the electrode, with its diffusion now being the rate-limiting step. Under these conditions, a peak is detected when the potential is scanned in the positive direction and superimposed onto the sigmoidal-shaped component. The effects of these two parameters are observed in the voltammetric behavior of DCHMA (Figure S1).

To obtain further insights into the catalytic reaction mechanism, the apparent number of electrons (n_{app}) exchanged during the controlled-potential bulk electrolysis of 0.75 mM Fc in the absence and presence of cyclohexylamine-

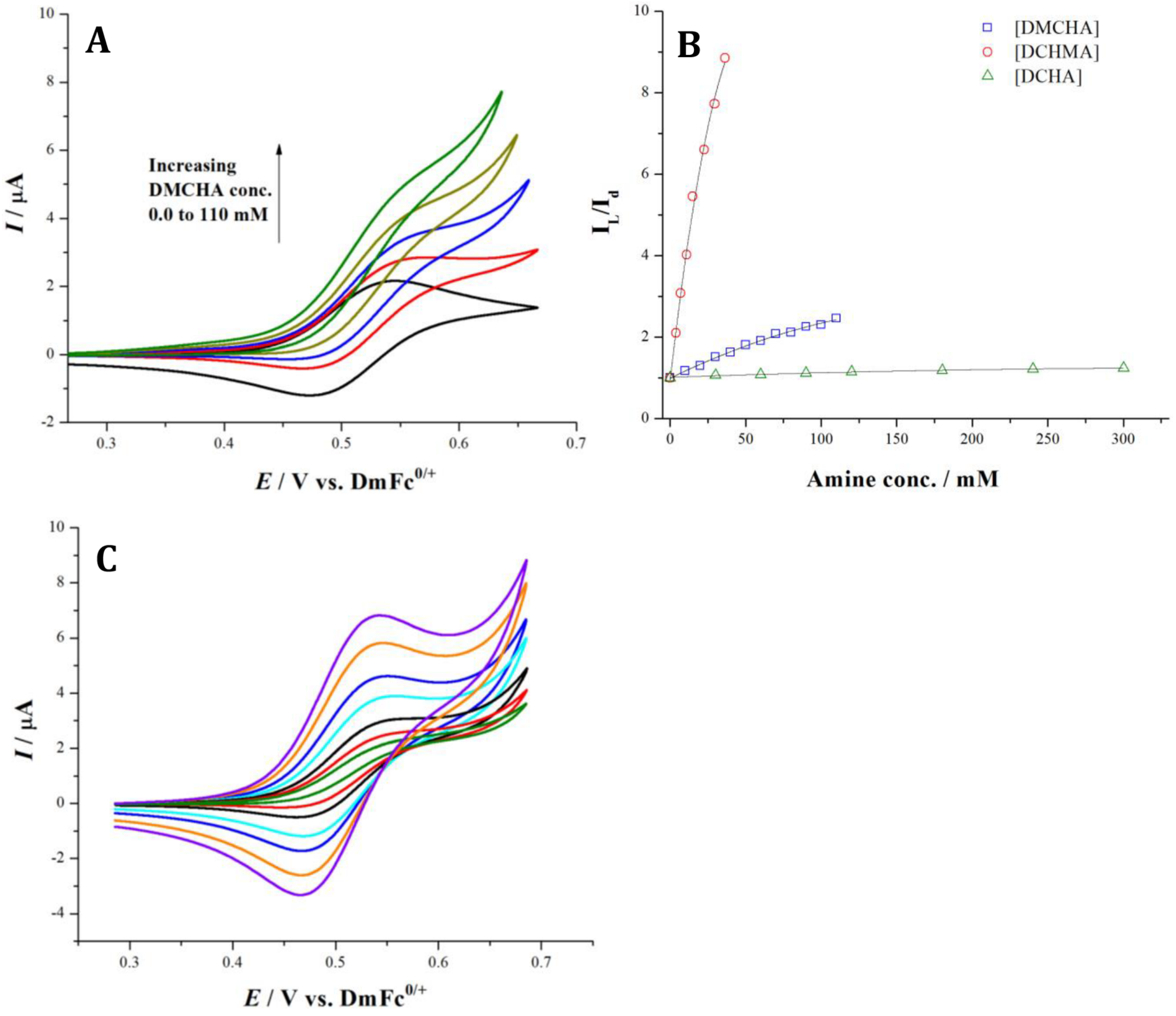


Figure 2. (A) CVs obtained for 0.75 mM Fc in acetonitrile (0.1 M $[Bu_4N][PF_6]$) at a glassy carbon electrode (d = 1.0 mm) over the potential region where the Fc oxidation occurs with the addition of 0.0, 20, 40, 70, and 110 mM DMCHA at a scan rate of 0.1 V s^{-1}. (B) Variation of the catalytic current (I_L/I_d) with the concentration of added DMCHA, DCHMA, and DCHA obtained at a scan rate of 0.1 V s^{-1}. (C) CVs obtained for 0.75 mM Fc in acetonitrile (0.1 M Bu_4NPF_6) in the presence of 20 mM DMCHA at scan rates of 0.02, 0.05, 0.1, 0.2, 0.3, 0.5, and 0.7 V s^{-1}.

containing compounds was determined in CH_3CN and CH_2Cl_2 containing 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte. To this end, the same procedure as that described before was implemented, which implies the selection of the electrolysis potential so that only the catalytic oxidation process takes place.[15] Also, the current obtained was recorded as a function of time until it decayed to about 2% of the initial value. Under the same conditions, controlled potential electrolysis experiments were undertaken in the absence of Fc and cyclohexylamines. The coulombs obtained in the last experiment were subtracted to the former one to obtain the Fc faradaic component. As expected, the total coulombs gave n_{app} = 1.0 ± 0.1 electrons per molecule of Fc in the absence of amine. However, n_{app} values of 2.1 ± 0.1 and 2.7 ± 0.2 electrons per molecule of Fc were observed for bulk electrolysis experiments containing 1:1 and 1:2 Fc/amine ratio, respectively, which implies that one electron per molecule of cyclohexylamine is transferred to Fc^+ during the catalytic reaction. This is in agreement with our previous observations using propylamine, diethylamine, pyrrolidine, and triethylamines.[15]

CVs of a mixture of 0.5 mM Fc and 2.0 mM DMCHA in acetonitrile (0.1 M $[Bu_4N][PF_6]$) before (Figure 3, curve *a*) and after (Figure 3, curve *b*) exhaustive controlled-potential bulk electrolysis was also obtained. The fact that neither DMCHA (oxidation process at around 0.871 V vs DmFc$^{0/+}$in Figure 3, curve *a*) nor its oxidation product (a secondary amine) formed during the catalytic reaction is detected by cyclic voltammetry at the end of the electrolysis experiment indicates that they are protonated and present as quaternary ammonium ions at the end of this experiment. The same result was observed during the BE of DCHMA and DCHA (Figure S2). This is in agreement with the observations of Adenier et al. during their studies on the direct electrooxidation of amines.[8]

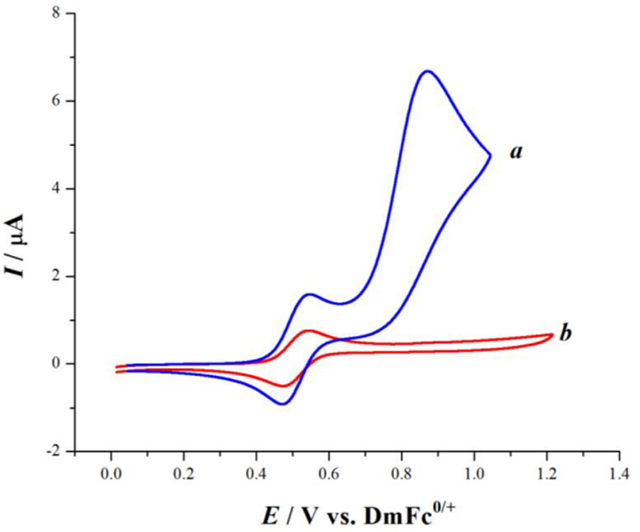
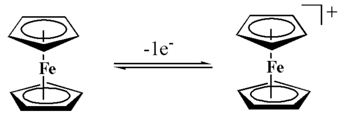


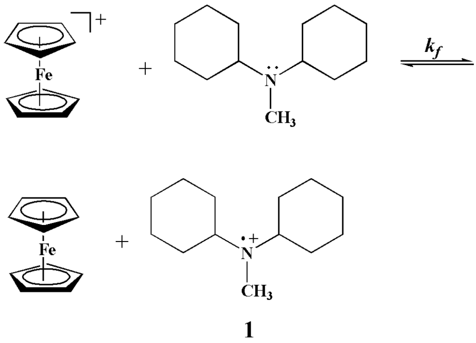
Figure 3. CVs obtained before (*a*) and after (*b*) exhaustive controlled potential electrolysis at 0.6 V vs DmFc$^{0/+}$ for 0.5 mM Fc in the presence of 2.0 mM DMCHA in acetonitrile (0.1 M $[Bu_4N][PF_6]$). Scan rate = 0.1 V s^{-1}, T = 21 ± 1 °C.

To identify the reaction products, controlled-potential bulk electrolyses of DMCHA, DCHMA, and DCHA were carried out in dichloromethane containing 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte. At the end of the process, the products were extracted with 3 × 10 mL of Milli-Q water, then treated with a 40% NaOH aqueous solution to deprotonate the amines and extracted again with 3 × 10 mL CH_2Cl_2. The organic layer was then dried and evaporated under vacuum. The oxidation products for DMCHA, DCHMA, and DCHA were identified as *N*-methylcyclohexylamine, *N*,*N*-dicyclohexylamine, and cyclohexylamine, respectively.

Taking into consideration all the previously mentioned results, it is possible to propose that the electrochemical oxidation of ferrocene to ferrocenium (eq 1) triggers the reaction sequence shown in eqs 2–6 (the global unbalanced reaction is represented in eq 7). In this mechanism, the dicyclohexylmethylamines transfers one electron to Fc$^+$ to regenerate Fc (EC′ mechanism) and affords radical cation **1** (eq 2), which can deprotonate following two possible paths to give a radical. One pathway is the formation of cyclohexyl radical **2** (eq 3), and the second option is the formation of methylene radical **3** (eq 4). These radicals (**2** or **3**, depending on the amine under study) may be involved in a disproportionation process to yield the starting amine and **4** (eq 5). From the BE results of DMCHA and DCHMA, it is possible to observe that the formation of radical **3** is preferential over that of radical **2**. However, in the absence of methyl groups, the formation of radical **2** occurs, as observable from the BE of DCHA. This may be explained by considering that planarity at iminium intermediate **4** (sp^2-hybridized carbon) is required (eq 5), which will be favored in the methyl group rather than in the cyclohexyl functional group. It seems worthwhile to point out that in the case of radical **3**, an enamine intermediate is not possible to be formed. Nevertheless, the dealkylation process still takes place, and the secondary amine is obtained as the reaction product. This is in agreement with observations formulated by Ross with similar tertiary amines.[23] Water molecules, present in the organic solvent or added during the product extraction, can react with **4** to yield formaldehyde and protonated secondary amine **5**. This protonation yields an electrochemically inactive ammonium ion, justifying the observed consumption of one electron per starting Fc molecule.



(1)



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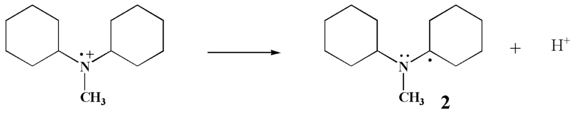

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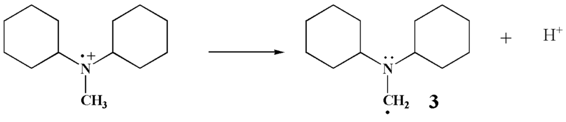
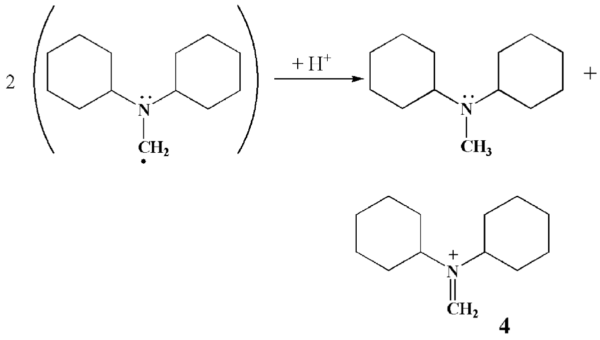
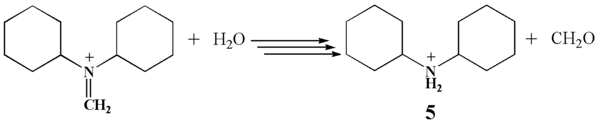


(4)

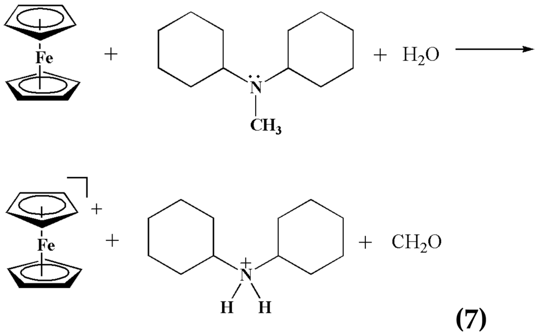


(5)



(6)

Global reaction:



(7)

The second-order rate constants, k_f, for homogeneous electron-transfer reactions between Fc$^+$ and the amines (eq 2) under study were estimated by comparison of experimental

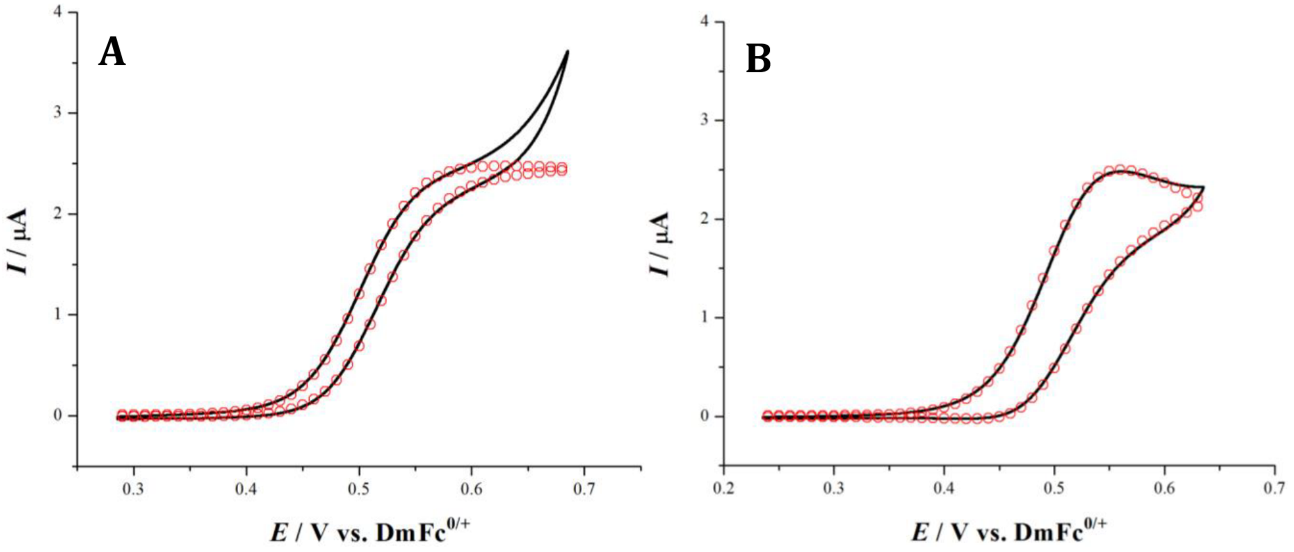


Figure 4. Comparison of experimental (—) and simulated (○) CVs obtained with a scan rate of 0.02 V s^{-1} at a glassy carbon electrode (1.0 mm diameter) for the oxidation of (A) 0.75 mM Fc in acetonitrile (0.1 M $[Bu_4N][PF_6]$) inal the presence of 20 mM DMCHA and (B) 0.85 mM Fc in the presence of 2.9 mM DCHMA. Simulation parameters: $T = 294$ K, A = 0.72 mm^2, $\alpha = 0.5$, $k° = 1$ cm s^{-1}, $K_{eq} = 1 \times 10^5$, $K_{eq\text{-}DISP} = 1 \times 10^3$, $k_{f\text{-}DISP}$ (DMCHA) = 10 M^{-1} s^{-1}, $k_{f\text{-}DISP}$ (DCHMA) = 2 M^{-1} s^{-1}, $E_f° = 0.5$ V, $C_{dl} = 0.40$ μF, $D_{Fc} = 2.3 \times 10^{-5}$ cm^2 s^{-1}.

CVs with digitally simulated ones obtained by using the mechanism outlined in eqs 1, 2 and 5. Figures 4 and S3 show some examples obtained at 20 mVs^{-1}. The simulations provide excellent agreement with experimental observations made over a wide range of catalyst concentrations (0.2−10 mM) and amine concentrations (0.20−15.0, 1.0−110, and 1.0−400 mM for DCHMA, DMCHA, and DCHA, respectively), when the rate constants of 460, 55, and 1.6 M^{-1} s^{-1} are employed, respectively (Table 1). Determinations of the rate constants were also performed at different scan rates (from 0.02 to 0.7 V s−1) to minimize the interference of natural convection in the electrochemical response, which is normally observed at scan rates ≤0.05 V s^{-1}. Significantly, k_f values decrease in the order DCHMA > DMCHA > DCHA, which is in agreement with the catalytic efficiency trend ($I_L/\gamma I_d$) observed (Table 1).

■ CONCLUSIONS

This work demonstrates that ferrocene can catalyze the homogeneous oxidation of amine in acetonitrile and dichloromethane containing 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte after its initial electrochemical oxidation. It was possible to propose an oxidation mechanism to account for the product formation by using cyclic voltammetry, bulk electrolysis, and digital simulations techniques in association with the respective product isolation. The catalytic reaction between ferrocenium and the secondary and tertiary amines followed a one-electron-oxidation mechanism with a considerable recovery of the catalyst at the end of the experiment. Both DCHMA and DMCHA proceed to yield a secondary amine product by the elimination of a methyl group. In absence of this alkyl group, as in the case of DCHA, the cycloalkyl group is then eliminated. The catalytic efficiency and the second-order rate constant for this last reaction is significantly slower than that observed for DCHMA and DMCHA and found to follow the order DCHA ≪ DMCHA < DCHMA. The results presented in this work should open up a new avenue to achieve simple, low-cost, and efficient amine oxidation, which could be useful in several areas of chemistry.

■ MATERIALS AND METHODS

Reagents and Chemicals. Ferrocene (Fc, 98%, Sigma-Aldrich), *N*,*N*-dimethylcyclohexylamine (DMCHA, 99%, Sigma-Aldrich), dicyclohexylamine (DCHA, 99%, Sigma-Aldrich), *N*,*N*-dicyclohexylmethylamine (DCHMA, 97%, Sigma-Aldrich), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, ≥99%, Sigma-Aldrich), acetonitrile (CH_3CN, ≥99.9%, Merck), and dichloromethane (CH_2Cl_2, ≥99.8%, Merck) were used as received from the manufacturer.

Instrumentation and Procedures. Electrochemical experiments were carried out in a standard three-electrode arrangement with an Interface1000 electrochemical workstation (Gamry, USA). A platinum wire was used as a counter-electrode, and an Ag/Ag^+ (0.01 M $AgNO_3$, 0.1 M $[Bu_4N][PF_6]$) double-junction reference electrode and an Ag/AgCl (CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$) single-junction quasi-reference electrode were used for studies in acetonitrile and dichloromethane, respectively. Nevertheless, all potential values are quoted relative to the decamethylferrocene/decamethylferrocenium ($DmFc^{0/+}$) potential scale, which was used before and after each experiment to monitor any possible drift of the reference electrode potential. A glassy-carbon (GC) working electrode with a diameter of 1.0 mm and an effective area of 0.72 mm^2 was used for cyclic voltammetric experiments. The area of the working electrode was determined from CVs using the peak current derived as a function of the square root of scan rate from the oxidation of a 1.0 mM Fc in CH_3CN (0.1 M Bu_4NPF_6) solution (Fc diffusion coefficient = 2.3×10^{-5} cm^2 s^{-1}) degassed with N_2 and with the application of the Randles−Sevcik relationship.[25] Before each voltammetric experiment, the working electrode was polished with 0.3 μm alumina slurry (Buehler, Lake Bluff, IL) on a clean polishing cloth (Buehler). After polishing, the electrode was rinsed with distilled water and acetone, and then dried with nitrogen gas.

Controlled-potential bulk electrolyses (BE) were performed both in acetonitrile and dichloromethane under nitrogen atmosphere (99.999%, BOC Australia) using a reticulated glassy carbon-working electrode, the previously mentioned reference electrodes, and a platinum-gauze counter electrode separated from the test solution by a fine-porosity glass frit. Dichloromethane was used as a solvent during the BE product identification.

All voltammetric experiments were carried out at ambient temperature (22 ± 1 °C). No IR_u compensation was performed during the voltammetric experiments. The commercially available software package DigiElch was used to simulate the voltammetric responses. LC-MS experiments were conducted using an LCMS-8040 LC/MS/MS System (Shimadzu). The mass spectrometer was operated in positive mode at a collision energy of −20 V. Nuclear magnetic resonance experiments were conducted using a Spinsolve 43 MHz Benchtop NMR Spectrometer (Magritek) and Fourier transform infrared spectroscopy experiments were conducted using an ALPHA FT-IR Spectrometer (Bruker).

Product Identification. *N-Methylcyclohexylamine.* Molar mass: 113 g/mol. Yield 40%. IR (neat): 3284 w, 2924 s, 2851 s, 2785 m, 1476 w, 1448m, 1368 m, 1146 m, 1128 m, 1095 m, 889 m, 785 w, 734 m, 542 w, 428 w. ^{1}H NMR ($CDCl_3$ with TMS, 43 MHz; Figures S4) δ_H: 2.42 (s, 3H, NCH_3), 2.49−1.38 (m, br, 12H, NH, CH and 5 × CH_2). ^{13}C NMR ($CDCl_3$ with TMS, 10 MHz; Figures S5) δ_C: 58.55 (CH), 33.62 (NCH_3), 33.33 (2 × $NCHCH_2$), 26.39 ($CH_2CH_2CH_2$), 25.09 (2 × $CHCH_2CH_2$). LC-MS: m/z (relative intensity): 113 (14), 95 (2), 85 (7), 81 (14), 77 (11), 70 (3), 68 (27), 66 (6), 58 (2), 57 (20), 56 (13), 55 (1), 45 (5), 43 (100), 39 (13).

Dicyclohexylamine. Molar mass: 181 g/mol. Yield 48%. IR (neat): 2920 s, 2851 s, 1448 m, 1126 m, 887 m, 703 m. ^{1}H NMR ($CDCl_3$ with TMS, 43 MHz; Figures S6) δ_H: 2.50 (m, 2H, 2 × NCH), 2.17−0.41 (m, br, 21H, NH, 10 × CH_2). ^{13}C NMR ($CDCl_3$ with TMS, 10 MHz; Figures S7) δ_C: 53.19 (2 × NCH), 34.65 (4 × $NCHCH_2$), 26.53 (2 × $CH_2CH_2CH_2$), 25.53 (4 × $CHCH_2CH_2$). LC-MS: m/z (relative intensity): 183 (6), 182 (87), 167 (20), 165 (1), 164 (3), 155 (7), 151 (3), 141 (16), 138 (6), 137 (6), 119 (7), 103 (7), 100 (15), 99 (5), 98 (10), 97 (18), 91 (3), 87 (1), 86 (1), 85 (3), 83 (100), 82 (4), 80 (3), 75 (3), 73 (9), 59 (3), 55 (5), 45 (3), 30 (5), 23 (3), 19 (1), 18 (1).

Cyclohexylamine. Molar mass: 99 g/mol. Yield 42%. IR (neat): 3366 w, 3278 w, 2924 s, 2854 s, 2750 w, 1606 w, 1460 m, 1370 w, 1149 w, 1090 w, 896 m, 829 m, 777 w, 554 w, 466 w. ^{1}H NMR ($CDCl_3$ with TMS, 43 MHz; Figures S8) δ_H: 2.49 (m, br, H, NCH), 1.85 to 1.07 (m, br, CH_2), 1.15 (s, NH_2). ^{13}C NMR ($CDCl_3$ with TMS, 10 MHz; Figures S9) δ_C: 50.72 (NCH), 37.23 (2 × $CHCH_2$), 26.01 ($CH_2CH_2CH_2$), 25.47 (2 × $CHCH_2CH_2$). LC-MS: m/z (relative intensity): 99 (60), 82 (18), 81 (7), 79 (42), 77 (8), 55 (26), 54 (14), 53 (26), 45 (7), 43 (100), 40 (8), 39 (10), 27 (8).

■ ASSOCIATED CONTENT

Supporting Information

. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00557.

> CVs over the potential region where the Fc oxidation occurs with the addition of different concentrations of DCHMA and DCHA, CVs before and after exhaustive controlled potential electrolysis of Fc in the presence of DCHMA and DCHA, comparison of experimental and simulated CVs, ^{1}H and ^{13}C NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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