Contents lists available at ScienceDirect





Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

The electrochemical reduction of 1,4-dichloroazoethanes: Reductive elimination of chloride to form aryl azines

Vittorio A. Sauro, David C. Magri, Jason L. Pitters, Mark S. Workentin*

Department of Chemistry, The University of Western Ontario, London, ON, Canada N6A 5B7

A R T I C L E I N F O

ABSTRACT

Article history: Received 8 March 2010 Received in revised form 19 April 2010 Accepted 21 April 2010 Available online 29 April 2010

Keywords: 1,4-Dichloroazoethanes Azines Cyclic voltammetry Electron transfer Radical ion A series of 1,4-dichloroazoethanes (1-X/Y, X and Y=4-NO₂, 4-CN, 4-CH₃ or 4-H) were studied in *N*,*N*-dimethylformamide using cyclic voltammetry, constant potential sweep voltammetry (CPSW) and constant potential electrolysis. The voltammograms of 1-X/Y exhibit an irreversible two-electron wave corresponding to dissociative electron transfer (DET) reduction of the carbon–chlorine bond resulting in formation of the azines 2-X/Y in quantitative yield. Additional redox waves correspond to the reversible reduction of the azines to the 2-X/Y^{•-} radical anion and 2-X/Y^{2–} dianion consecutively, with the exception of 1-NO₂/NO₂ where both NO₂ groups are reduced simultaneously in a two-electron reversible wave. Thermodynamic and kinetic parameters were determined from CPSW: the standard reduction potentials (E°) vary between -0.7 and -1.3 V versus SCE as a function of electron-withdrawing substituent; the heterogeneous rate constants (k_{het}) are consistent with a slow heterogeneous electron transfer with values ranging from 10^{-3} to 10^{-5} cm s⁻¹; the transfer coefficients (α) for 1-NO₂/NO₂ and 1-NO₂/H are greater than 0.5, indicative of a stepwise DET mechanism for the C–Cl bond cleavage while the remaining 1-X/Y compounds have α values between 0.35 and 0.5, and the intrinsic barriers are all significantly lower than predicted for a concerted DET, thereby also suggesting a stepwise DET mechanism.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The azo (N=N) bond is a relatively labile group often accompanied by the loss of N₂ under a variety of thermal and photochemical conditions [1–7]. The fragmentation of the C–N bond is rationalized to occur by homolytic cleavage upon photolysis via a radical pathway [4–8]. Conversely, the electrochemical reduction of azo compounds in aprotic solvents generally involves two sequential one-electron reductions of the N=N to the radical anion and dianion, respectively [5]. In the presence of a proton donor, the electrochemical reduction results in the transformation of the N=N to the hydrazone NH–NH by a two-electron mechanism [5,9].

Homolytic cleavage is also typical of carbon-halide (C–X) bonds. The electrochemical reduction of C–X bonds has long been used as model systems for developing dissociative electron transfer (DET) theory [11–14]. Dissociative reduction of a molecule with a weak σ bond results when electron transfer (ET) is accompanied by bond cleavage. Provided ET and bond breaking occur in a single step, within the timeframe of a vibration of a bond, concerted DET results on acceptance of the electron in the σ^* orbital. However, ET and bond cleavage may occur in two successive steps involving a

radical-anion intermediate species, in which case the mechanism proceeds by a stepwise DET mechanism. Alkyl halides and aryl halides are the classic examples of compounds to undergo both concerted and stepwise DET, respectively [15,16].

The first family of compounds shown to undergo both concerted and stepwise DET was the benzyl halides [11,12]. Benzyl halides have an accessible π^* orbital available in addition to the σ^* orbital of the C-X bond. The nitro-substituted benzyl halides (bromides or chlorides) react via a stepwise reductive cleavage while the less electron-withdrawing substituents (including CN, H, CH₃) follow a concerted pathway. An important parameter for distinguishing between a stepwise and concerted DET mechanism is the intrinsic barrier (ΔG_0^{\neq}), that is the activation free energy when the driving force for the reaction is zero. In the limiting case of concerted DET, the (ΔG_0^{\neq}) is much larger as it contains contributions from both the reorganization energy (λ_o) and the bond dissociation energy (BDE) from the cleaving bond. However, the (ΔG_0^{\neq}) is significantly smaller when the bond cleavage step is an intramolecular DET from an initially formed radical ion of the antenna group to the σ^* of the breaking bond [12]. Many other bonds have been shown in recent years to undergo DET including molecular systems with O-O [12,17] and S-S [12a,18] bonds. This latter body of work has validated and further assisted in developing Savéant's DET theory [11].

We were interested in examining the electrochemical reduction of 1,1'-dichloro-1,1'-diaryl-1,1'azoethanes, more generally

^{*} Corresponding author. Tel.: +1 519 661 2111x86319; fax: +1 519 661 3022. *E-mail address*: mworkent@uwo.ca (M.S. Workentin).

^{0013-4686/\$ –} see front matter 0 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2010.04.080



Scheme 1. The photodissociation of 1,4-dichloroazoethanes via C-N bond cleavage.

referred to as 1,4-dichloroazoethanes. In addition to an azo moiety, these compounds also have two reducible benzyl halide groups. In previous photochemical studies of 1,4-dichloroazoethanes, azines (2,3-diaza derivatives of butadienes -C=N-N=C-) were isolated as products [1,5,10]. The reaction was also found to yield a significant amount of radical coupling and oxygenated products due to the formation of a carbon radical intermediate with loss of molecular nitrogen (Scheme 1) [5,10]. Considering that 1,4-dichloroazoethanes exhibit the loss of dinitrogen upon irradiation via cleavage of the C–N bonds, we were interested in examining if under electrochemical conditions a competition would exist between C–Cl versus C–N reductive cleavage, and whether this competition could be controlled by a change in the aryl substituent.

In this work, the electrochemical reduction of a series of seven symmetrical and unsymmetrical 1.4-dichloroazoethanes (1-X/Y, where X and Y are either 4-NO₂, 4-CN, 4-CH₃ or 4-H) were studied in N,N-dimethylformamide using cyclic voltammetry, convolution potential sweep voltammetry (CPSV) and constant potential electrolysis. These compounds provide an unprecedented example of systems containing two halides, not on adjacent carbon atoms, that form azine products upon electrochemical reduction. Bulk electrolysis experiments revealed that dissociative reduction of 1.4-dichloroazoethanes results in the loss of both chlorine atoms to yield azines in guantitative yield (Scheme 2). CPSV and application of DET theory allowed for the determination of a number of thermodynamic and kinetic parameters including the standard reduction potential (E^{o}) and standard heterogeneous rate constant (k_{het}^{0}) . Irrespective of the substituents, rather low intrinsic barriers were determined throughout the series, thereby suggesting a stepwise DET mechanism in which the azo group significantly contributes to lowering the LUMO energy.

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich and used as received unless otherwise stated. Spectroscopic grade *N*,*N*-dimethylformamide (DMF) was distilled under a nitrogen atmosphere at reduced pressure over calcium hydride. Tetraethylammonium perchlorate (TEAP), from Kodak, was recrystallized three times from ethanol and dried under vacuum at $60 \,^{\circ}$ C and stored in a vacuum dessicator. Ferrocene was purified by sublimation.

2.2. Instrumentation

NMR spectra were recorded on a Varian Gemini 300 MHz (300.08 MHz for ¹H and 75.46 MHz for ¹³C) or a Varian Mercury 400 MHz (400.08 MHz for ¹H and 100.60 MHz for ¹³C) instrument. Chemical shifts were measured in deuterated chloroform and reported in parts per million downfield from tetramethylsilane. Gas chromatography analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 10 meter HP-5 column and an FID detector. UV-vis spectra were recorded on a Varian Cary 100 spectrometer. Melting points were recorded using a Gallenkamp melting point apparatus and are uncorrected. Elemental analysis was performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

2.3. Cyclic voltammetry

Experiments were performed using either a Princeton Applied Research (PAR) 283 or 263 potentiostat interfaced to a personal computer running PAR M270 software. Measurements were conducted in a water-jacketed glass cell maintained at a constant temperature of 25 °C under an argon atmosphere. The glass cell was stored overnight in an oven maintained at 110 °C and assembled hot while flushing with argon. The working electrode was a 3 mm glassy carbon rod (Tokai) sealed in a glass tube. It was polished with 1 µm diamond paste, cleaned by sonication in 2propanol and dried with a cool stream of air. The counter electrode was a 1 cm² platinum flag. The quasi-reference electrode was a silver wire contained in a glass tube sealed with a porous ceramic tip and filled with a 0.1 M solution of TEAP. Ferrocene ($E^{0} = 0.470 \text{ V}$ versus SCE in DMF) was added to the solution afterwards as an internal reference to calibrate the potentials versus the saturated calomel electrode. Positive feedback internal resistance compensation was applied to minimize the effects of the solution resistance. Linear sweep voltammograms for convolution potential sweep voltammetry were recorded using the same set-up. Convolution analysis was performed using custom-made analysis software.

2.4. Constant potential coulometry

100 mg of a 1,4-dichloroazoethane was dissolved in 25 mL of 0.1 M TEAP/DMF solution maintained at a constant temperature



 $X,Y = NO_2, CN, H, CH_3$

Scheme 2. The reaction equation for the reduction of 1,4-dichloroazoethanes 1-X/Y to 2-X/Y azines.

of 25 °C. Argon was continuously bubbled into solution with vigorous stirring to eliminate oxygen. The working electrode was a platinum mesh or rotating disk electrode with a 12 mm glassy carbon tip. The counter electrode was a platinum coil separated from the bulk solution by a 2 mm thick layer of activated alumina and a sintered glass disk. The appropriate constant potential was applied using either a Princeton Applied Research (PAR) 283 or 263 potentiostat. Exhaustive electrolysis was monitored by cyclic voltammetry. Afterwards, the DMF was removed in vacuo while keeping the electrolysis mixture under 40 °C. The recovered solid mixture was dissolved in dichloromethane and distilled water and transferred to a separatory funnel. The aqueous layer was extracted three times. The organic layers were combined, washed with distilled H₂O twice, dried with MgSO₄, filtered and evaporated under vacuum. The remaining solid residue was analyzed by GC and ¹H NMR.

2.5. Syntheses of the 1,4-dichloroazoethanes

All 1-X/Y were synthesized in a fumehood by chlorination of the corresponding acetophenone azines (2-X/Y) and purified by recrystallization [19–21]. Excess chlorine gas was condensed into a round-bottom flask containing neat 2-X/Y or a suspension of 2-X/Y in CH₂Cl₂. The suspension was stirred at -60 °C for 0.5 h and then slowly warmed to room temperature. During this time, most of the Cl₂ gas evaporates from the reaction mixture. Any remaining gas was removed under vacuum. The crude 1-X/Y was recrystallized from a hexanes/ethyl acetate mixture with slight warming (below 30 °C). The recrystallization solution of 1-X/Y was cooled in dry ice and the resulting solid filtered and dried under vacuum. The purity of the 1-X/Y was confirmed by melting point determination and elemental analysis.

1,1'-Dichloro-1,1'-diphenyl-1,1'-azoethane (1-H/H): [19] m.p. = 98–99 °C decomposition with gas evolution; ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 2.22(s, 6H), 7.37(m, 6H), 7.58(m, 4H); ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 141.0, 128.7, 128.6, 126.4, 94.5, 30.1; UV-vis (MeCN): $\lambda_{\rm max}$ = 235 nm, ε = 1980 cm⁻¹ M⁻¹; elemental analysis, calc. %C(62.55), H(5.26), det. %C(62.54), H(5.70).

1,1'-Dichloro-1,1'-bis(4-methylphenyl)-1,1'-azoethane (1-CH₃/ CH₃): [10] m.p. = 118–119 °C decomposition with gas evolution; ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 2.21(s, 6H), 2.35(s, 6H), 7.19(d, 4H), 7.44(d, 4H); ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 140.0, 131.8, 128.2, 123.2, 93.9, 30.2; UV-vis (MeCN): $\lambda_{\rm max}$ = 234 nm, ε = 12400 cm⁻¹ M⁻¹; elemental analysis, calc. %C(64.48), H(6.02), det. %C(64.58), H(6.24).

1,1'-Dichloro-1,1'-bis(4-nitrophenyl)-1,1'-azoethane (1-NO₂/NO₂): [10] m.p. = 156–159 °C decomposition with gas evolution; ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 2.20(s, 6H), 7.81(d, 4H), 8.25(d, 4H); ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 147.4, 130.8, 127.6, 123.8, 93.4, 30.7; UV-vis (MeCN): $\lambda_{\rm max}$ = 278 nm, ε = 17284 cm⁻¹ M⁻¹; elemental analysis, calc. %C(48.38), H(3.56), det. %C(50.07), H(3.57). The discrepancy in %C is due to trace recrystallization solvent in the sample, evidenced by the NMR spectrum. This solid was dried under vacuum and its purity was verified by NMR spectroscopy prior to use.

1,1'-Dichloro-1,1'-bis(4-cyanophenyl)-1,1'-azoethane (**1**-CN/CN): m.p. = 114–117 °C decomposition with gas evolution; ¹H NMR (300 MHz, CDCl₃): $\delta_{\rm H}$ 2.17(s, 6H), 7.73(m, 8H); ¹³C NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ 145.7, 132.4, 127.3, 118.1, 112.9, 93.5, 30.5; UV-vis (MeCN): $\lambda_{\rm max}$ = 266 nm, ε = 3150 cm⁻¹ M⁻¹; elemental analysis, calc. %C(60.52), H(3.96), det. %C(60.70), H(3.99).

1,1'-Dichloro-1-(4-cyanophenyl)-1'-phenyl-1,1'-azoethane (1-CN/H): m.p. = 79–80 °C decomposition with gas evolution; ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.17(s,3H), 2.22(s,3H), 7.38(m, 3H), 7.54(d, 2H), 7.72(m, 4H); ¹³C NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 146.1, 140.4, 132.4, 128.9, 128.6, 127.3, 126.3, 118.3, 112.7, 94.7, 93.2, 30.4, 30.1; UV-vis (MeCN): $\lambda_{\rm max}$ = 266 nm, ε = 2000 cm⁻¹ M⁻¹;

elemental analysis, calc. %C(61.46), H(4.56), det. %C(61.27), H(4.37).

1,1'-Dichloro-1-(4-nitrophenyl)-1'-phenyl-1,1'-azoethane (1-NO₂/H): [20] m.p. = 83–84 °C decomposition with gas evolution; ¹H NMR (400 MHz, CDCl₃: $\delta_{\rm H}$ 2.19(s, 3H), 2.23(s, 3H), 7.39(m, 3H), 7.54(d, 2H), 7.80(d, 2H), 8.25(d, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 147.9, 140.4, 129.0, 128.6, 127.7, 126.3, 123.7, 94.7, 93.0, 30.6, 30.1; UV-vis (MeCN): $\lambda_{\rm max}$ = 245 nm, ε = 6150 cm⁻¹ M⁻¹; elemental analysis, calc. %C(54.56), H(4.30), det. %C(54.21), H(4.40).



Fig. 1. Cyclic voltammograms of 2.0 mM (a) **1**-H/CH₃, (b) **1**-CH₃/CH₃, (c) **1**-H/H, (d) **1**-CN/H, (e) **1**-CN/CN, (f) **1**-NO₂/H and (g) **1**-NO₂/NO₂ in 0.1 M TEAP/DMF at 0.2 V s⁻¹ with a glassy carbon electrode. The arrows indicate the potential sweep direction in all the CVs.

1,1'-Dichloro-1-(4-methylphenyl)-1'-phenyl-1,1'-azoethane (1-CH₃/H): m.p. = 92–93 °C decomposition with gas evolution; ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ 2.20(s, 6H), 2.34(s, 3H), 7.17(d, 2H), 7.39(m, 5H), 7.55(m, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ 141.0, 138.7, 137.9, 129.2, 128.7, 128.5, 126.4, 126.3, 94.5, 94.4, 30.1, 29.9, 21.1; UV-vis (MeCN): $\lambda_{\rm max}$ = 218 nm, ε = 8220 cm⁻¹ M⁻¹; elemental analysis, calc. %C(63.55), H(5.66), det. %C(63.36), H(5.57).

3. Results

The syntheses of the 1-X/Y compounds were performed by chlorination of the corresponding acetophenone azines [19–21]. The details and spectral characterization appear in Section 2. The electrochemistry of the series of seven 1-X/Y compounds were investigated in N,N-dimethylformamide (DMF) containing 0.1 M tetraethylammonium perchlorate (TEAP) at a glassy carbon electrode. Fig. 1 illustrates the reductive cyclic voltammograms for the complete series of compounds at 0.2 V s⁻¹. Each voltammogram is characterized by an initial two-electron irreversible cathodic wave A, followed by a second reversible wave B (See Fig. 1c). This second wave corresponds to a one-electron reduction of the product 2-X/Y compounds, with the exception of 1-NO₂/NO₂ where this reversible wave corresponds to a two-electron reduction of the corresponding 2-NO₂/NO₂. With the exception of 1-NO₂/NO₂, a third reduction wave is observed at more negative potentials. When at least one of the substituents is a cyano or nitro group, wave C is a reversible couple (Fig. 1d-f). Table 1 summarizes the observed peak potentials for wave A, the standard potentials for wave B, and the peak potentials (Fig. 1a-c) and standard potentials (Fig. 1d-f) for wave C. An identifiable trend is that as the substituents attached to the phenyl ring become more electron-donating, the waves corresponding to A and B are observed at more cathodic potentials.

Table 2 lists specific data corresponding to wave A for the **1**-X/Y series. In each case, the first reduction wave is irreversible at all scan rates investigated (up to 25 V s^{-1}). The peak potential (E_p) of wave A was observed to shift to more negative potentials upon increasing the scan rate (ν). The scan rate normalized peak currents ($i_p/\nu^{1/2}$) were found to decrease with increasing scan rate, typical for systems undergoing DET controlled by slow heterogeneous kinetics. The peak width at half current height $|E_{p/2} - E_p|$ follows a trend of increasing from 60 to 109 mV as the substituents become more electron-donating. The variation of E_p with the logarithm of the scan rate ($\log \nu$) is linear with the slope ranging from 38 to 87. Furthermore, addition of a non-nucleophilic proton donor, such as trifluoroacetic acid (TFE), has no effect on wave A [22].

Table 1

Reduction potentials of the 1,4-dichloroazoethanes in 0.1 M TEAP/DMF solution at a glassy carbon electrode.

| Fig. 1, label | Fig. 1, label 1 -X/Y | | $E_{p(A)}^{a,b}$ | $E^{o}_{(B)}^{a,b,c}$ | $E_{(C)}^{o}^{a,b,d}$ | |
|---------------|-----------------------------|-----------------|------------------|-----------------------|-----------------------|--|
| | x | Y | | | | |
| g | NO ₂ | NO ₂ | -0.795 | -0.937 | _e | |
| f | NO ₂ | Н | -0.832 | -0.972 | -1.526 | |
| e | CN | CN | -1.074 | -1.377 | -1.597 | |
| d | CN | Н | -1.161 | -1.559 | -1.925 | |
| с | Н | Н | -1.250 | -1.902 | -2.295^{f} | |
| b | CH ₃ | CH₃ | -1.273 | -1.987 | -2.394^{f} | |
| a | CH ₃ | Н | -1.275 | -1.941 | -2.337 ^f | |

^a V versus SCE in DMF/0.1 M TEAP.

^b Peak potentials at 0.1 V s^{-1} .

^c E^{o} for the reversible redox couple of **1**-X/Y.

^d E^{o} for the third reduction wave of the **1**-X/Y unless otherwise noted.

^e No third reduction wave observed.

^f Irreversible at all scan rates up to 25 V s⁻¹.

Table 2

Electrochemical data for the initial irreversible reduction wave for **1**-X/Y in 0.1 M TEAP/DMF solution.

| 1-X/Y | | $E_{p/2}^{a,b}$ | $ E_{\rm p/2} - E_{\rm p} ^{\rm c,b}$ | $-\partial E_{\rm p}/\partial \log \nu^{\rm c}$ | n ^d |
|-----------------|-----------------|-----------------|---------------------------------------|---|----------------|
| NO ₂ | NO ₂ | -0.735 | 60 | 38 | 1.92 |
| NO ₂ | Н | -0.763 | 69 | 47 | 1.94 |
| CN | CN | -0.975 | 99 | 87 | 2.02 |
| CN | Н | -1.061 | 100 | 86 | 2.01 |
| Н | Н | -1.145 | 105 | 86 | 2.09 |
| CH ₃ | CH ₃ | -1.164 | 109 | 82 | 2.16 |
| CH ₃ | Н | -1.166 | 109 | 82 | 2.01 |
| | | | | | |

^a V versus SCE in DMF/0.1 M TEAP.

 $^{\rm b}$ At 0.1 V s⁻¹ scan rate.

^c mV.

^d Number of electrons determined by constant potential electrolysis in F mol⁻¹.

Product studies and comparison with authentic samples confirmed that waves B and C correspond to the formation of the acetophenone azines (2-X/Y) [21]. Quantitative formation of 2-X/Y was observed by constant potential electrolysis experiments, where solutions of 1-X/Y were electrolyzed at a potential slightly negative to the E_p of wave A until no trace of 1-X/Y remained (see Fig. 2). In each case, 2 F mol⁻¹ was consumed (Table 2). The cyclic voltammograms after exhaustive electrolysis were identical to the cyclic voltammograms of authentic 2-X/Y [21]. The products were isolated from the electrolysis mixture and confirmed to be 2-X/Y using ¹H NMR spectroscopy, GC and MS analysis. Hence, the second and third reductive waves observed in the CVs of 1-X/Y are due to the one-electron reductions of the corresponding 2-X/Y radical anions and dianions, respectively, with the exception of the 2-NO₂/NO₂ where the second wave is a two-electron reduction [21].

The symmetry factors (α values) for wave A, which is the initial heterogeneous ET to the 1,4-dichloroazoethanes, were evaluated to gain insight into the reaction mechanism. Three independent approaches were employed including the peak width at each scan rate (Eq. (1)), the linear regression of E_p over a range of scan rates to obtain an average value (Eq. (2)), and the apparent value from the potential dependence of $\ln k_{het}$ from CPSV analysis (Eq. (3)) [11,24]. The first two methods are simpler in that only a data point



Fig. 2. Cyclic voltammograms before (dashed) and after (solid) the addition of $2 \,\mathrm{Fmol}^{-1}$ of charge during the constant potential electrolysis of **1**-CN/CN in 0.1 M TEAP/DMF at 0.2 V s⁻¹.

| Table | 3 |
|-------|---|
| | |

Data derived from convolution sweep potential voltammetry and estimates of the α values for the 1-X/Y series of compounds at a glassy carbon electrode.

| 1 -X/Y | | α ^a | $\alpha_{avg}{}^{b}$ | $\alpha_{app}{}^{c}$ | E ^o _{1-X/Y} d,e | $D_{1-X/Y}^{f}$ | $\Delta G_{0}^{\neq g}$ | $\log k_{\rm het}^{\rm o}$ |
|-----------------|-----------------|---|----------------------|----------------------|-------------------------------------|-----------------|-------------------------|----------------------------|
| NO ₂ | NO ₂ | 0.79 ^h 0.79 ⁱ 0.74 ^j | 0.75 | 0.84 | -0.599 | 8.3 | 2.0 | -4.4 |
| NO ₂ | Н | 0.69 ^h 0.69 ⁱ 0.68 ^j | 0.62 | 0.71 | -0.545 | 9.6 | 3.8 | -5.4 |
| CN | CN | 0.48 ^h 0.45 ⁱ 0.38 ^g | 0.34 | 0.39 | -0.904 | 8.2 | 7.1 | -3.3 |
| CN | Н | 0.47 ^h 0.43 ⁱ 0.41 ^g | 0.34 | 0.37 | -0.981 | 9.2 | 6.4 | -3.3 |
| Н | Н | 0.45 ^h 0.43 ⁱ 0.40 ^g | 0.34 | 0.35 | -1.084 | 11.0 | 5.8 | -3.1 |
| CH ₃ | CH₃ | 0.44 ^h 0.41 ⁱ 0.39 ^g | 0.36 | 0.34 | -1.111 | 9.5 | 4.0 | -3.1 |
| CH ₃ | Н | 0.44^{h} 0.42^{i} 0.38^{g} | 0.35 | 0.35 | -1.075 | 10.1 | 4.4 | -3.3 |

^a Determined by Eq. (1) at various scan rates. See footnotes h-j.

^b Determined by Eq. (2).

1 05 07

^c Determined by Eq. (3).

^d From extrapolation of α data to 0.5 from several experiments.

^e V versus SCE in DMF/0.1 M TEAP.

f 10⁻⁶ cm² s⁻¹.

^g Determined from the experimental α -*E* data by Eq. (9) in kcal mol⁻¹; for comparison the theoretical stepwise ΔG_o^{\neq} are 3.1, 3.8 and 6.2 kcal mol⁻¹ by the Marcus (Eq. (10)), Hush (Eq. (11)) and Bard (Eq. (12)) approaches, respectively.

 j 1.0 V s⁻¹.

or two are examined from the cyclic voltammograms whereas the last method examines the potential dependence over the entire set of data. A summary of the α data from all three methods are presented in Table 3. The **1**-NO₂/NO₂ and **1**-NO₂/H have α values ranging from 0.62 to 0.84 depending on the method of evaluation. The fact that the values are greater than 0.5 suggests the initial electron transfer occurs via a stepwise mechanism [11]. The other five **1**-X/Y compounds have α values within the range of 0.35–0.50, which falls within the mixed kinetic region where both a stepwise and a concerted DET mechanism may be in competition [11,17c].

$$\alpha = \frac{1.85KI}{F(E_{p/2} - E_p)}$$
(1)

$$\alpha_{\rm avg} = \frac{RT}{2F} \left(-\frac{\partial (\ln \nu)}{\partial E_{\rm p}} \right) \tag{2}$$

$$\alpha_{\rm app} = -\frac{RT}{F} \left(\frac{\partial (\ln k)}{\partial E} \right) \tag{3}$$

Convolution potential sweep voltammetry was used to evaluate thermodynamic and kinetic parameters for the direct reduction of **1**-X/Y in 0.1 M TEAP/DMF solution over a range of scan rates from 0.1 to 25 V s^{-1} [23]. Table 3 also summarizes this data. The technique involves the subtraction of background currents from the voltammograms at each corresponding scan rate and the resultant data transformed into sigmoidal-shaped curves via the convolution integral (Eq. (4)) [23]. From the limiting plateau current, the diffusion coefficients were determined to range from 8.3×10^{-6} to $1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in 0.1 M TEAP/DMF solution (Eq. (5)). The potential dependence of the heterogeneous rate constant (k_{het}) was derived from the convoluted current curves. The heterogeneous kinetics, log k_{het}^0 , in Table 3 are consistent with an irreversible

electrode reaction [24,25]. The log k_{het}^o values, estimated from interpolation of the second order polynomial fit to the heterogeneous kinetics are low, but typical for dissociative systems, ranging from -3.1 to -5.4 [11,12]. Derivatization of the ln k_{het} -E data over small intervals for each scan rate results in the determination of the potential dependence of the apparent transfer coefficient, α_{app} (Eq. (3)), uncorrected for the effect of the electrode double-layer. From the linear α -E relationship, the standard reduction potential was determined by extrapolation to $\alpha = 0.5$ (Eq. (6)). Despite the observed reduction being electrochemically irreversible, the technique allows for the thermodynamically significant $E_{1-X/Y}^o$ to be easily determined. The $E_{1-X/Y}^o$, which range from -0.60 to -1.1 V, decrease as a function of electron-donating substituent ability.

$$I_{\rm lim} = \pi^{-1/2} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \tag{4}$$

$$I_{\rm lim} = nFAD^{1/2}C*$$
(5)

$$\alpha = 0.5 + \frac{F}{8\Delta G_0^{\neq}} (E - E^{\circ}) \tag{6}$$

4. Discussion

The standard potentials $E_{1-X/Y}^{\circ}$ for all the compounds reported in Table 1 are within 300 mV of the observed peak potential E_p (wave A). In a stepwise ET mechanism, the peak potential is normally close to the thermodynamic standard reduction potential where $\alpha = 0.5$ by definition [24]. However, in a concerted DET reduction, the observed peak potential appears at a much more negative potential due to the large activation overpotential that must be overcome to stretch and break the cleaving bond, which results in

 $^{^{}h}$ 0.1 V s⁻¹.

 $^{^{}i}$ 0.5 V s⁻¹.



Scheme 3. Possible reaction pathways for the reduction of 1-X/Y to 2-X/Y.

much lower experimental α value, typically below 0.3, for example, as observed with benzyl chlorides [15].

As previously mentioned, the $\log k_{het}^o$ values are low ranging from -3.1 to -5.4. Unexpectedly, the measured kinetics for $1-NO_2/NO_2$ and $1-NO_2/H$ are the lowest in the series. We believe that the k_{het} values should be similar to the other 1-X/Y compounds. The window of accessible α data was quite narrow for $1-NO_2/NO_2$ and $1-NO_2/H$, covering only 100 mV of data, which results in a greater degree of error during the determination of the $E_{1-X/Y}^o$ from the extrapolation of the data and accounts for the more than one order of magnitude discrepancy.

The application of DET theory was also used to determine the intrinsic barrier (ΔG_0^{\neq}), the solvent reorganization energy (λ_0) and bond dissociation energy (BDE). The intrinsic barrier is diagnostic for distinguishing between a concerted and stepwise mechanistic pathway. In the stepwise case, ΔG_0^{\neq} only has a contribution from λ_0 so that the classic Marcus–Hush model applies (Eq. (7)). For the concerted case, Savéant's model is used to evaluate the ΔG_0^{\neq} , which includes a contribution for the BDE (Eq. (8)). ΔG_0^{\neq} was determined from the slope of the α –*E* convolution data (Eq. (9)). The determined ΔG_0^{\neq} (Table 3) values are significantly smaller than those determined for other C–Cl systems including benzyl chlorides [15]. The results suggest 1-X/Y undergoes a stepwise reductive cleavage for all the compounds investigated.

$$\Delta G_0^{\neq} = \frac{\lambda_0}{4} \tag{7}$$

$$\Delta G_0^{\neq} = \frac{\lambda_0 + \text{BDE}}{4} \tag{8}$$

$$\frac{\partial \alpha}{\partial E} = \frac{1}{8\Delta G_0^{\neq}} \tag{9}$$

A major difference between the Marcus and Savéant ET models is the magnitude of ΔG_o^{\neq} . Hence, estimates for λ_o can be helpful in distinguishing between a concerted or stepwise DET mechanism [18]. Several approaches exist for estimating λ_o , as shown by Eqs. (10–12), based on the molecular and solvent parameters (where D_{op} and D_s are the optical and static dielectric constants) [24]. These approaches provide reasonable estimates of λ_o when there is negligible contribution from the internal reorganization energy. To account for ET at only a portion of the acceptor 1-X/Y molecule, an effective radius approach was used (Eq. (13)) [11a–b, 17g–h]. The theoretical ΔG_o^{\neq} values are obtained by substituting the results from Eqs. (10–12) into Eq. (7), which yields 3.1, 3.8 and 6.2 kcal mol⁻¹ by the Marcus (Eq. (10)), Hush (Eq. (11)) and Bard (Eq. (12)) approaches, respectively. These estimated ΔG_o^{\neq} are in relatively good agreement with the experimental values, which range from 2.0 to 7.1 kcal mol⁻¹, thereby suggesting that there is no apparent contribution from the BDE. Hence, the reasonable fits with the Marcus model (Eq. (7)) suggests the reduction occurs via a stepwise DET mechanism throughout the series of compounds.

$$\lambda_{\text{oMarcus}} = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_s}\right) \left(\frac{1}{4a}\right) \tag{10}$$

$$\lambda_{\text{oHush}} = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_{\text{s}}}\right) \left(\frac{1}{2a}\right) \tag{11}$$

$$\lambda_{\text{oBard}} = \frac{2.08}{a} \tag{12}$$

$$a = \frac{a_{\rm Cl}^{-}(2a_{\rm 5-X/Y} - a_{\rm Cl}^{-})}{a_{\rm 5-X/Y}}$$
(13)

Scheme 3 illustrates two possible heterogeneous reduction mechanisms for the series of 1,4-dichloroazoethanes. The diagnostic thermodynamic parameters suggest the initial 1-X/Y reduction proceeds via formation of a radical-anion intermediate involving acceptance of an electron into a delocalized π^* orbital energy followed by an intramolecular dissociative electron transfer to a C–Cl bond. Afterwards, a number of other elementary reaction steps occur ultimately resulting in the formation of 2-X/Y and chloride anions. The unsymmetrical substituted 1-X/Y are expected to undergo reductive cleavage of the C–Cl bond nearest the most electron-withdrawing substituent as similarly observed in the reduction of the C=N bond in the 2-X/Y [21].

After dissociative reduction of a C–Cl bond, a benzylic carbon radical is formed. The mechanism could then precede either by a rapid radical rearrangement leading to the expulsion of a chlorine atom (route 1) which is subsequently reduced, or reduction of the carbon radical followed by an anionic rearrangement followed by elimination of chloride anion (route 2). The mechanistic pathway depends on whether the carbon radical formed upon C-Cl fragmentation is immediately reduced to an anion intermediate depending on the overpotential, as in route 2, and the activation barrier that must be overcome for reorganization of the molecular structure and expulsion of Cl[•], which is then readily reduced $(E_{Cl^{\bullet}/Cl^{-}} = +1.81 \text{ V})$ versus SCE) [26] as in case 1. The reduction potentials of the carbon radicals can be approximated from the analogous substituted benzyl radicals [27], although the E^o of each radical is expected to be substituent dependent. For example, for 1-CN/CN the E_p is at -1.074 V whereas the E° for the 4-CN benzyl radical is -0.77 V so that heterogeneous reduction of the carbon radical is energetically feasible [27]. Conversely, for 1-H/H the E_p is at -1.250 V whereas the E° for the benzyl radical is -1.45 V versus SCE [27]. In this case, reduction of the **1**-H/H[•] is an uphill process with a lower k_{het} . The inductive effect of an azo group on the E^{o} of benzyl radicals is not known, but it is anticipated to shift *E*^o to more positive potentials due to its electron-withdrawing properties ($\sigma_1 = 0.30$ for -N=N-Ph) [29]. From the mechanistic pathway we would expect to observe coupling products or other products derived from the radical intermediate (route 1). The absence of this observation suggests the mechanism proceeds by route 2, although neither can be ruled out. A third possible mechanism, involves the double simultaneous (or successive but at similar potentials) dissociative reduction with loss of both chlorides to yield the dibenzylic diradical, which is a minor resonance structure better written as the azine. A similar mechanism was ruled out by Savéant and coworkers in the reduction of a number of vicinal dihalides, otherwise known as 1,2dichloro-1,2-diphenylethanes [16f]. Given the stepwise nature of the dissociative reduction for 1-X/Y such a mechanism is considered unlikely.

Vicinal dihalides have been also studied by Lund and coworkers [30]. The CVs exhibited an irreversible two-electron reduction wave followed by a more negative reversible one-electron wave. The first wave was attributed to reductive cleavage of the C-X bonds followed by elimination of the second halogen to yield electroactive E-stilbene products. Although they did not apply Savéant DET theory, they did suggest a concerted DET mechanism. In contrast, we show that 1,4-dichloroazoethanes react by a stepwise DET mechanism. The key difference between the two classes of compounds is the azo group, which appears to contribute to lowering the π^* orbital energy level of all the **1**-X/Y compounds. Other families of compounds have been shown to have unexpectedly low intrinsic barriers regardless of the substituent on the aryl moiety. In the case of diaryl disulfides, the ET mechanism was within the mixed kinetic region between the two mechanistic extremes of stepwise and concerted [12a,18]. In our recent study of 3,3,6,6tetraaryl-1,2-dioxanes, we discovered that the intrinsic barriers were inconsistent with a purely concerted DET to the O-O bonds [17k]. Density functional theory calculations illustrated that the LUMO was not localized on the O-O bond, but rather delocalized over a large molecular framework including the equatorial aryl rings, the adjacent C–O bond and the O–O bond.

5. Conclusions

The present study on the electrochemical reduction of a series of substituted 1,4-dichloroazoethanes, 1-X/Y, provides an unprecedented illustration of molecular systems containing two halides, separated by three bonds, that react through a dissociative electron transfer mechanism to yield azine products. The initial reduction proceeds by DET to cleave a C-Cl bond. The low intrinsic barriers suggest the reduction proceeds by a stepwise DET throughout the series in contrast to benzyl halides and vicinal dihalides. We postulate the azo moiety facilitates the stepwise pathway by lowering the energy of the LUMO over the bulk of the molecular architecture, although a concerted DET may also be competitive in some cases. The stable carbon radical formed after dissociation is then reduced directly by the electrode as the reduction potentials of the radicals are generally expected to be more positive than the applied electrode potential [17g,27], resulting in an anionic intermediate, and the expulsion of chloride to form 2-X/Y azines. Unlike the photochemical reactions, no coupling products were observed from carbon radical intermediates. Hence, we provide an efficient route to obtaining pure azines in quantitative yield.

Acknowledgements

The financial support of the Natural Science and Engineering Research Council of Canada, Canadian Foundation for Innovation, ORCDF, and the University of Western Ontario (ADF) is greatly appreciated. VAS thanks the OGS program for a scholarship. DCM thanks the OGSST program for a scholarship.

References

- [1] P.S. Engel, Chem. Rev. 80 (1980) 99.
- [2] P.S. Engel, S. Duan, G.B. Arhancet, J. Org. Chem. 62 (1997) 3537.
- [3] P.S. Engel, S.L. He, W.B. Smith, J. Am. Chem. Soc. 119 (1997) 6059.
- S.K. Danek, D.P. Kelly, A.K. Serelis, J. Org. Chem. 52 (1987) 2911.
- [5] S. Patai, in: S. Patai (Ed.), The Chemistry of the Hydrazo, Azo and Azoxy Groups, John Wiley & Sons, New York, 1975.
- C.F. Billera, T.B. Dunn, D.A. Barry, P.S. Engel, J. Org. Chem. 63 (1998) 9763
- [7] P.S. Engel, L. Pan, K.H. Witmire, I. Guzman-Jimenez, J. Org. Chem. 65 (2000) 1016.
- [8] S. Engel, L. Pan, Y. Ying, L.B. Alemany, J. Am. Chem. Soc. 123 (2001) 3706.
- [9] J.P. Stradins, V.T. Glezer, in: A.J. Bard, H. Lund (Eds.), Azo, Azoxy and Diazo Compounds, vol. 13, Marcel Dekker Inc., New York, 1979.
- [10] N. Levi, D.S. Malament, J. Chem. Soc. Perkin Trans. II (1976) 1249.
- [11] (a) J.-M. Savéant, in: D. Bethel (Ed.), Advances in Physical Organic Chemistry, vol. 26, Academic Press, New York, 1990, p. 1; (b) J.-M. Savéant, in: P.S. Mariano (Ed.), Advances in Electron Transfer Chemistry, vol. 4, JAI Press, Greenwich, CT, 1994, p. 53; (c) J.-M. Savéant, Acc. Chem. Res. 26 (1993) 455; (d) J.-M. Savéant, in: T. Tidwell (Ed.), Advances in Physical Organic Chemistry, vol. 35, Academic Press, New York, 2000, p. 117; (e) C. Costentin, M. Robert, J.-M. Savéant, Chem. Phys. 324 (2006) 40; (f) C. Costentin, L. Donati, M. Robert, Chem. Eur. J. 15 (2009) 785. [12] (a) F. Maran, D.D.M. Wayner, M.S. Workentin, in: T.T. Tidwell (Ed.), Advances
- in Physical Organic Chemistry, vol. 36, Academic Press, New York, 2001, p. 85; (b) S. Antonello, F. Maran, Chem. Soc. Rev. 34 (2005) 418.
- [13] R.A. Rossi, A.B. Pierini, A.B. Penenory, Chem. Rev. 103 (2003) 71.
- [14] A. Houmam, Chem. Rev. 108 (2008) 2180.
- [15] Examples of aryl halides: (a) C.P. Andrieux, I. Gallardo, J.M. Savéant, K.B. Su, J. Am. Chem. Soc. 108 (1986)
 - 638; (b) C.P. Andrieux, A.L. Gorande, J.-M. Savéant, J. Am. Chem. Soc. 114 (1992) 6892:

(c) C.P. Andrieux, C. Comgellas, J. Kanoufi, J.-M. Savéant, A. Thiebault, J. Am. Chem. Soc. 119 (1997) 9527;

(d) C.P. Andrieux, E. Differding, M. Robert, J.-M. Savéant, J. Am. Chem. Soc. 115 (1993) 6592;

(e) C.P. Andrieux, J.-M. Savéant, A. Tallec, R. Tardivel, C. Tardy, J. Am. Chem. Soc. 119 (1997) 2420

(f) R. Fuhlendorff, D. Occhialini, S.U. Pedersen, H. Lund, Acta, Chem. Scand, 43 (1989) 803:

- (g) D. Occhialini, S.U. Pedersen, H. Lund, Acta. Chem. Scand. 44 (1990) 715; (h) D. Occhialini, J.S. Kristensen, K. Daasbjerg, H. Lund, Acta. Chem. Scand. 46
- (1992)474
- [16] Examples of alkyl halides:

(a) L. Pause, M. Robert, J.-M. Savéant, J. Am. Chem. Soc. 122 (2000) 9829; (b) A. Cardinale, A.A. Isse, A. Gennaro, M. Robert, J.-M. Savéant, J. Am. Chem. Soc 124 (2002) 13533.

- (c) K. Daasbjerg, S.U. Pedersen, H. Lund, Acta Chem. Scand. 43 (1989) 876;
- (d) T. Lund, H. Lund, Acta Chem. Scand. B 41 (1987) 93;
- (e) L. Pause, M. Robert, J.-M. Savéant, J. Am. Chem. Soc. 121 (1999) 7158;
- (f) D. Lexa, J.-M. Savéant, K.B. Su, D.L. Wang, J. Am. Chem. Soc. 109 (1987) 6464;
- (g) H. Jensen, K. Daasbjerg, J. Chem. Soc. Perkin Trans. 2 (2000) 1251;
- (h) K. Daasbjerg, T.B. Christensen, Acta Chem. Scand. 49 (1995) 128;
- (i) X.-M. Zhang, J. Chem. Soc. Perkin Trans. 2 (1993) 2275;
- (j) C. Costentin, J.-M. Savéant, J. Am. Chem. Soc. 122 (2000) 2329;
- (k) C. Costentin, P. Hapiot, M. Medebielle, J.-M. Savéant, J. Am. Chem. Soc. 122 (2000) 5623
- [17] (a) M.S. Workentin, F. Maran, D.D.M. Wayner, J. Am. Chem. Soc. 117 (1995) 2120:
 - (b) S. Antonello, F. Maran, J. Am. Chem. Soc. 119 (1997) 12595;
 - (c) S. Antonello, F. Maran, J. Am. Chem. Soc. 121 (1999) 9668;
 - (d) S. Antonello, M. Musumeci, D.D.M. Wayner, F. Maran, J. Am. Chem. Soc. 119 (1997) 9541:
 - (e) M.S. Workentin, R.L. Donkers, J. Am. Chem. Soc. 120 (1998) 2664;
 - (f) R.L. Donkers, F. Maran, D.D.M. Wayner, M.S. Workentin, J. Am. Chem. Soc. 121 (1999) 7239:
 - (g) R.L. Donkers, M.S. Workentin, Chem. Eur. J. 7 (2001) 4012;
 - (h) D.C. Magri, M.S. Workentin, Org. Biomol. Chem. 1 (2003) 3418;
 - (i) D.C. Magri, M.S. Workentin, Org. Biomol. Chem. 18 (2008) 3354;
 - (j) D.C. Magri, M.S. Workentin, Chem. Eur. J. 14 (2008) 1698;
 - (k) D.L.B. Stringle, D.C. Magri, M.S. Workentin, Chem. Eur. J. 16 (2010) 178.
- [18] (a) T.B. Christensen, K. Daasbjerg, Acta Chem. Scand. 51 (1997) 307;
- (b) K. Daasbjerg, H. Jensen, R. Benassi, F. Taddei, S. Antonello, A. Gennaro, F. Maran, J. Am. Chem. Soc. 121 (1999) 1750;

(c) S. Antonello, R. Benassi, G. Gavioli, F. Taddei, F. Maran, J. Am. Chem. Soc. 124 (2002) 7529;

(d) S. Antonello, K. Daasbjerg, H. Jensen, F. Taddei, F. Maran, J. Am. Chem. Soc. 125 (2003) 14905.

- [19] D.S. Malament, J.M. McBride, J. Am. Chem. Soc. 92 (1970) 4586.
- [20] A.F. Hegarty, J.A. Kearney, J. Org. Chem. 40 (1975) 3529.
 [21] V.A. Sauro, M.S. Workentin, J. Org. Chem. 66 (2001) 831.
- [22] 2,2,2-Trifluoroethanol did cause the two one-electron waves, B and C, to merge into a single two-electron wave with increasing acid concentrations.
- [23] (a) J.C. Imbeaux, J.-M. Savéant, J. Electroanal. Chem. 44 (1973) 169; (b) J.-M. Savéant, D. Tessier, J. Electroanal. Chem. 61 (1975) 251.
- [24] A.J. Bard, L.R. Faulkner, Electrochemical Methods. Fundamentals and Applications, John Wiley & Sons, New York, NY, 1980.
- [25] J.C. Eklund, A.M. Bond, J.A. Alden, R.G. Compton, Perspectives in Modern Voltammetry: Basic Concepts and Mechanistic Analysis, vol. 32, Academic Press, 1999.
- [26] D.D.M. Wayner, in Handbook of Organic Chemistry, Redox Properties, vol. 2, p. 363.
- [27] (a) D.D.M. Wayner, D.J. McPhee, D. Griller, J. Am. Chem. Soc. 110 (1988) 132; (b) B.A. Sim, P.H. Milne, D. Griller, D.D.M. Wayner, J. Am. Chem. Soc. 112 (1990) 6635;
- (c) P. Hapiot, V.V. Konovalov, J.-M. Savéant, J. Am. Chem. Soc. 117 (1995) 1428. [29] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165.
- [30] (a) H. Lund, E. Hobolth, Acta Chem. Scand. B 30 (1976) 895;
- (b) T. Lund, C. Bjorn, H.S. Hansen, A.K. Jensen, T.K. Thorsen, Acta Chem. Scand. 47 (1993) 877;
 - (c) H. Lund, H.L. Kristensen, Acta Chem. Scand. B 33 (1979) 495;
 - (d) H. Balslev, K. Daasbjerg, H. Lund, Acta Chem. Scand. 47 (1993) 1221.