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

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ABSTRACT

A series of 1,4-dichloroazoethanes (**1**-X/Y, X and Y = 4-NO_2, 4-CN, 4-CH_3 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/$Y^{\bullet-}$ radical anion and **2**-X/Y^{2-} dianion consecutively, with the exception of **1**-NO_2/NO_2 where both NO_2 groups are reduced simultaneously in a two-electron reversible wave. Thermodynamic and kinetic parameters were determined from CPSW: the standard reduction potentials (E^o) 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**-NO_2/NO_2 and **1**-NO_2/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.

1. Introduction

The azo (N═N) bond is a relatively labile group often accompanied by the loss of N_2 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, CH_3) follow a concerted pathway. An important parameter for distinguishing between a stepwise and concerted DET mechanism is the intrinsic barrier ($\Delta G_0^{\neq}$), that is the activation free energy when the driving force for the reaction is zero. In the limiting case of concerted DET, the ($\Delta G_0^{\neq}$) 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 ($\Delta G_0^{\neq}$) 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

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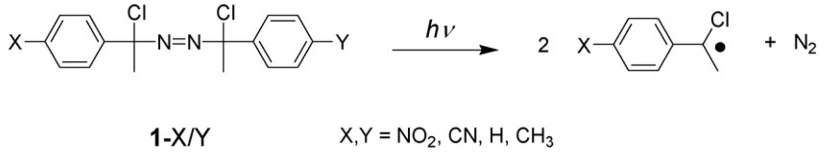


Scheme 1. The photodissociation of 1,4-dichloroazoethanes via C–N bond cleavage.

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-NO_2, 4-CN, 4-CH_3 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 quantitative 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^o_{het}). 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 °C and stored in a vacuum dessicator. Ferrocene was purified by sublimation.

2.2. Instrumentation

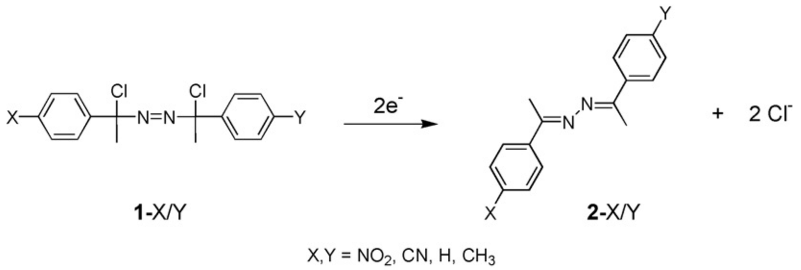
NMR spectra were recorded on a Varian Gemini 300 MHz (300.08 MHz for ^{1}H and 75.46 MHz for ^{13}C) or a Varian Mercury 400 MHz (400.08 MHz for ^{1}H and 100.60 MHz for ^{13}C) instrument. Chemical shifts were measured in deuterated chloroform and reported in parts per million downfield from tetramethylsilane. 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 2-propanol and dried with a cool stream of air. The counter electrode was a 1 cm^2 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^o = 0.470 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



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