

POLAROGRAPHIC AND POTENTIOSTATIC REDUCTION OF CARBODIIMIDES: A MECHANISTIC STUDY

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Abstract

The polarographic reduction of aromatic carbodiimides in anhydrous aprotic solvents goes through a carbene intermediate by a diffusion controlled process in two one-electron steps. The first step is the rate-determining step and converts the carbodiimide to a radical anion (6) that reduces further by a fast one-electron step to a carbene dianion intermediate (7). This abstracts an oxygen, along with protons, from the solvent to give diphenyl urea (9) or reduces further to methylene dianiline (12).

Introduction

Polarography is a technique with diverse applications [1-2]. One of the most important uses of the polarographic technique is in the study and elucidation of the reaction mechanism in organic chemistry [2-4]. In this work we would like to report the use of this technique to elucidate the mechanistic pathway by which carbodiimides reduce. In this regard, seven different aromatic carbodiimides with different electron withdrawing and contributing groups were prepared [5], each of these compounds was reduced polarographically in anhydrous dimethylformamide.

The number of electrons involved in the reductions in conjunction with diffusion current constants, helps us to postulate the intermediates that are formed in the non-aqueous media. Diffusion controlled reduction waves, if they occur, eliminate the possibility of kinetic or adsorption currents interfering or occurring simultaneously during the reduction process.

Hammett free energy diagrams of half-wave potentials versus polar substituent constant can help to elucidate the intermediate in an electrochemical reduction [6], consequently the half-wave potentials of substituted carbodiimides were determined and linear free-energy

graphs were drawn to provide additional evidence for the chemical intermediates in this electrochemical reduction.

In the potentiostatic study of these carbodiimides in different anhydrous aprotic solvents [dimethylformamide (DMF) and acetonitrile], we considered the effect of the oxygenated solvent (DMF) and a non-oxygenated one (acetonitrile) in order to determine and establish the mechanism of the reaction.

Experimental Section

General Method

Tetra-n-butyl ammonium bromide (Eastman reagent grade) was recrystallized twice in ethyl acetate (Fisher reagent grade). Acetonitrile (Mallinckrodt nano grade), and N,N-dimethylformamide (Fisher reagent grade) were refluxed over sodium hydride and potassium carbonate, respectively, and then distilled through a 71 cm fractionation column under dry nitrogen.

The polarograms were obtained by using a Heath Model EUW-401, which contained a Heath operational Amplifier EUW-19 A, a Heath Recorder EUW-20 A, and a Heath polarographic Model EUA-12-2. The calibration of the polarograph was done according to the Heath Model

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UW-401 Manual in which the zero initial setting, sweep rate and hold drift current were calibrated.

The three-electrode polarograph in this study consisted of a dropping mercury electrode (dme) as the working electrode, a platinum wire as a counter electrode, and a silver/silver bromide electrode as the reference electrode.

All polarograms were obtained at four different (40, 50, 60 and 70 cm) mercury heights in a water bath thermostated at $25 \pm 0.1^\circ\text{C}$. The electrode was a Sargent Model (S-1947) dropping mercury electrode (6 to 12 seconds) which was cut to 12 cm in length. The mass of a drop of mercury was obtained by collecting nine separate samples, 20 drops each, in distilled water at 25°C and 0.05 ± 0.05 cm mercury height at zero potential. Then water was decanted and the mercury was dried and weighed. The average and average deviation was 6.92 ± 0.02 mg/drop.

The average drop-time and average deviation (3.45 ± 0.05 sec) was obtained in three trials, 20 drops per trial, under the same experimental conditions. The reference electrode was constructed in the laboratory from an eighteen-gauge silver wire according to the method of Biolchini [7]. Carbodiimides were prepared according to Campbell's procedure for synthesizing carbodiimides [5], in which phospholene oxide is used as a catalyst [8].

Preparation of 3-methyl-1-phenyl-3-phospholene-1-oxide

A mixture of 27.1 ml (28.5 g, mmole) of dichlorophenyl phosphine (Aldrich), 60.0 ml (769 mmole) of isoprene

(Matheson) and 0.40 g (2 mmole) of 2,6-di-tert-butyl-p-cresol (Aldrich) were allowed to stand at room temperature in hood for seven days. After this time, the solid product was dissolved in 150 ml of ice water, and 100 ml of hexane was added. The pH was adjusted to between 5 and 6 by the addition of sodium bicarbonate and the solution was extracted with three-150 ml portions of chloroform and dried over calcium sulfate.

A reduced pressure from the water aspirator was used to evaporate the solvent and concentrate the residue to approximately 10 ml. The residue was vacuum distilled to produce 6 ml (40% yield) of a white oil, b. p. $160-162^\circ\text{C}$ at 0.4-0.45 torr (lit. b.p. $152-154^\circ\text{C}$ at 0.35-0.40 torr) [8].

General Procedure for Polarographic Reduction of Carbodiimides

The polarograms of seven different carbodiimides were obtained at four different mercury heights (40, 50, 60, and 70 cm). The polarographic solutions were $1 \pm 0.58 \times 10^{-3}$ M of the corresponding carbodiimide and 0.175 M of the supporting electrolyte: tetra-n-butyl ammonium bromide in anhydrous dimethyl formamide. As an example, the polarogram of bis-(p-methoxy phenyl)-carbodiimide in DMF is shown in Figure 1.

General Procedure for Potentiostatic Reduction of Carbodiimides

In this work, the Beckman Electroscan 30 was used as the potentiostat which had a reference voltage control span

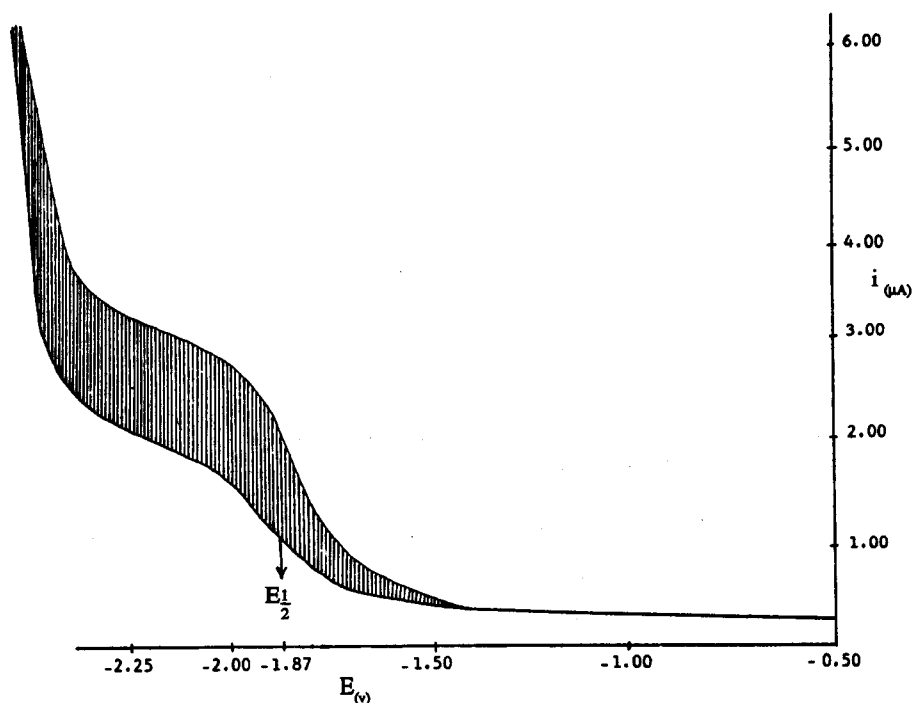


Figure 1. Polarogram of bis-(p-methoxyphenyl)-carbodiimide in DMF

of ± 5.0 V with ± 10 mV accuracy. The current capacity was 0-100 mA with $\pm 3\%$ accuracy, and the maximum output voltage was ± 30 volts. A mercury pool cathode was used as the working electrode, a platinum spiral wire as the anode and a silver/silver bromide electrode as the reference electrode.

Twenty milliliters of [tetra-n-butyl ammonium bromide solution 2.82 g (8.74 mmole) in 50 ml of dimethylformamide or acetonitrile], was added to the anode and another 20 ml of it to the cathode of the cell containing 1.00 g (5.00 mmole) of diphenyl carbodiimide. The cell was placed in a constant temperature bath at 0°C and was stirred whilst dry nitrogen was passed through it. The initial potential of the reduction was set at -1.95 volts versus the reference electrode. The total reduction time was 10 and 20 hrs in DMF and acetonitrile, respectively. At the end of the reductions, the color of the catholyte was dark-green, and the anolyte, dark-red. The anolyte color was indicative of the presence of bromine from oxidation of bromide anion. In DMF, the catholyte was rotary evaporated to a dark viscous liquid (2.821 g) which was washed with 50 ml of anhydrous ether. The residue after washing with 20 ml of H_2O was crystallized from 95% ethyl alcohol to give 0.624 g (1.530 mmole, 57% yield) of white crystalline diphenylurea m.p. 236-237 $^\circ\text{C}$, IR (KBr) 3280, 1601 cm^{-1} (lit. m.p. 234-236 $^\circ\text{C}$).

In acetonitrile after the catholyte was rotary evaporated, the residue, a dark gummy material (2.62 g), was washed with 100 ml of boiling hexane and after the removal of solvent, the residue was recrystallized twice from 20 ml of hexane to give 0.496 g (2.44 mmole, 46% yield) of white methylene dianiline, m.p. 95-98 $^\circ\text{C}$ IR (KBr) 3390, 3050, 1490 cm^{-1} , mass spectrum (70 eV) m/e (rel. intensity) m $^+$ 197 (25), 105 (20), 93 (100).

The % yield based on the mA current flow was approximately 60% in acetonitrile and over 100% in

dimethylformamide.

Results and Discussion

For this mechanistic study, seven different carbodiimides were prepared according to the Campbell procedure [5]. These compounds along with their diffusion currents [6], the mercury heights and square root of these heights are listed in Table 1. From the polarograms, half-wave potentials and i_d 's were obtained. The results are shown in Table 2.

The polarographic reduction of the carbodiimides was diffusion controlled as indicated in Figure 2. It has been shown that for an irreversible electrolytic process from Zuman and Hammett's equation (1,2), equation (3) can be obtained [9], to account for the effect of different substituents attached to the benzene ring.

$$\Delta E_{\frac{1}{2}} = \frac{2.3 RT}{(\Delta \alpha - n)_r F} (\Delta \log K^0) R' \quad (1)$$

$$(\Delta \log K) R = \rho_r \sigma_x \quad (2)$$

$$E_{\frac{1}{2}} = \rho_r \sigma_x \quad (3)$$

In this equation, the term $(\Delta \alpha - n)_r$ is the difference in the products of the transfer coefficient, α , and the number of electrons, n , which are transferred in the potential determining step for the parent compound and a compound with a substituent R' . The factors T , R , and F represent absolute temperature, gas constant, and faraday constant, respectively. The term $(\Delta \log K^0)$ is the difference in the rate constants for the electrode process for unsubstituted and substituted compounds. By using this equation and plotting $E_{\frac{1}{2}}$ versus σ_x , the Hammett total polar substituent constant [9] (Fig. 3) can be obtained. The reaction constant,

Table 1. Diffusion current (μA) of carbodiimides versus mercury heights (cm) at 25°C

Carbodiimides	Hg. Ht.	40	50	60	70
	$\sqrt{\text{Hg. Ht}}$	6.32	7.05	7.76	8.37
		Diffusion current (μA)			
Bis- (p- methoxyphenyl)-carbodiimide		1.44	1.78	2.05	2.35
4,4'- ditolyl carbodiimide		1.58	1.74	2.12	2.31
3,3' - ditolyl carbodiimide		1.51	1.75	1.82	2.06
Diphenyl carbodiimide		2.96	3.04	3.20	4.00
Bis- (o- fluorophenyl)-carbodiimide		0.966	1.35	1.48	1.64
Bis- (p- bromophenyl) - carbodiimide		0.731	0.877	1.27	1.54
Bis - (p- chlorophenyl) - carbodiimide		0.99	1.30	1.58	

Table 2. The half-wave potentials versus diffusion currents (i_d) and diffusion current (I_d) at 60 cm mercury heights and 25°C

Carbodiimides	i_d (μA)	I_d (μA)*	$E_{1/2}$
Bis- (p- methoxyphenyl)-carbodiimide	2.05	1.30	1.87
4,4'- Ditolyl carbodiimide	2.12	1.34	1.78
3,3' - Ditolyl carbodiimide	1.82	1.15	1.77
Diphenyl carbodiimide	3.20	2.02	1.74
Bis- (o- fluorophenyl)-carbodiimide	1.48	0.937	1.62
Bis- (p- bromophenyl) - carbodiimide	1.27	0.804	1.54
Bis- (p- chlorophenyl) - carbodiimide	1.58	1.00	1.48

* $I_d = \frac{i_d}{cm^{2/3} t^{1/6}}$, where $cm^{2/3} t^{1/6}$ is 1.58.

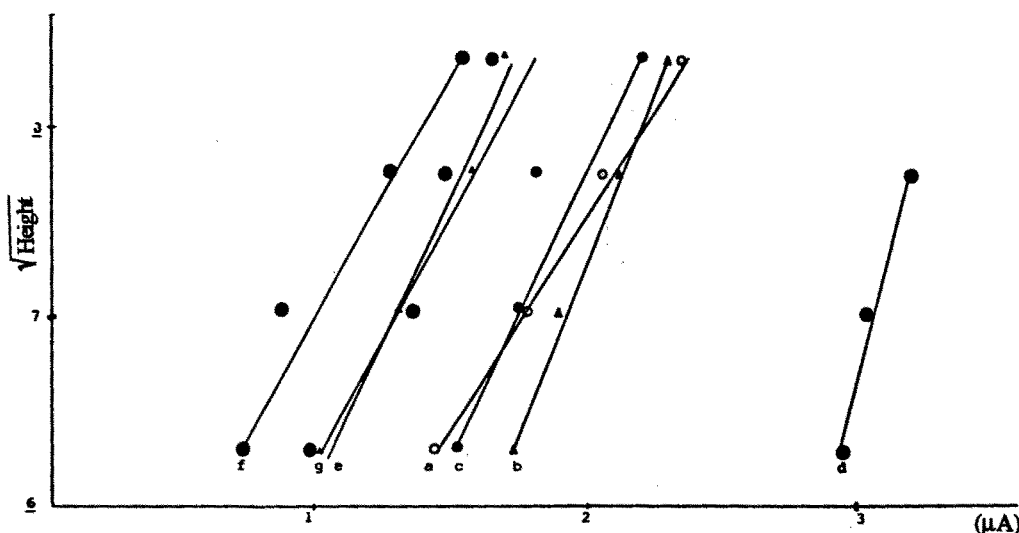


Figure 2. Diffusion currents versus heights for (a), bis- (p-methoxyphenyl)-carbodiimide; (b), 4,4-ditolyl carbodiimide; (c), 3,3-ditolyl carbodiimide; (d), diphenyl carbodiimide; (e), bis- (o-fluorophenyl)-carbodiimide; (f), bis- (p-bromophenyl)-carbodiimide, (g), bis- (p-chlorophenyl)-carbodiimide.

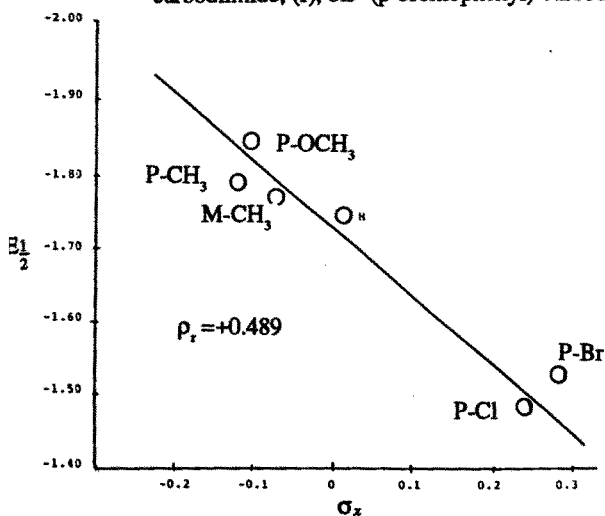


Figure 3. Graph of $E_{1/2}$ values versus sigma values of substituent groups on carbodiimides

$\rho_r = 0.489$ can be calculated from the slope of this straight line and from its sign and magnitude one can conclude that there is a mechanistic relationship between the half-wave potential and the substituent groups. It can be shown [10] that since ρ_r is positive (0.489) for the polarographic reduction, it is a good indication that the neutral carbodiimide is the reactant in the rate-controlling step, and thus the possibility of the radical-anion being a reactant in the rate-controlling step is eliminated. The number of electrons in the rate-controlling step is obtained from Meites's method [11], equation (4), (Fig. 4).

$$E_{dmc} = E_{1/2} - \frac{0.0542}{\alpha n} \log \left(\frac{i}{i_d - i} \right) \quad (4)$$

It has been shown that when αn is in the range of 0.4 to 0.6 [11], there is a one-electron rate-controlling step. The

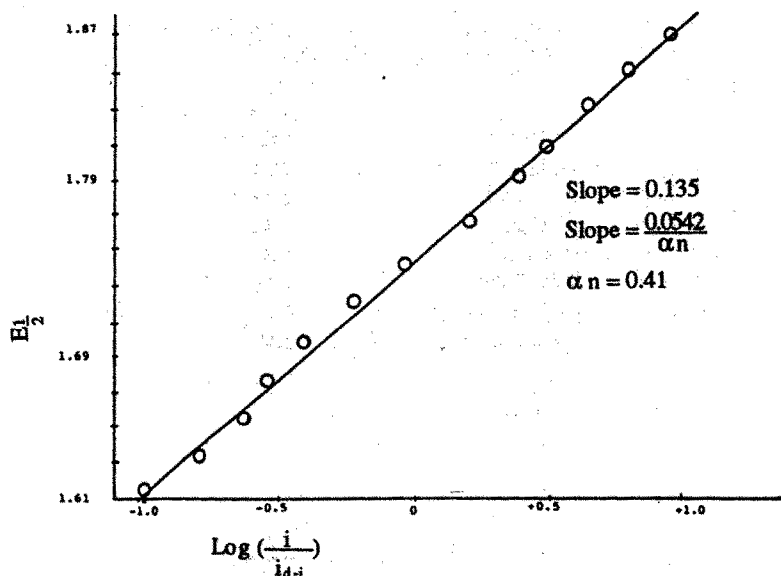


Figure 4. Graph of $E_{1/2}$ values versus $\log \frac{i}{I_d - i}$ of diphenylcarbo diimide at 60 cm mercury height

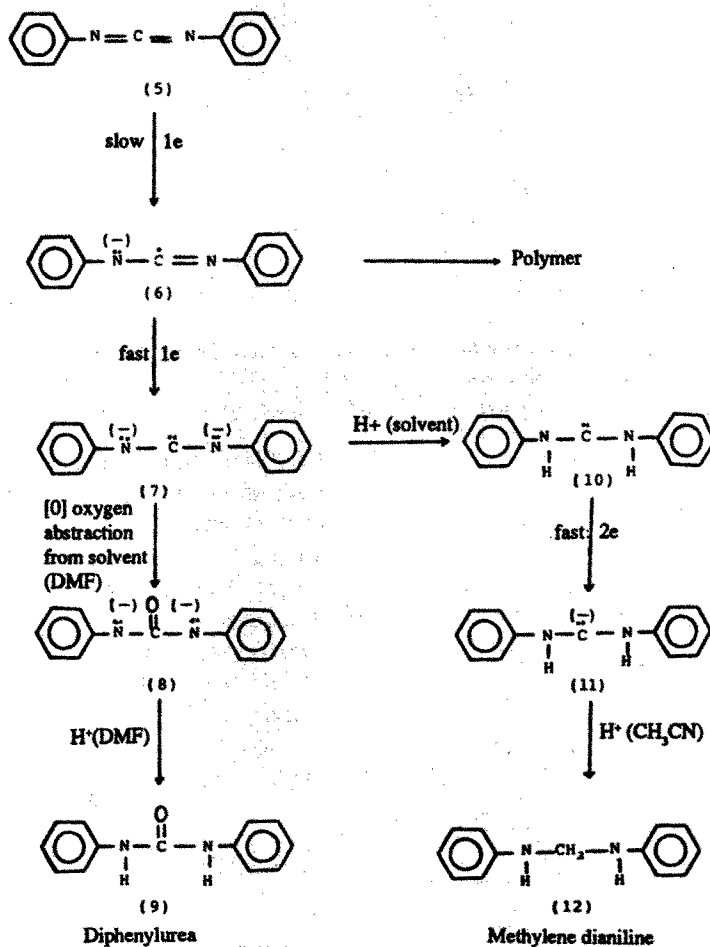


Figure 5. Reduction process of diphenyl carbodiimide in DMF and acetonitrile

slope, from Figure 4, was 0.41 for diphenyl carbodiimide. This is consistent with a mechanism which postulates the addition of one electron in the rate-controlling step. Therefore, the Hammett's plot plus the one electron addition in the rate-controlling step support the mechanism postulated in Figure 5.

A proof for the total number of electrons involved in a mechanism can be obtained by comparing the diffusion current constant with those of known reducible compounds. If one compares two reducible species with equal diffusion coefficients, D , the number of electrons should be equal in their respective polarograms.

Trans-stilbene is a compound with two phenyl rings which approximates the size of diphenyl carbodiimide and is known to undergo a two electron reduction in DMF. By comparing its diffusion coefficient with that of diphenyl carbodiimide, one can conclude that diphenyl carbodiimide is also reduced by the total number of two electrons [12].

In order to unequivocally prove the mechanism which shows that there are to tally two electrons consumed in this reduction, the intermediate dianion (7) reduction product should be established. This intermediate product abstracts an oxygen from the solvent (3), and therefore this proof, along with the potentiostatic reduction in an aprotic non-oxygenated anhydrous solvent, such as acetonitrile, which results in methyl dianiline (12) rather than diphenyl urea (9), the only product in DMF, is another proof of this

proposed mechanism.

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