Electrometric studies on the reduction of the azomethine bond in schiff bases and the effect of substituent on it

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The peak potential (Ep) of benzaldehyde (Bz) and its schiff bases with aniline, 3- and 4-OH-, 4-OCH$_3$-, 4-Cl- and 4-NO$_2$-anilines in CH$_3$OH are determined at HMDE employing voltammetric techniques. The results are discussed in terms of influence of the substituent on phenylimino ring affecting electrochemical behaviour of $-CH=N-$ bond. The shift in Ep values of schiff bases is examined on the basis of effect of substituent with respect to Bz (ΔEp') and with parent benzylidene-aniline (1) (ΔEp"). It is found that $-CH=N-$ reduction step involved transfer of two electrons and the reduction process is diffusion controlled and irreversible. The kinetic parameters have been evaluated and used to calculate Hammett constant (σ_x). The characteristic potentials (ΔEp") versus σ_x plot has shown linear relationship and the reaction constant, rho ($\rho_\pi, -CH=N-$), has been determined from the slope value. The positive value of ρ_π, $-CH=N-$ indicates the nucleophilic nature of the electrode process. The CPC experiments have shown that in the reduction process of the studied schiff bases except benzylidene-4'-nitroaniline, where there is a transfer of six electrons, there is transfer of two electrons. The reduction products after CPC experiments, have been characterised by the chemical tests and the spectral studies (UV and IR). A reduction mechanism is proposed on the basis of voltammetric measurements and product analysis.

Recently, studies on cyclic voltammetric behaviour of the schiff bases derived from 2-hydroxynaphthaldehyde with 2-, 3-, 4-OH-, 4-Cl- and 4-NO$_2$-anilines in CH$_3$OH, C$_2$H$_5$OH and aqueous C$_2$H$_5$OH (1:1, v/v) have been reported[1]. The schiff bases viz. 2-hydroxynaphthalidene 2'-, 3'-, 4'-CH$_3$- and -OCH$_3$-anilines in CH$_3$OH have also been studied voltammetrically and the mechanism of electroreduction process was shown[2]. In continuation of the work done earlier, an attempt is made to study the influence of substituent of phenylimino ring on voltammetric behaviour of

schiff bases of the type Ar$-CH=N-$Ar', where Ar $= -C_6H_5$ and Ar' $= -C_6H_5$ (1); $-C_6H_4$-3'-OH (2); $-C_6H_4$-4'-OH (3); $-C_6H_4$-4'-OCH$_3$ (4); $-C_6H_4$-4'-Cl (5) and $-C_6H_4$-4'-NO$_2$ (6). The diffusion coefficient, D$_{ox}$, and the kinetic parameters (αn_a and $k^0_{f,h}$) of the schiff bases (1)-(6) of their reduction process, at HMDE in CH$_3$OH have been determined at three different temperatures. The values of Hammett substituent constant (σ_x) have also been calculated from $k^0_{f,h}$ values to evaluate the reaction constant, $\rho_\pi, -CH=N-$.

Experimental

The schiff bases viz. benzylidene-aniline (m.p. 49.5°C); benzylidene-3'-hydroxyaniline (m.p. 108.5°C); benzylidene-4'-hydroxyaniline (m.p. 111.2°C); benzylidene-4'-methoxyaniline (m.p. 70.4°C); benzylidene-4'-chloroaniline (m.p. 62.6°C) and benzylidene-4'-nitroaniline (m.p. 117.1°C) were prepared and their purity is verified on the basis of melting points and the TLC analysis (using 2.5% KMnO$_4$ in dil. H$_2$SO$_4$) in benzene ethylacetate system. Mercury (BDH) was washed with 4% HNO$_3$ and the acid free mercury was distilled under reduced pressure for HMDE. Stock solutions (0.01 M) of the depolariser were prepared in distilled CH$_3$OH. Experimental concentration of each depolariser was taken as 1.0 mM and the ionic strength of the solution was maintained constant using 0.1 M LiCl (BDH) in CH$_3$OH. Voltammetric measurements of the test solution were made at three different temperatures viz. 293, 298 and 303 ± 0.5 K, after deaerating by purified N$_2$ gas using 384-B Polarographic analyser equipped with Houstan DMP-40 digital plotter and PAR 303 SMDE/HMDE assembly as described earlier[1]. The effective area of HMDE was 0.016 cm^2.

Controlled potential coulometric (CPC) experiments were performed with the help of PAR model 173 potentiostat coupled with PAR model 179 integrator. A coulometric cell of three electrode configuration viz. mercury pool cathode, a platinum wire counter electrode (separated from main solution by a glass frit) was used with SCE as reference electrode. The compounds were studied, before and after coulometry by UV and IR spectra to have knowledge about structural changes occurred in the electrolytic process.

Table 1 – The CV data and the peak separation ($\Delta Ep'$ and $\Delta Ep''$) value for schiff bases of type $Ar - CH = N - Ar'$ in CH_3OH. [Schiff base] = 1.0 mM; $\mu = 0.1$ M LiCl; W.E. = HMDE; R.E. = Ag/AgCl (Cl$^-$ satd.) $\nu = 0.2$ Vs^{-1}

Schiff base/ aldehyde	Substituent on Ar' ring	$- Ep$, V			$Ep' = [Ep_{(alde.)} - Ep_{(S.B.)}]$, V			$Ep'' = (Ep_x - Ep_H)$, V		
		293	298	303 K	293	298	303 K	293	298	303 K
*	–	1.550	1.540	1.530	–	–	–	–	–	–
1	H	1.340	1.330	1.320	– 0.210	– 0.210	– 0.210	–	–	–
2	3'-OH	1.346	1.340	1.334	– 0.204	– 0.200	– 0.196	– 0.006	– 0.010	– 0.014
3	4'-OH	1.370	1.355	1.330	– 0.180	– 0.185	– 0.192	– 0.030	– 0.025	– 0.018
4	4'-OCH$_3$	1.539	1.528	1.515	– 0.011	– 0.012	– 0.015	– 0.199	– 0.198	– 0.195
5	4'-Cl	1.333	1.320	1.308	– 0.217	– 0.220	– 0.222	0.007	0.010	0.012
6	4'-NO$_2$ a)	0.792	0.785	0.777	– 0.758	– 0 775	– 0.753	–	–	–
	b)	1.140	1.135	1.130	– 0.410	– 0.405	– 0.400	0.200	0.195	0.190

a) peak of NO$_2$ group; b) peak of $- CH = N -$ bond; * Benzaldehyde.

Results and discussion

All the studied compounds gave well defined voltammograms (CV and SWV). Benzaldehyde and its schiff bases in CH_3OH have exhibited a cathodic peak respectively at $- 1.540$ V and in the range $- 1.135$ to $- 1.528$ V at 298 K. Schiff base (6) gave an additional cathodic peak which is attributed to reduction of $- NO_2$ group to hydroxyamine ($- NHOH$). The absence of anodic counterpart in reverse scan and negative shift of Ep with increasing scan rate (ν), in all the cases, reveal the irreversible nature of the electrode process. The cyclic and square wave voltammograms of schiff base (1) are depicted in Fig. 1A. The plots of i_{p_c} versus $\nu^{1/2}$ (50-500 m Vs^{-1}) for parent aldehyde and its schiff bases were found linear and passing through the origin have indicated that the reduction process is diffusion controlled. The plots of i_{p_c} versus $\nu^{1/2}$ for benzaldehyde and the schiff base (1) at 298 K are shown in inset Fig. 1A. The Ep, $\Delta Ep' = [Ep_{(alde.)} - Ep_{(schiff base)}]$ and $\Delta Ep'' = [Ep_{(schiff base derivative)} - Ep_{(parent schiff base(1))}]$ values at three different temperatures are given in Table 1. The Ep values and their shift viz. $\Delta Ep'$ and $\Delta Ep''$ as noted are associated with the nature of the substituent on phenylimino ring. The Ep values are found to decrease and $\Delta Ep'$ values are found to increase with the increase in temperature. The decrease in Ep values may be because of increased solubility and hence mobility of organic compound[3] whereas rise in $\Delta Ep'$ values may be ascribed to the difference in mobility of the parent aldehyde and the schiff base derived from it.

Figure 1B shows comparative reduction of benzaldehyde and the schiff base (1) in CH_3OH at 298 K. Examining the Ep and $\Delta Ep'$ values (Table 1) it is observed that $- CH = N -$ moiety of schiff bases (1)-(6) is reduced at positive potentials than that of $- CHO$ group of parental aldehyde. These observations are in concurrence with our earlier observation[1,2] and observations of others[4,5]. Further, reduction of dipolar $- NO_2$ group occurs at less negative potential to that of $- CH = N -$ and $- CHO$ groups[6].

The Ep values of all the studied schiff bases show the ease of reduction of $- CH = N -$ bond in the order $6 > 5 > 1 > 2 > 3 > 4$ which may be due to varied strength of resonance and polar effects exerted by the substituent on Ar' ring.

The potential shift with respect to parent aldehyde ($\Delta Ep'$) is in the range $- 0.012$ V to $- 0.405$ V at 298 K. The ease of reduction on the basis of $\Delta Ep'$ values follow the trend $4 > 3 > 2 > 1 > 5 > 6$ which is mainly due to the nature and the position of the substituent present on phenylimino ring (decreasing trend in electron donation of the substituent is 4'-OCH$_3$ > 4'-OH > 3'-OH > -H and the decreasing trend in electron withdrawal as 4'-NO$_2$ > 4'-Cl > -H). Among 3'-/4'-OH groups, 3'-OH group facilitates the reduction, as resonance effect being least at 3' position for electroactive group. This is consistent with the predictions made for similar groups on nitrobenzene derivatives by Gupta and Chatterjee[7].

The potential shift with respect to parent schiff base (1) ($\Delta Ep''$) is found in the range $- 0.010$ V to $+ 0.195$ V at 298 K. The values of $\Delta Ep''$ showing the effect of substituent on phenylimino ring follow the trend $4 > 3 > 2 > 5 > 6$. The Ep values of $- CH = N -$ bond is found shifted negatively in the range $- 0.010$ V to $- 0.198$ V for 4'-OCH$_3$ and 3'-/4'-OH derivatives and positively with $+ 0.010$ V to $+ 0.195$ V for 4'-NO$_2$ and 4'-Cl derivatives
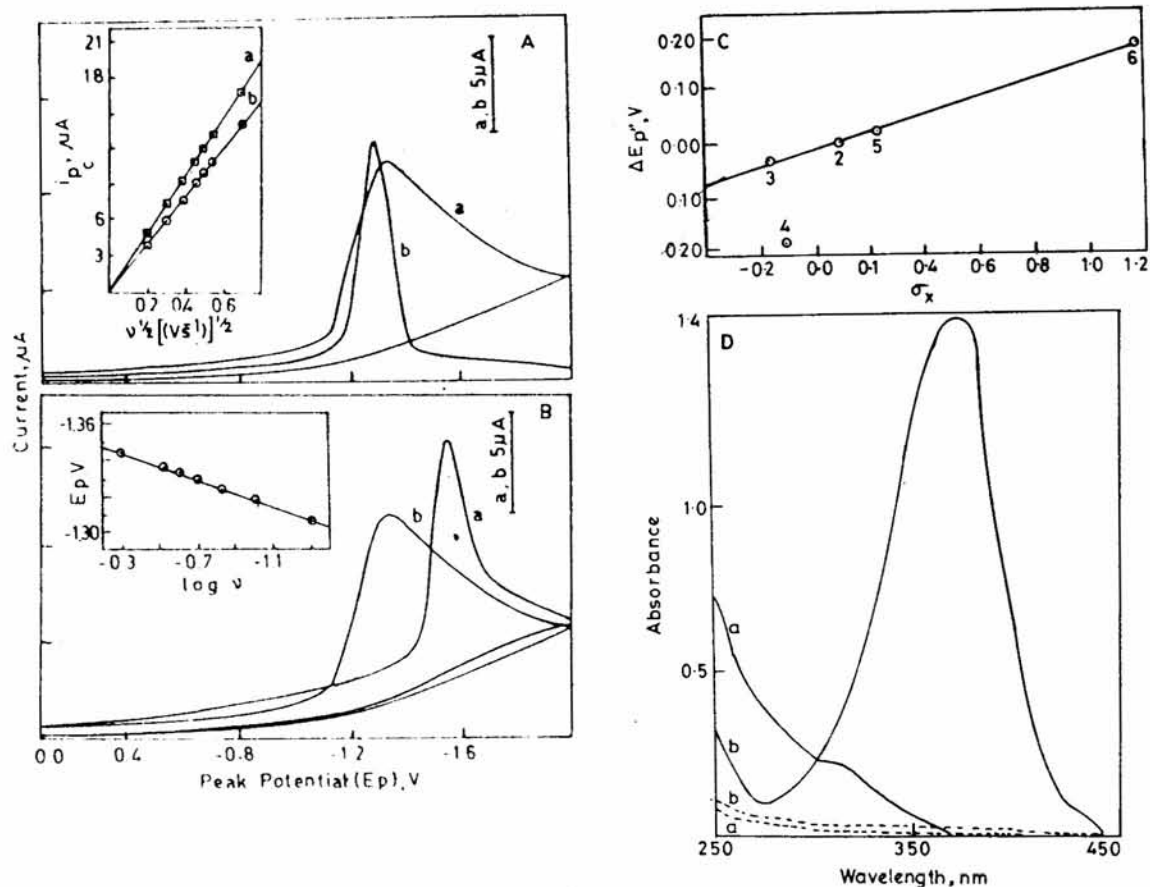
Fig. 1 – (A) Typical cyclicvoltammogram (a) and square wave voltammogram (b) of the schiff base (1) in CH₃OH at 298 K. In-set: Plot of ipc versus $v^{1/2}$ for benzaldehyde (a) and schiff base (1) (b) in CH₃OH at 298 K. Conc. = 1.0 mM; μ = 0.1 M LiCl; W.E. = HMDE; R.E. = Ag/AgCl (Cl⁻ satd.); v = 0.2 Vs⁻¹. (B) A comparative cyclicvoltammograms of benzaldehyde (a) and schiff base (1) (b) in CH₃OH at 298 K. Inset: Plot of Ep versus log v for the reduction of schiff base (1) in CH₃OH at 298 K. Conc. = 1.0 mM; μ = 0.1 M LiCl; W.E. = HMDE; R.E. = Ag/AgCl (Cl⁻ satd.); v = 0.2 Vs⁻¹. (C) Plot of ΔEp″ versus σ_x values for schiff bases (1)-(6) in CH₃OH at 298 K. Conc. = 1.0 mM; μ = 0.1 M LiCl; v = 0.2 Vs⁻¹. (D) UV absorption spectra of schiff base (1) (a) and (6) (b) before coulometry (——) and after complete coulometric reduction (......) in CH₃OH at 298 K.

respectively at 298 K. Among 4'-OCH₃ and 3'-/4'-OH derivatives, the trend of negative shift of Ep or ΔEp' is in the order 4'-OCH₃ > 4'-OH > 3'-OH which is likely to be due to electron dona-tion by resonance effect to the reaction centre (–CH=N–). The positive shift i.e. ease of re-duction of 4'-NO₂ and 4'-Cl follows the order 4'-NO₂ > 4'-Cl derivative which is likely to be due to more pronounced extramobile π-electron system of the dipolar –NO₂ group (as –R > –I) than that of 4'-Cl derivative (as –I > –R), because of more electronegative nature of chlorine atom.

The ease of reduction of –CH=N– bond in all the studied schiff bases with respect to parent aldehyde and the schiff base (1) is 6 > 5 > 2 > 3 > 4. This is likely to be due to a decrease in the electrophilicity of reaction at the reaction centre, which inhibits the migration of electron in the molecule. The schiff base (6) is having more electrophilic properties due to the presence of dipolar –NO₂ group with extramo-bile π-electron system.

The CPC experiment suggests that except the schiff base (6), all the schiff bases in CH₃-OH consume two electrons during –CH=N– bond reduction process, which is consistent with our earlier observation[2] and the observation of others[6] for –CH=N– bond reduction. The schiff base (6) consumes total six electrons of which four for the reduction of –NO₂ group at the potential –0.8 V and the other two for the reduction of –CH=N– bond at –1.55 V.

Diffusion coefficients

The diffusion coefficient values, (D$_{ox}$), of the azomethine group of the schiff bases (1)-(6) have been determined at 293, 298 and 303 ± 0.5 K from the slope of the plot i_{p_c} versus $v^{1/2}$. The cal-

Table 2 – Kinetic parameters for reduction of $-CH=N-$ bond of schiff bases (1)-(6) at HMDE at 293, 298 and 303 ± 0.5 K.
[Schiff base] = 1.0 mM; $\mu = 0.1$ M LiCl; W.E. = HMDE (0.016 cm^2); $\nu = 0.2$ Vs^{-1}.

Schiff base	Substituent on Ar' ring	Temp. ±0.5 K	αn_a (Ep – logν)	$D_{ox} \times 10^6$ cm^{2}s^{-1}	$k_{f,h}^0$ cms^{-1} at E = 0 volt	σ_x
1	–H	293	0.822	4.56	3.739×10^{-20}	—
		298	0.838	4.90	2.633×10^{-20}	—
		303	0.867	5.12	1.040×10^{-20}	—
2	3'-OH	293	0.798	4.38	4.647×10^{-20}	0.094
		298	0.814	4.70	3.278×10^{-20}	0.095
		303	0.840	4.94	1.297×10^{-20}	0.096
3	4'-OH	293	0.817	4.31	2.489×10^{-20}	−0.177
		298	0.841	4.96	1.748×10^{-20}	−0.178
		303	0.878	5.15	6.883×10^{-21}	−0.179
4	4'-OCH$_3$	293	0.715	4.32	2.892×10^{-20}	−0.111
		298	0.728	4.65	2.035×10^{-20}	−0.112
		303	0.749	4.95	8.023×10^{-21}	−0.113
5	4'-Cl	293	0.795	3.70	6.285×10^{-20}	0.226
		298	0.799	3.72	4.492×10^{-20}	0.232
		303	0.808	4.00	1.779×10^{-20}	0.233
6	4'-NO$_2$	293	0.776	4.11	5.610×10^{-19}	1.176
		298	0.786	4.62	3.955×10^{-19}	1.177
		303	0.810	5.02	1.585×10^{-19}	1.182

culated D_{ox} values at 298 K are in the range 3.72×10^{-6} to 4.96×10^{-6} cm^2 s^{-1} (Table 2).

Electrokinetic parameters

The electrokinetic parameters viz. transfer coefficient αn_a and the standard heterogeneous forward rate constant $(k_{f,h}^0)$ for all the studied schiff bases have been calculated, at 293, 298 and 303 ± 0.5 K from the CV data, using Eq. (1a)[8]

$$Ep = \frac{1.14\, RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F} \ln \frac{k_{f,h}^0}{D_{ox}^{1/2}} - \frac{RT}{2\alpha n_a F} \ln(\alpha n_a \nu) \quad \dots (1a)$$

and taking the slope and the intercept respectively of the plot[9] of Ep versus log ν.

Assuming αn_a to be the same for the parent compound and the derivative, the difference in their peak potentials at the same scan rate is

$$\Delta Ep'' = Ep_x - Ep_H$$
$$= \frac{RT}{\alpha n_a F} \left[\ln\left(\frac{k_{f,h}^0}{D_{ox}^{1/2}}\right)_x - \ln\left(\frac{k_{f,h}^0}{D_{ox}^{1/2}}\right)_H \right] \quad \dots (1b)$$

where Ep_x and Ep_H are the peak potentials of derivative and parent schiff base respectively.

The plot of Ep versus log ν for the reduction of schiff base (1) in CH$_3$OH at 298 K is depicted in inset Fig. 1B. All the calculated αn_a and $k_{f,h}^0$ (re-

ported at E = 0 volt) values are given in Table 2. The αn_a and D_{ox} values are found to increase while $k_{f,h}^0$ values are found to decrease with the increase in temperature, which account the shift of reduction potential towards positive (anodic) side.

Substituent constant σ_x values

The substituent constant σ_x is defined[10] as

$$\sigma_x = \log k_x - \log k_H \quad \dots (2a)$$

where k_x and k_H represent the rate constants for the substituted and unsubstituted molecules respectively and the corresponding relationship for the substituent effect in an irreversible reduction process[11] is given by Eq. (2b)

$$\sigma_x = \log(k_{f,h}^0)_x - \log(k_{f,h}^0)_H \quad \dots (2b)$$

where $(k_{f,h}^0)_x$ and $(k_{f,h}^0)_H$ are standard heterogeneous rate constant of substituted and unsubstituted schiff base (1) respectively. The values of σ_x determined using Eq. (2b) are noted in Table 2. It has been found that σ_x values are depending on the nature and the position of the substituent on phenylimino ring. The values of σ_x, except schiff base (6), are almost the same with the corresponding value reported by Hammett[12] and Jaffe[13], on the basis of calculation made using ion-

isation constant of benzoic acid and its derivatives in H_2O at 25°C. The σ_x value of 4'-NO_2 group is becoming strong through resonance (cross conjugation) with the reaction centre[14].

Correlation of $\Delta Ep''$ with Hammett constant (σ_x)

Zuman[15] reported a linear relation between the reduction potential and the σ_x values. It has been shown that when αn_a and D_{ox} of the parent compound and its derivatives are nearly the same[8], the $\Delta Ep''$ at the same scan rate can be correlated with σ_x values to get the reaction constant ρ_π, $-CH=N-$ (Eq. 2c), which explains the ease of quantitative reduction.

Equation (2c) is the simplified form of Eq. (1b) given as,

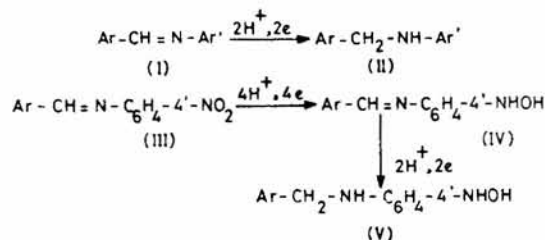$$\Delta Ep'' = \rho_{\pi, -CH=N-} \cdot \sigma_x \qquad \ldots (2c)$$

Plot of $\Delta Ep''$ versus σ_x (Fig. 1c) reveals the linear relation with positive value of reaction constant $\rho_{\pi, -CH=N-}$ which is equal to 0.159 V, $r = 0.98$, $s = 0.027$, $s_\rho = 0.022$ at 298 K for the series of schiff bases (1)-(6). The positive value of $\rho_{\pi, -CH=N-}$ indicates the nucleophilic[10,13] nature of the electrode process, i.e. electron uptake of the depolariser is the rate determining step and the reaction is facilitated because of low electron density[13,15] at the reaction centre. These results prove that the substituent has appreciably affected the reduction of $-CH=N-$ bond by its polar and resonance effect through phenylimino ring.

The $\rho_{\pi, -CH=N-}$ value is independent of substituent and depends on temperature and the medium of investigation. The $\rho_{\pi, -CH=N-}$ values found to decrease with rise in temperature for the studied medium.

Reduction mechanism

The CPC reduction products are characterised by monitoring UV spectra in the wavelength range 250-400 nm. Figure 1D indicates that with the progress of electrolysis of schiff bases (1) and (6) the initial λ_{max} around 320 nm [$\simeq$ 380 nm for schiff base (6)] display a systematic decline and there is no absorbance peak above 250 nm and onwards after complete electrolysis. The dye test and the 2, 3, 5, 6-tetrachlorobenzoquinone test for chemical analysis of primary aromatic amine gave a negative response. All experimental evidences of CV, UV spectral and chemical test indicate that above electrode process in schiff bases (1)-(6) (I/III) is irreversible and diffusion controlled with two electrons reduction ($-CH=N-$) reaction transferring the reactant to an inactive secondary amine ($-CH_2-NH-$) (II/V). In the case of schiff base (6) (III), prior to two electron

reduction of $-CH=N-$ bond, the $-NO_2$ group also reduces to $-NHOH$(IV)[16] by taking four electrons and then transferring it into (V) by two electrons reduction.

$$Ar-CH=N-Ar' \xrightarrow{2H^+, 2e} Ar-CH_2-NH-Ar'$$
$$\text{(I)} \qquad\qquad \text{(II)}$$

$$Ar-CH=N-C_6H_4-4'-NO_2 \xrightarrow{4H^+, 4e} Ar-CH=N-C_6H_4-4'-NHOH$$
$$\text{(III)} \qquad\qquad\qquad\qquad \text{(IV)}$$
$$\downarrow 2H^+, 2e$$
$$Ar-CH_2-NH-C_6H_4-4'-NHOH$$
$$\text{(V)}$$

This is consistent with the explanation given for the reduction of $-CH=N-$ bond[17] and for the $-NO_2$ group[18]. Further, IR studies of CPC reduction products gave broad band $\simeq 3400$ cm^{-1} also representing the existence of secondary amine group (II/V) and the absence of stretching bonds for $-NO_2$ group indicate its reduction. Thus the spectral observations of UV and IR are also consistent with the suggested mechanism.

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