

Comparison between Heterogeneous and Homogeneous Electron Transfer in *p*-Phenylenediamine Systems

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The one-electron oxidation of selected *p*-phenylenediamines to form the corresponding radical cations has been studied at a Pt electrode in dimethylformamide and acetonitrile solutions containing 0.1 mol dm⁻³ NaClO₄. The standard redox potentials, the diffusion coefficients and the standard rate constants have been evaluated in the range between room temperature and the melting point of the respective solvent using cyclic voltammetry. It has been shown that the dynamics of solvent reorientation affects the heterogeneous electron-transfer rate, as opposed to the homogeneous process. The free energies of activation are much greater in the heterogeneous than in the homogeneous case. Both results are explained by the different shape of the activated complexes, consisting of one or two ellipsoidal molecules.

Electron-exchange reactions are activated processes. The observed rate constant, k_s , is related to the overall free-energy barrier, ΔG^* , and the pre-exponential term, A , by

$$k_s = A \exp(-\Delta G^*/RT). \quad (1)$$

According to the 'encounter pre-equilibrium' model,¹⁻⁴ the formation of a precursor complex of the reactants (in homogeneous reactions) or of the system reactant-electrode (in heterogeneous reactions) precedes the activated electron transfer. With this assumption A is given by

$$A = \kappa_{el} \nu_n K_p \quad (2)$$

where ν_n is the effective nuclear frequency factor (the frequency of surmounting the free-energy barrier in the classical high-temperature limit), κ_{el} is the electronic transfer coefficient and K_p is the association constant of the precursor complex. Generally K_p can be expressed by the Eigen equation.⁵ Another expression for K_p is found if it is assumed that the transfer takes place preferentially within a small range of distances δr .⁶⁻⁸ Then for homogeneous reactions:

$$K_p = 4\pi\bar{r}^2\delta\bar{r}N \exp[-w(d)/RT] \quad (3)$$

and for heterogeneous reactions:

$$K_p = \delta\bar{r} \exp[-w(d)/RT] \quad (4)$$

where \bar{r} is the mean particle radius, N is Avogadro's constant and $w(d)$ is the energy required to transfer the reacting particle from the bulk solution to the reaction site. In the electrochemical case $w(d)$ is equivalent to the so-called 'Frumkin correction'. ν_n may be approximated in the two-mode model used^{9,10} by the mean frequencies of molecular vibration, ν_v , and solvent reorientation, ν_o .

Generally two limiting cases are discussed: In the first the pre-exponential term is

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controlled by inner vibrations of the reactant, whereas in the second it is controlled only by the dynamics of solvent reorientation *via* the longitudinal relaxation time, τ_L , of the given solvent. The latter is valid¹¹ if

$$P(\lambda) = \nu_i[\lambda_i/(\lambda_i + \lambda_o)]^{\frac{1}{2}} \exp(-\lambda_i/4RT) > \tau_L^{-1} \quad (5)$$

where λ_i and λ_o are the inner and outer reorganization energies in the sense of Marcus's theory.^{12,13} In this case ν_n may be expressed as follows.¹⁴⁻¹⁶

$$\nu_n = \tau_L^{-1}(\lambda_o/16\pi RT)^{\frac{1}{2}} \quad (6)$$

If, however, the reaction rate is controlled by molecular vibrations³

$$\nu_n = \nu_i[\lambda_i/(\lambda_i + \lambda_o)]^{\frac{1}{2}} \quad (7)$$

The latter approximation is questionable and leads to pre-exponential terms much higher than observed.¹⁷ It has to be assumed that in this case the electronic transfer coefficient is small ($\kappa_{el} \ll 1$).¹⁸

Generally λ_i as well as λ_o are different for homogeneous and heterogeneous reactions. Up to now the theories of electron-transfer reactions were tested for the heterogeneous case mostly from experiments at one temperature. To our knowledge only for some aquo- and amino- complexes in aqueous solutions¹⁹ has the temperature dependence of electron-transfer kinetics in both homogeneous and heterogeneous cases been simultaneously studied.

For *p*-phenylenediamines the homogeneous electron exchange has been studied extensively,^{17,20,21} but the corresponding heterogeneous reaction in dimethylformamide and acetonitrile only at one temperature²² and for unsubstituted *p*-phenylenediamine in different solvents.²³ It was found that the solvent reorientation dynamics play an important role in the electrochemical case,²³ whereas the homogeneous reaction is independent of τ_L .

The explanation of this problem was the purpose of this work. We have studied the first oxidation step of selected *p*-phenylenediamines (PPD), forming stable radical cations



for a wide range of temperatures in dimethylformamide and acetonitrile.

Experimental

Materials

All amines used [*p*-phenylenediamine (PPD), *N,N*-dimethyl-*p*-phenylenediamine (DMPPD), *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPPD) and 2, 3, 5, 6-tetramethyl-*p*-phenylenediamine (DAD)] were commercial products, purified by vacuum sublimation or distillation. Analytical-grade NaClO_4 was dried at 120 °C. Analytical-grade ferrocene (Fc) was used as received. Acetonitrile (ACN) and dimethylformamide (DMF) were dried and purified for electrochemical use in the conventional manner.²⁴

Apparatus

To obtain the transfer rate constant cyclic voltammetry was used. The measuring system for cyclic voltammetry was constructed from a Wenking VSG 72 voltage scan generator and a home-built potentiostat. The cyclic voltammograms were stored in a Nicolet 2020 digital oscilloscope. To compensate the ohmic drop a current-follower configuration with negative input impedance was used.^{25,26} The working electrode was a Pt disc with an area of 0.011 cm² and was polished before each use with diamond paste. The counter electrode was a platinum wire and the reference electrode was an aqueous saturated

Table 1. Electrochemical parameters and diffusion coefficients D for oxidation of selected p -phenylenediamines at 20 °C

solvent	solute	$E^\circ/\text{V vs. Fc/Fc}^+$	$D/\text{cm}^2 \text{ s}^{-1}$	$k_s/\text{cm s}^{-1}$	$(dE/dT)/\text{mV K}^{-1}$
DMF	PPD	-0.28	9.1×10^{-6}	0.092	0.91
	DMPPD	-0.34	7.4×10^{-6}	0.23	0.79
	TMPPD	-0.29	10.9×10^{-6}	0.19	0.54
	DAD	-0.37	10.8×10^{-6}	0.080	1.10
ACN	PPD	-0.11	20.6×10^{-6}	0.6 ^a	1.21

^a Extrapolated value.

calomel electrode with an agar plug. An additional platinum wire was dipped in the solution and was connected *via* a 0.1 μF capacitor to the reference electrode. The role of this wire was to shunt the high-frequency components of the applied signal from the reference electrode.²⁷

All potentials at room temperature were also referred to ferrocene/ferricinium (Fc/Fc^+).

Procedure

The standard heterogeneous rate constants, k_s , were evaluated from the observed differences between anodic and cathodic peak potentials ΔE of the cyclic voltammograms using the relationship of Nicolson.²⁸ ΔE could be measured with a precision of *ca.* 2 mV for potential scan rates between 0.1 and 100 V s^{-1} (depending on k_s). The diffusion coefficients D and the standard redox potentials E° were also determined from cyclic voltammograms recorded at scan rates of 0.1–1 V s^{-1} .

The error limit of the electrochemical parameters was *ca.* 20% for k_s , 10% for D , and 5 mV for E° .

All measurements were carried out in solutions deaerated with pure argon at different temperatures > -60 °C. The reference electrode was kept at room temperature (20 °C). The concentrations of supporting electrolyte (NaClO_4) and reactants were 0.1 and 0.001 mol dm^{-3} , respectively.

The working electrode was immersed in the deaerated solution and cycled many times in the potential range ± 0.2 V around the redox potential of the system studied. By this procedure reproducible results were obtained, although the surface state is not well defined.

Results

Dimethylformamide Solutions

For all systems studied, current–potential curves with nearly equal anodic and cathodic peak currents were obtained.

A summary of the evaluated electrochemical parameters (at 20 °C) is presented in table 1. The results agree very well with the literature data.^{22, 23}

With increasing temperature the standard redox potentials are shifted to more positive values (table 1). This indicates negative solvation entropies for the studied radical cations, but the effect is not large, only somewhat greater than for metallocenes²⁹ and is close to the values for quinones.³⁰ It is concluded that the aromatic radical cations are relatively weakly solvated. The results indicate also that the association between radical cations and ClO_4 anions is small. This is in agreement with the independence of the standard redox potentials of the concentration of the supporting electrolyte.²³

For DMF as solvent the energy of activation for the diffusion process is *ca.* 30% greater than the energy of activation for viscosity, as in the case of quinones.³¹ Since the electrode reaction rates could be measured between $-60\text{ }^{\circ}\text{C}$ and $+20\text{ }^{\circ}\text{C}$ (213–293 K), the activation parameters could be obtained rather precisely.

Acetonitrile Solutions

In this solvent all reactions studied were much faster than in dimethylformamide. Therefore the rate constants could not be measured at room temperature with the method used. Although the reactions were slower at low temperatures, precise measurements were only possible with PPD. For all other systems studied even at $-30\text{ }^{\circ}\text{C}$ the rate constants exceeded 0.2 cm s^{-1} . Since the melting point of 0.1 mol dm^{-3} NaClO_4 solutions lay between -50 and $-60\text{ }^{\circ}\text{C}$, the useful temperature range was too small to measure the activation parameters precisely. Even for PPD it was impossible to obtain k_s at $20\text{ }^{\circ}\text{C}$. This disagrees with the results of Pluschke²² and Opałó,²³ but their values $k_s = 0.17\text{ cm s}^{-1}$ and $k_s = 0.22\text{ cm s}^{-1}$, respectively, are close to the limit of classical cyclic voltammetry. Therefore in ACN solutions only the PPD/PPD⁺ system could be measured with the required precision, and only kinetic data for this system will be discussed further.

The temperature dependence of the other electrochemical parameters (D and E°) can be interpreted in the same way as in DMF solutions.

Discussion

Heterogeneous Kinetics

To determine the activation parameters exactly the temperature dependence of the pre-exponential factor has to be known. With the experimental values of λ_o (for DMF solutions *ca.* 100 kJ mol^{-1} , see later) and calculated values of λ_i (*ca.* 10 kJ mol^{-1} at 293 K ^{17, 20})† it is found from the inequality of Ovchinnikova^{11a} [eqn (5)] that $P(\lambda) > \tau_L^{-1}$. Therefore we tried to interpret the experimental results using eqn (6) and (4) with $w(d) = 0$ using the following expression for k_s .^{29, 32}

$$k_s = \kappa_{el} \delta r \tau_L^{-1} (\lambda_o / 16\pi RT)^{\frac{1}{2}} \exp[-(\lambda_o + \lambda_i) / 4RT]. \quad (9)$$

Although in the above equations λ_i and λ_o as well as τ_L are temperature dependent, to a first approximation λ_i and λ_o may be assumed to be constant. This is allowed since in the heterogeneous case λ_i is small compared with λ_o . Also the term $(1/n^2 - 1/\epsilon)$ in λ_o [cf. eqn (11)] varies by only 3% within the temperature range used. If the temperature dependence of τ_L can be described as²⁹

$$\tau_L^{-1} = A_L \exp(-H_L / RT) \quad (10)$$

from eqn (9) a linear relationship between $\ln(k_s T^{\frac{1}{2}})$ and $1/T$ should be observed with a slope equal to $(\lambda_i/4 + \lambda_o/4 + H_L)$ and an intercept equal to $\ln A_L \kappa_{el} \delta r (\lambda_o / 16\pi R)^{\frac{1}{2}}$.

Dielectric relaxation data for DMF as well as for ACN are incomplete, but with the available values^{33, 34} it is possible to estimate A_L and H_L for both DMF and ACN. A_L are 33.2×10^{12} and $4.3 \times 10^{12}\text{ s}^{-1}$, and H_L are 4.6 and 4.2 kJ mol^{-1} for ACN and DMF, respectively.

In fig. 1 $\ln(k_s T^{\frac{1}{2}})$ is plotted *vs.* $1/T$. Linear relationships with correlation coefficients always better than 0.99 are found. The experimentally obtained values of intercepts and slopes for all systems studied are presented in table 2.

From the experimental slope the sum of λ_i and λ_o can be obtained after subtraction

† In ref. (17) and (20) the calculated values of λ_i for the homogeneous case have to be multiplied by 2; therefore for the heterogeneous λ_i the given values can be used.

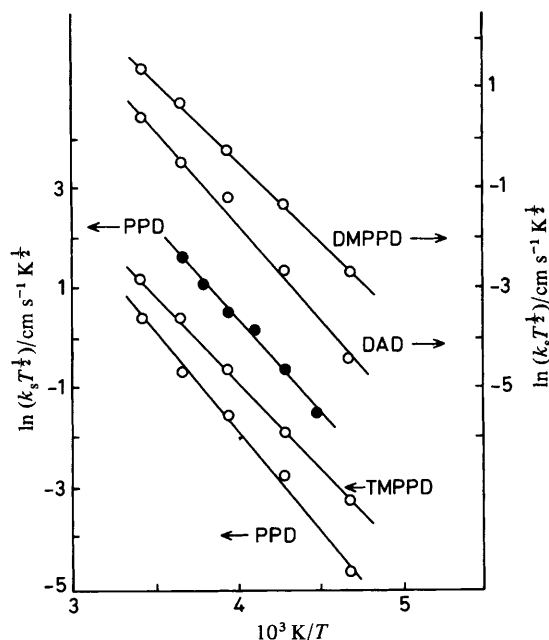


Fig. 1. $\ln(k_s T^{3/2})$ as a function of T^{-1} for *p*-phenylenediamines studied in dimethylformamide (○) and acetonitrile (●). Temperature range 213–293 K.

Table 2. Experimental kinetic parameters for electro-oxidation of selected *p*-phenylenediamines

solvent	solute	$(\lambda_0/4) + (\lambda_1/4) + H_L$ /kJ mol ⁻¹	$\lambda_0 + \lambda_1$ /kJ mol ⁻¹	$A_L \kappa_{el} \delta r (\lambda_0 / 16\pi R)^{1/2}$ /cm s ⁻¹ K ^{1/2}
DMF	PPD	32.5	113	10.3×10^6
	DMPPD	26.3	88	2.0×10^6
	TMPPD	29.0	99	5.1×10^6
	DAD	30.6	106	4.7×10^6
ACN	PPD	30.7	104	4.2×10^6

of H_L . The calculated values of λ_1 (10 kJ mol⁻¹ at the mean temperature of the experiments²⁰) are small compared with the experimental λ_0 of ca. 100 kJ mol⁻¹.

To calculate λ_0 the classical Marcus theory^{12,13} can be used, in which λ_0 is given as a function of the polarity parameter $\gamma = (1/n^2 - 1/\epsilon)$ of the solvent, depending on its refractive index n and dielectric constant ϵ , and the geometric parameter

$$g \approx (1/2)(1/\bar{r} - 1/2d)$$

where \bar{r} is the 'effective' radius of the reacting particle and d is the distance from the electrode surface when electron transfer occurs:

$$\lambda_0 = (e_0^2 N / 8\pi\epsilon_0) (1/n^2 - 1/\epsilon) (1/\bar{r} - 1/2d). \quad (11)$$

According to eqn (11) λ_0 depends strongly on \bar{r} and d . In the spherical approximation \bar{r} can be calculated from the molar volume of the substances studied. Large values of λ_0 indicate that the image interaction of the reactant with the electrode can be neglected

Table 3. Calculated kinetic parameters for electro-oxidation of selected *p*-phenylenediamines

solvent	solute	spherical model		ellipsoidal model		$A_v \kappa_{el} \delta r (\lambda_o / 16\pi R)^{1/2}$ /cm s ⁻¹ K ^{1/2}
		\bar{r}/nm	$\lambda_o/\text{kJ mol}^{-1}$	\bar{r}/nm	$\lambda_o/\text{kJ mol}^{-1}$	
DMF	PPD	0.33	97	0.278	115	4.3×10^5
	DMPPD	0.37	87	0.294	109	4.2×10^5
	TMPPD	0.34	91	0.406	79	3.6×10^5
	DAD	0.4	76	0.317	101	4.0×10^5
ACN	PPD	0.33	111	0.278	131	3.5×10^6

^a Calculated with λ_o from the ellipsoidal model and $\kappa_{el} \delta r = 60$ pm.

($d = \infty$) as was proposed by Hale.³⁵ The values of r and λ_o for the spherical approximation with $d = \infty$ are given in table 3.

If the molecule is approximated by an ellipsoid with the semi axes $a > b > c$, $1/r$ is expressed by^{20,36}

$$1/\bar{r} \approx (a^2 - c^2)^{1/2} / F(\alpha, \phi) \quad (12)$$

where $\phi = \arcsin(a^2 - c^2)^{1/2} / a$; $\alpha = \arcsin[(a^2 - c^2)/(a^2 - b^2)]^{1/2}$ and $F(\alpha, \phi)$ is the elliptic integral of the first kind. The values of \bar{r} and λ_o for this model (with the assumption $d = \infty$) are also given in table 3. The semiaxes are obtained from crystallographic data [see ref. (20)]. λ_o for heterogeneous processes, calculated from both models, differ by less than ca. 20% if the image charges are neglected ($d \rightarrow \infty$).

In table 3 the calculated values of the pre-exponential factor are also given, calculated with λ_o values from the ellipsoidal model and with values of $\kappa_{el} \delta r$ equal to 60 pm.³⁷ The agreement between theory and experiment (table 2) is satisfactory. For values of $\kappa_{el} \delta r = 60$ pm it can be assumed that the reaction is adiabatic for the closest approach of the reactant to the electrode surface ($\kappa_{el} = 1$).^{37,38}

For interpretation the apparent standard rate constants k_s have been used. This may be correct in view of the results presented in ref. (23). For the PPD system it was found that k_s is nearly independent of the concentration of the supporting electrolyte. Moreover E° values (see table 2) are close to the estimated zero-charge potential of the Pt electrode in perchlorate solutions [cf. ref (23) and references therein]. Therefore the measured values of k_s can be taken as 'true' values, not influenced by the potential drop in the diffuse layer. Measured (table 2) and calculated (table 3) data of the pre-exponential and the exponential terms of k_s correspond well.

Comparison between Heterogeneous and Homogeneous Electron-transfer Kinetics

The logarithm of the homogeneous electron self-exchange rate constant of *p*-phenylenediamines was found to be independent of τ_L but proportional to the solvent polarity parameter γ . This can be discussed in terms of the classical Marcus model without considering solvent relaxation phenomena.^{17,20,21}

We assume that the different behaviour is connected with the structure of the activated complex in both cases, expressed by the differences in λ_i and in the geometric parameter g . Since two molecules are involved in homogeneous processes, $\lambda_i(\text{hom}) = 2 \lambda_i(\text{het})$ [in the present case at 298 K: $\lambda_i(\text{hom}) \approx 20$ kJ mol⁻¹].^{20,32}

The geometric parameter for homogeneous processes is $g = 1/\bar{r} - 1/2d$, where $2d$ is the distance between the molecule centres. For spherical molecules $2d \geq 2r$ and for ellipsoids $2d \geq 2r$, since the minimum distance is given by the smallest semiaxis, c . If the image interaction can be neglected [$d(\text{het}) \rightarrow \infty$] one obtains for spherical molecules $g(\text{hom}) = g(\text{het}) \approx 1/2r$. For ellipsoids, however, $g(\text{hom})$ may be much smaller than $g(\text{het})$, the minimum value being $g(\text{hom}) \approx 1/\bar{r} - 1/2c$.

The experimental values of $\lambda_o(\text{hom})$ were *ca.* 40 kJ mol⁻¹²⁰ for *p*-phenylenediamines, compared with 100 kJ mol⁻¹ found for $\lambda_o(\text{het})$ (see table 3). With the rather small $\lambda_o(\text{hom})$ and $\lambda_i(\text{hom})$ always greater than $\lambda_i(\text{het})$ it results from the inequality of Ovchinnikova [eqn (11a)] that $P(\lambda)_{\text{het}} > P(\lambda)_{\text{hom}}$.³⁹ For *p*-phenylenediamines $P(\lambda)_{\text{hom}} \approx \tau_L^{-1}$, $P(\lambda)_{\text{het}} < \tau_L^{-1}$. The homogeneous electron exchange may therefore be just a borderline case, whereas in the heterogeneous reaction the solvent dielectric relaxation dynamics prevail.

Conclusion

It has been shown that the experimental results for the heterogeneous electron transfer in *p*-phenylenediamine systems can be discussed in terms of an 'encounter pre-equilibrium' model in which the pre-exponential term is determined by solvent reorientation dynamics. The larger value of λ_i for homogeneous reactions explains the independence of electron-transfer kinetics on solvent reorientation dynamics in this case.

For electron-transfer reactions it is generally expected that heterogeneous processes should be more likely to be controlled by dielectric relaxation properties of the solvent than homogeneous processes.

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