

# The Effect of Tetraalkylammonium Ions on the Heterogeneous Charge Transfer Kinetics for the Reduction of Benzonitrile and Dinitromesitylene in DMF

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The kinetics of the heterogeneous charge transfer during the reduction of benzonitrile in DMF containing different tetraalkylammonium ions have been studied at mercury electrodes. The simple Frumkin double layer correction, which assumes that electron transfer takes place at the outer Helmholtz plane, could not be applied to the data. Only the smallest tetraalkylammonium cations adsorb specifically to the electrode. For tetraalkylammonium ions containing one or more methyl groups specific adsorption was observed at negative potentials. Activation energies ranging from 20 to 40 kJ/mol were observed for the charge transfer processes on going from large to small electrolyte cations. It was shown that the simple Frumkin correction does apply to processes taking place near the potential of zero charge, for example during the reduction of dinitromesitylene in DMF. A model is discussed in which the site of charge transfer is not necessarily the outer Helmholtz plane and is different for different processes.

A number of heterogeneous charge transfer kinetic studies of the reduction of organic compounds at mercury electrodes in aprotic solvents has been carried out in order to test double layer theory on simple outer-sphere electron transfer processes.<sup>1-4</sup> In most cases only a single electrolyte has been used in the studies and under these conditions the theory holds quite well. The simplest version of double layer theory assumes

that charge transfer takes place at the outer Helmholtz plane (OHP) and that the effect of the double layer can be accounted for by the so-called Frumkin correction.<sup>5</sup> However, when studying the effect of different electrolytes, deviations from the simple theory are observed. Baranski and Fawcett have shown that it cannot be assumed that the electron transfer takes place at the OHP.<sup>6</sup> They also proposed a model similar to the one discussed in this paper.

In order to compare the rates of heterogeneous and homogeneous electron transfer reactions, it is necessary to have an adequate understanding of the influence of the double layer. In recent years, attempts have been made to explain discrepancies between experimental and theoretical results. Some deviations can be accounted for by considering the effect of ion-pairing, specific adsorptions and of the negatively charged electrode.

A phenomenon which has not been adequately investigated is the effect of the size of tetraalkylammonium ions on the rate of reduction of organic compounds. Several years ago it was shown that the heterogeneous rate constants for the reduction of a number of organic compounds is increased dramatically as the size of the cation is decreased.<sup>7,8</sup> This effect has been attributed to changes in the double layer with the different cations<sup>9</sup> but this has not really been demonstrated. From a practical viewpoint, this phenomenon can be of great importance. For example, it has been shown that electrode kinetic studies of the reactions of some anion radicals of

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diazo compounds can be carried out using  $\text{Me}_4\text{N}^+$  as the electrolyte cation while such studies are not possible when the cation is  $\text{Bu}_4\text{N}^+$  due to very slow electron transfer.<sup>10,11</sup>

This investigation was carried out to gain more detailed information on the effect of tetraalkylammonium ions on the rate of heterogeneous charge transfer during the reduction of some organic compounds.

## EXPERIMENTAL

The instrumentation, cells, electrodes, reference electrodes, and solvent purification procedures were identical to those used previously.<sup>12</sup> The unsymmetrical electrolytes,  $\text{Bu}_3\text{MeNI}$ ,  $\text{Bu}_2\text{Me}_2\text{NI}$  and  $\text{BuMe}_3\text{NI}$  were prepared according to standard procedures. The benzonitrile was reagent grade and used without further purification. Dinitromesitylene was prepared by nitration of mesitylene.

**Determination of double layer capacitances.** The double layer capacitances ( $C_{dl}$ ) were determined by A.C. voltammetry.<sup>13</sup> The method involves measuring the in phase  $i_1$  and out-of-phase  $i_2$  components of the current and  $C_{dl}$  is then calculated from eqn. (1)

$$C_{dl} = (i_1^2 + i_2^2) / \omega A V i_2 \quad (1)$$

where  $\omega$  is the angular frequency,  $A$  is the electrode area, and  $V$  is the amplitude of the sine wave. A 10 mV peak-to-peak amplitude and a frequency of 1000 Hz were used. The potential of zero charge for a mercury electrode is  $-0.21$  V vs. S.C.E.<sup>14</sup>

**Determination of the heterogeneous charge transfer coefficient.** The transfer coefficient ( $\alpha$ ) was determined by A.C. measurements. Reversible potentials were determined by the position of the maximum of the fundamental total magnitude signal for frequencies ranging from 10 to 1000 Hz. The phase angle maxima were determined with frequencies ranging from 1000 to 5000 Hz. The transfer coefficient was calculated using eqn. (2) where  $(E_{dc})_{\max}$  is the potential at the maximum phase angle. The error in the determination of  $\alpha$  was less than  $\pm 0.01$ .

$$(E_{dc})_{\max} = E_{\text{rev}} + (RT/nF) \ln(\alpha/(1-\alpha)) \quad (2)$$

**The determination of the diffusion coefficient.** At low frequencies the electron transfers of interest in this study are diffusion controlled and under these conditions the magnitude of the fundamental current ( $I$ ) is proportional to the

square root of the diffusion coefficient,  $I(\omega) = f(D^{1/2})$ . The value reported for benzonitrile<sup>4</sup> was taken as a standard in order to determine other values.

**The determination of the electrode area.** The electrode area ( $A$ ) was determined by linear sweep voltammetry. At low sweep rates, where the electron transfer can be considered to be reversible, the peak current is proportional to the  $A$ . Measurements were carried out on the reduction of benzonitrile.

**The determination of heterogeneous rate constants.** The heterogeneous rate constants ( $k_s$ ) were determined by derivative cyclic voltammetry.<sup>14</sup> The method has been described in detail.

## RESULTS AND DISCUSSION

The differential capacitance at the mercury–*N,N*-dimethylformamide (DMF) interface has been studied by a number of researchers. Recent studies by Fawcett, Ikeda and Sellan<sup>15</sup> employed several tetraalkylammonium ions and led to the conclusion that ionic specific adsorption is negligible.

In order to test for an effect of the size of tetraalkylammonium ions on the differential capacitance, we systematically varied the supporting electrolyte cation from  $\text{Me}_4\text{N}^+$  to  $\text{Hx}_4\text{N}^+$

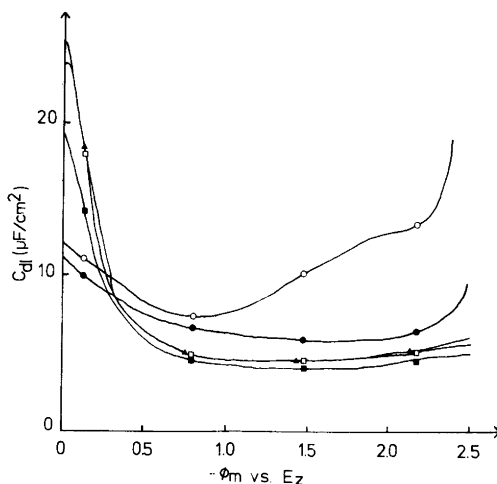


Fig. 1. The double layer capacitance as a function of the potential for some tetraalkylammonium ions.  $\circ$ , 0.1 M  $\text{Me}_4\text{NBF}_4$ ;  $\square$ , 0.1 M  $\text{Pr}_4\text{NBF}_4$ ;  $\bullet$ , 0.1 M  $\text{Et}_4\text{NBF}_4$ ;  $\blacksquare$ , 0.1 M  $\text{Bu}_4\text{NBF}_4$ ;  $\blacktriangle$ , 0.1 M  $\text{Hx}_4\text{NClO}_4$ .

(tetrahexylammonium ion). The results are illustrated in Fig. 1. With the exception where  $\text{Me}_4\text{NBF}_4$  was the supporting electrolyte, the differential capacitance was relatively constant at potentials ranging from about  $-0.5$  to  $-2.5$  V vs.  $E_z$ , the potential of zero charge. The differential capacity does depend upon the size of the  $\text{R}_4\text{N}^+$  and increases as the cation decreases in size.

With all of the symmetrical  $\text{R}_4\text{N}^+$  except  $\text{Me}_4\text{N}^+$ , the differential capacitance was observed to be independent of cation concentration. This indicates that there is no specific adsorption of cations in these cases in the potential region studied. However, the situation is quite different with  $\text{Me}_4\text{N}^+$  in which case the differential capacitance increased at negative potentials and was observed to be dependent upon the cation concentration (Fig. 2). The minima observed at  $E_z$  at the lowest concentrations indicate that specific adsorption at  $E_z$  is negligible in these cases.

Differential capacitance data using some unsymmetrical cations, with varying number of methyl and butyl groups, are shown along with that for  $\text{Me}_4\text{N}^+$  and  $\text{Bu}_4\text{N}^+$  in Fig. 3. The capacitance with the unsymmetrical cations increases at negative potentials as it does with  $\text{Me}_4\text{N}^+$ , indicating specific adsorption. The degree of specific adsorption is dependent upon the

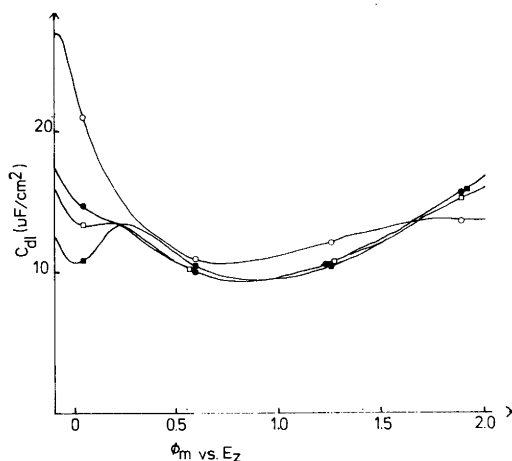


Fig. 2. The double layer capacitance as a function of the potential for different concentrations of  $\text{Me}_4\text{NBF}_4$ :  $\circ$ , 0.1 M  $\text{Me}_4\text{NBF}_4$ ;  $\bullet$ , 0.05 M  $\text{Me}_4\text{NBF}_4$ ;  $\square$ , 0.025 M  $\text{Me}_4\text{NBF}_4$ ;  $\blacksquare$ , 0.01 M  $\text{Me}_4\text{NBF}_4$ .

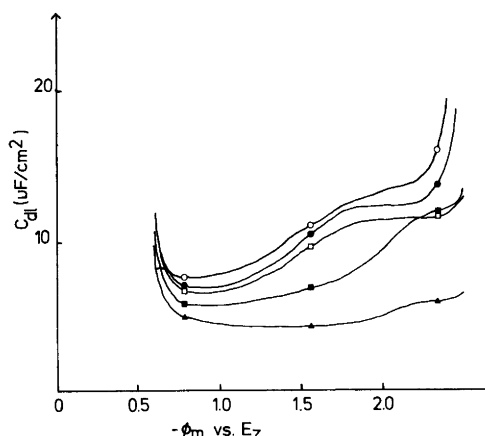


Fig. 3. The double layer capacitance as a function of the potential for some unsymmetrical alkylammonium ions:  $\circ$ , 0.1 M  $\text{Me}_4\text{NBF}_4$ ;  $\bullet$ , 0.1 M  $\text{Me}_3\text{BuNI}$ ;  $\square$ , 0.1 M  $\text{Me}_2\text{Bu}_2\text{NI}$ ;  $\blacksquare$ , 0.1 M  $\text{MeBu}_3\text{NI}$ ;  $\blacktriangle$ , 0.1 M  $\text{Bu}_4\text{NI}$ .

number of methyl groups in the cation and, at any given potential, increases with increasing number of methyl groups. The potential range studied was limited to  $-0.5$  to  $-2.3$  V vs.  $E_z$  since the iodide counter ion adsorbs at more positive potentials.

The results discussed in the preceding paragraphs suggest that it is possible to vary the double layer properties over a wide range by the variation of the nature of the tetraalkylammonium ion of the supporting electrolyte. Thus, heterogeneous kinetic studies in which significant variations in the cations are made should provide a much more stringent test of the applicability of double layer theories than those in which either a single or a limited number of cations are employed. We chose to study the kinetics of heterogeneous charge transfer to two substrates, benzonitrile and dinitromesitylene. The reason for these choices is that benzonitrile (BN) is reduced at a potential well removed from  $E_z$  where substantial double layer corrections are necessary and dinitromesitylene reduces near the  $E_z$  where double layer corrections, in the absence of specific adsorption, are small.

The most commonly used double layer correction is given by the Frumkin equation, (3), where  $\phi_r$  is the potential of the

$$k_s^{\text{app}} = k_s^{\text{corr}} \exp[(an - z)(\phi_r F/RT)] \quad (3)$$

**Table 1.** The effect of electrolyte cation on the heterogeneous rate constant for the reduction of benzonitrile.

Electro- lyte	$-\phi_2/$ mV	$k_s^{\text{app}}/$ $\text{cm s}^{-1}$	$k_s^{\text{corr}}/$ $\text{cm s}^{-1}$	$\lambda^a$	$-\phi_r/$ mV
Hx <sub>4</sub> N <sup>+</sup>	125.0	0.13	1.48	-0.45	181.2
Bu <sub>4</sub> N <sup>+</sup>	117.6	0.45	4.44	0	117.6
Pr <sub>4</sub> N <sup>+</sup>	124.8	1.10	13.2	0.42	72.4
Et <sub>4</sub> N <sup>+</sup>	125.4	1.20	13.8	0.46	67.7
Me <sub>4</sub> N <sup>+</sup>	142.8	4.5	72.4	1	0

<sup>a</sup>  $|\phi_r| = |\phi_2| (1-\lambda)$ ,  $\lambda$  is chosen so that  $k_s^{\text{corr}} = 4.5 \text{ cm s}^{-1}$ .

pre-electrode site, *i.e.* the potential at that distance from the electrode where the electron transfer takes place. In the simplest case, this potential is assumed to be that at OHP and can be calculated from eqn. (4)

$$\phi_r = 2(RT/F) \sinh^{-1} (q_m/8RT\epsilon C) \quad (4)$$

where  $q_m$  is the electrode charge,  $\epsilon$  is the dielectric constant and  $C$  is the electrolyte concentration.

At the potential where benzonitrile is reduced, the double layer capacitance increases as the cation size decreases. This would make the Frumkin correction term larger for the smaller cations and the apparent heterogeneous rate constant,  $k_s^{\text{app}}$ , would be expected to decrease. However, the opposite trend is observed experimentally. As shown in Table 1, the corrected

**Table 2.** The effect of Bu<sub>4</sub>NBF<sub>4</sub> concentration on the heterogeneous rate constant for the reduction of benzonitrile.

[Bu <sub>4</sub> NBF <sub>4</sub> ] (M)	$-\phi_2/$ mV	$k_s^{\text{app}}/$ $\text{cm s}^{-1}$	$k_s^{\text{corr}}/$ $\text{cm s}^{-1}$	$\lambda^a$	$-\phi_r/$ mV
0.01	176.0	0.17	5.25	0.04	169.0
0.025	152.8	0.26	5.10	0.04	146.7
0.05	135.1	0.35	4.86	0.03	131.0
0.10	117.6	0.45	4.44	0	117.6

<sup>a</sup> See note <sup>a</sup> in Table 1.

**Table 3.** The effect of Pr<sub>4</sub>NBF<sub>4</sub> concentration on the heterogeneous rate constant for the reduction of benzonitrile.

[Pr <sub>4</sub> NBF <sub>4</sub> ] (M)	$-\phi_2/$ mV	$k_s^{\text{app}}/$ $\text{cm s}^{-1}$	$k_s^{\text{corr}}/$ $\text{cm s}^{-1}$	$\lambda^a$	$-\phi_r/$ mV
0.01	183.5	0.74	26.3	0.49	93.6
0.025	160.0	1.12	25.3	0.55	72.0
0.05	142.4	1.16	18.6	0.51	69.8
0.01	124.8	1.16	13.2	0.42	72.4

<sup>a</sup> See note <sup>a</sup> in Table 1.

**Table 4.** The effect of Et<sub>4</sub>NBF<sub>4</sub> concentration on the heterogeneous rate constant for the reduction of benzonitrile.

[Et <sub>4</sub> NBF <sub>4</sub> ] (M)	$-\phi_2/$ mV	$k_s^{\text{app}}/$ $\text{cm s}^{-1}$	$k_s^{\text{corr}}/$ $\text{cm s}^{-1}$	$\lambda^a$	$-\phi_r/$ mV
0.01	184.2	1.63	58.8	0.72	51.6
0.025	160.8	1.5	34.4	0.65	56.3
0.05	143.0	1.35	21.9	0.57	61.5
0.10	125.4	1.20	13.8	0.46	67.7

<sup>a</sup> See note <sup>a</sup> in Table 1.

rate constants,  $k_s^{\text{corr}}$ , increase as the cation size decreases. Discrepancies of the same type were found by Corrigan and Evans<sup>9</sup> during the reduction of 2-methyl-2-nitrobutane and by Kakutani *et al.*<sup>16</sup> in studying the reduction of some nitrobenzenes. In both cases the effects were attributed to double layer effects.

A further test of the simple theory can be made by changing the electrolyte concentration during rate constant determinations. Results of experiments of this type are given in Tables 2, 3 and 4 using Bu<sub>4</sub>NBF<sub>4</sub>, Pr<sub>4</sub>NBF<sub>4</sub> and Et<sub>4</sub>NBF<sub>4</sub>, respectively. In all cases, the values of  $k_s^{\text{corr}}$  increase substantially with decreasing electrolyte concentration. The conclusion we arrive at is, that if the data can be accounted for in terms of eqn. (3), the pre-electrode site cannot be at the OHP.

In order to find a model which is capable of explaining all of the results, the double layer can be divided into two distinct regions, according to the Stern treatment.<sup>20</sup> The two regions are the compact layer, encompassing the space from the electrode surface to the OHP, and the diffuse

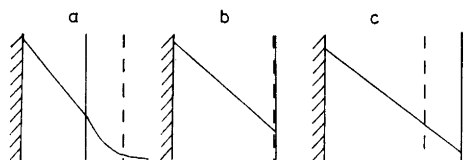


Fig. 4. A schematic picture of the double layer. --- pre-electrode site; ———, outer Helmholtz plane. a.  $1 \leq \lambda$  and  $\lambda \geq 0$ . b.  $\lambda = 0$ . c.  $\lambda \phi_2 \leq \phi_m$  and  $\lambda < 0$ .

layer, which is from the OHP out to the end of the diffuse layer.

If we assume that there exists a pre-electrode site at a certain distance from the electrode which is independent of the size of the electrolyte cation, OHP will be situated differently for the different electrolytes. It is commonly assumed that the potential falls linearly to the OHP in the compact layer and asymptotically to zero from the OHP in the diffuse layer.<sup>20</sup> The parameter  $\lambda$  is defined so that  $|\phi_r| = |\phi_2| (1 - \lambda)$  where  $\phi_r$  is the potential at the pre-electrode site. Then for  $\lambda \leq 1$  and  $\lambda > 0$ ,  $\lambda = 0$  and  $\lambda \phi_m < \phi_2$  and  $\lambda < 0$  the pre-electrode site will be in the diffuse layer, at the OHP, and in the compact layer, respectively. Fig. 4 shows the potential drop in the double layer for the various cases.

From the capacitance data we can conclude that  $\text{Me}_4\text{N}^+$  adsorbs specifically to the electrode. If the coverage is large the potential will drop to zero at the inner Helmholtz plane, IHP, and the apparent rate constant should equal the true value without need for correction. If we assume this to be the case, we can evaluate  $\lambda$  in other cases. In Table 1, we note that  $k_s^{\text{corr}}$ , where the correction was made assuming the pre-electrode

site to be the OHP, with  $\text{Bu}_4\text{N}^+$  as the electrolyte cation is nearly the same as the  $k_s^{\text{app}}$  with  $\text{Me}_4\text{N}^+$ . The model then calls for the pre-electrode site to be near the OHP when  $\text{Bu}_4\text{N}^+$  is the supporting electrolyte cation. For the smaller cations the pre-electrode site will be in the diffuse layer while it will be situated in the compact layer for cations larger than  $\text{Bu}_4\text{N}^+$ . The values of  $\lambda$  listed in Table 1 are those that give  $k_s^{\text{corr}}$  equal to  $k_s^{\text{pp}}$  for the case where the supporting electrolyte cation was  $\text{Me}_4\text{N}^+$ . In Table 1,  $\phi_2$  is the potential at the OHP and  $\phi_r$  is that evaluated according to the model.

The distance,  $x_2$ , from the electrode to the OHP can be estimated from the solvated radii of the tetraalkylammonium cations in DMF<sup>17</sup> if we assume that there is one layer of solvent molecules between the electrode and the OHP. In order to estimate the radii for cations for which data are not available, the radii were plotted as a function of the number of carbon atoms in the alkyl groups and a reasonably linear relationship was observed. Using these radii and a radius of 6.5 Å for DMF<sup>16</sup> resulted in the  $x_2$  listed in Table 5. Since we have concluded that  $x_r$ , the distance from the electrode to the pre-electrode site, is independent of the electrolyte cation and that with  $\text{Bu}_4\text{N}^+$  this corresponds to the OHP,  $x_r$  according to our model is 11.6 Å. We can estimate  $\phi_r$ , the potential at  $x_r$ , for  $\text{Hx}_4\text{N}^+$  since the potential is assumed to drop linearly to the OHP. In this case,  $\phi_2 = -125$  mV and  $k_s^{\text{app}} = 0.13$  cm/s (Table 1). A linear potential drop gives  $\phi_r = -247$  mV and a corrected rate constant of 15.9 cm/s. This value is clearly too large, but the example does show that a small change in the pre-electrode site makes a large difference in the corrected rate constant.

An attempt was made to test the validity of the relation,  $k_s^{\text{app}} = k_s^{\text{corr}}$  for  $\text{Me}_4\text{N}^+$ . The apparent

Table 5. The distance to the outer Helmholtz plane for the different electrolytes.

Electrolyte	Radii (Å)	$x_2$ (Å)
$\text{Me}_4\text{N}^+$	3.88	10.38
$\text{Et}_4\text{N}^+$	4.28 <sup>a</sup>	10.78
$\text{Pr}_4\text{N}^+$	4.68	11.18
$\text{Bu}_4\text{N}^+$	5.12	11.62
$\text{Hx}_4\text{N}^+$	5.93 <sup>a</sup>	12.43

<sup>a</sup> The value is taken from the linear plot of radii = f (number of carbon atoms).

Table 6. The effect of the unsymmetrical electrolyte cations on the heterogeneous rate constant for the reduction of benzonitrile.

Electrolyte	$k_s^{\text{app}}$ /cm s <sup>-1</sup>
$\text{Bu}_4\text{NI}$	0.45
$\text{Bu}_3\text{MeNI}$	5 ± 2
$\text{Bu}_2\text{Me}_2\text{NI}$	6 ± 2
$\text{BuMe}_3\text{NI}$	3 ± 2
$\text{Me}_4\text{NBF}_4$	4.5

**Table 7.** Determination of the heterogeneous rate constant for the reduction of benzonitrile as a function of temperature.

0.1M <i>T</i> (K)	Hx <sub>4</sub> N <sup>+</sup> <i>k<sub>s</sub><sup>a</sup></i>	0.1M <i>T</i> (K)	Bu <sub>4</sub> N <sup>+</sup> <i>k<sub>s</sub><sup>a</sup></i>	0.1M <i>T</i> (K)	Pr <sub>4</sub> N <sup>+</sup> <i>k<sub>s</sub><sup>a</sup></i>	0.1M <i>T</i> (K)	Et <sub>4</sub> N <sup>+</sup> <i>k<sub>s</sub><sup>a</sup></i>
282	0.057	261	0.134	256	0.312	254	0.256
304	0.075	274	0.241	275	0.623	263	0.581
323	0.121	284	0.322	284	0.794	284	2.34
349	0.272	295	0.457	294	1.06	295	4.7
		318	0.790				

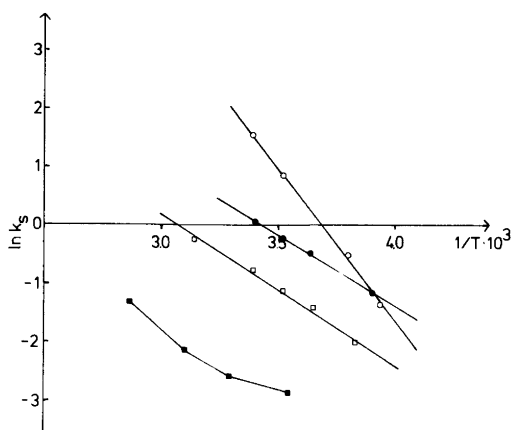
<sup>a</sup> Apparent *k<sub>s</sub>*-values in cm s<sup>-1</sup>.

rate constant for the reduction of benzonitrile in DMF in the presence of Me<sub>4</sub>N<sup>+</sup> was determined at several electrolyte concentrations and found to be constant within experimental error. This is a rapid process and considerable error is associated with the measurement of the rate constants, *i.e.* of the order of  $\pm 50\%$ , which makes the independence of *k<sub>s</sub><sup>app</sup>* on electrolyte concentration somewhat tenuous. In order to gain more confidence in this proposal, kinetic experiments were carried out using the unsymmetrical cations as well. The data are summarized in Table 6. In all cases, the error is relatively large but *k<sub>s</sub><sup>app</sup>* are equal, within experimental error to the value obtained with Me<sub>4</sub>N<sup>+</sup> as the cation.

Heterogeneous kinetic studies were carried out over a range of temperatures using some of the electrolytes. The data are shown in Table 7. The

activation energies were evaluated by plotting  $\ln k_s^{\text{app}}$  as a function of  $1/T$  (Fig. 5). The plots are reasonably linear in all cases except when the electrolyte was Hx<sub>4</sub>NBF<sub>4</sub>. The activation parameters for the other electrolytes are given in Table 8. The values of *E<sub>a</sub>* are nearly the same for Bu<sub>4</sub>NBF<sub>4</sub> and Pr<sub>4</sub>NBF<sub>4</sub> as electrolytes but nearly twice as great for Et<sub>4</sub>NBF<sub>4</sub>. The expected pre-exponential factor is given by  $Z = RT/2\pi M$  where *M* is the molecular weight of the substrate.<sup>18</sup> This relationship gives  $Z = 6.8 \times 10^3$  which is close to that observed for Bu<sub>4</sub>N<sup>+</sup> and Pr<sub>4</sub>N<sup>+</sup>. However, the value when Et<sub>4</sub>N<sup>+</sup> was the electrolyte is 5 powers of 10 too great.

Since the heterogeneous charge transfer rate constants cannot be corrected in a simple way, it is expected that the transfer coefficients will also vary with the nature of the electrolyte.<sup>19</sup> How-

**Fig. 5.** Arrhenius plots for some tetraalkylammonium ions. ○, Et<sub>4</sub>NBF<sub>4</sub>; ●, Pr<sub>4</sub>NBF<sub>4</sub>; □, Bu<sub>4</sub>NBF<sub>4</sub>; ■, Hx<sub>4</sub>NClO<sub>4</sub>.**Table 8.** The activation energy for the reduction of benzonitrile.

Electrolyte	<i>E<sub>a</sub></i> /kJ mol <sup>-1</sup>	<i>A</i>
Bu <sub>4</sub> NBF <sub>4</sub>	21.2	$2.6 \cdot 10^3$
Pr <sub>4</sub> NBF <sub>4</sub>	20.1	$4.0 \cdot 10^3$
Et <sub>4</sub> NBF <sub>4</sub>	43.6	$2.4 \cdot 10^8$

**Table 9.** The reversible potential and the transfer coefficient for the reduction of benzonitrile.

Electrolyte	$-E_{\text{rev}}$ /mV	$\alpha$
Me <sub>4</sub> NBF <sub>4</sub>	2652.7	0.520
Et <sub>4</sub> NBF <sub>4</sub>	2652.5	0.534
Pr <sub>4</sub> NBF <sub>4</sub>	2649.4	0.535
Bu <sub>4</sub> NBF <sub>4</sub>	2650.4	0.530

Table 10. The effect of electrolyte cation on the heterogeneous rate constant for the reduction of dinitromesitylene.

Electrolyte	$-\phi_2/\text{mV}$	$k_s^{\text{app}}/\text{cm s}^{-1}$	$k_s^{\text{corr}}/\text{cm s}^{-1}$	$\lambda^a$	$-\phi_r/\text{mV}$
$\text{Me}_4\text{N}^+$	101.3	0.84	6.0	0	101.3
$\text{Et}_4\text{N}^+$	95.6	1.2	7.7	0	95.6
$\text{Pr}_4\text{N}^+$	102.9	1.08	8.0	0	102.9
$\text{Bu}_4\text{N}^+$	95.4	0.95	6.1	0	95.4
$\text{Hx}_4\text{N}^+$	103.0	0.42	3.1	-0.4	61.5

<sup>a</sup> See note <sup>a</sup> in Table 1.

ever, this was not observed to be the case. The transfer coefficients, listed in Table 9, were observed to be very nearly the same for all of the electrolytes. The reversible potential was also observed to be independent of the nature of the supporting electrolyte cation. The latter indicates that ion-pairing between the anion radical and the cations cannot be the source of the discrepancies.

The experimental results for the reduction of benzonitrile are difficult to explain within the realm of any model. The discrepancies could be due to the very negative charge on the electrode as previously discussed by Fawcett *et al.*<sup>6,19</sup> In order to test for the dependence on the electrode potential, we chose to study the reduction of dinitromesitylene which takes place at  $-0.9\text{ V vs. }E_z$ . In this potential region none of the supporting electrolyte cations studied are specifically adsorbed to the electrode. The results are summarized in Table 10. Within experimental error, the corrected rate constants were observed to be constant with all electrolytes except  $\text{Hx}_4\text{NBF}_4$ . This indicates that the simple Frumkin correction is applicable to the data and that the electron transfer can be assumed to take place at the OHP. With  $\text{Hx}_4\text{NBF}_4$  as the electrolyte cation there are still discrepancies. The  $\lambda$  value indicates that the pre-electrode site is in the compact layer in this case.

The data from the kinetic experiments on the reduction of dinitromesitylene can be incorporated in the description of the model if we neglect the unexplained results when  $\text{Hx}_4\text{NBF}_4$  is the electrolyte. Since with the other electrolytes the Frumkin correction appears to be valid for this process we propose that, at potentials not too far removed from  $E_z$ , the OHP is the preferred pre-electrode site. At more negative potentials,

the pre-electrode site will be located approximately at the same distance,  $x_r$ , from the electrode, independent of the size of the electrolyte cation. In the case of  $\text{Bu}_4\text{N}^+$ ,  $x_r$  corresponds closely to  $x_2$ . Charge transfer in the presence of tetraalkylammonium ions smaller than  $\text{Bu}_4\text{N}^+$  would be retarded at OHP and therefore takes place in the diffuse layer. In the case of cations with greater radii than  $\text{Bu}_4\text{N}^+$ , the potential at the OHP is sufficiently reduced due to the larger value of  $x_2$  that the pre-electrode site can penetrate the OHP and charge transfer takes place in the compact layer. This model predicts that the Frumkin correction will be valid for all tetraalkylammonium ions with effective radii equal to or smaller than  $\text{Bu}_4\text{N}^+$  up to some value of the electrode potential above which electron transfer is retarded at the OHP for the smaller cations and charge transfer begins to take place in the diffuse layer. The value of  $x_r$  then is predicted to be potential dependent and happens to coincide with  $x_2$  during the reduction of benzonitrile. The model also predicts that  $x_r$  will always be less than  $x_2$  for cations of greater radii than  $\text{Bu}_4\text{N}^+$ .

Although the model described above accounts for the double layer corrections necessary in the case of the two substrates used in this study, much further work would be necessary to twist the generality of the model.

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