

## Role of the Carboxy Proton in Heterogeneous Electron Transfer to *o*-Nitrobenzoic Acid

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Heterogeneous electron transfer (ET) to *o*-nitrobenzoic acid has been investigated in *NN*-dimethylformamide containing tetrabutylammonium perchlorate. Although primary anion radicals undergo fast homogeneous decay, voltammetric measurements allowed the ET rate constant to be determined at various temperatures. These rate constants are abnormally low for an aromatic nitro derivative, even *ortho*-substituted, as also shown by comparison with the ET rate constant for methyl *o*-nitrobenzoate, which is at least two orders of magnitude higher. However, the e.s.r. spectrum demonstrates the presence of a hydrogen bond in *o*-nitrobenzoic acid anion radical, which is not present in the parent molecule, showing that the ET process entails significant structural change. The latter rather than solvent reorganisation around the charge of the anion-radical, localised by the *ortho* effect, is believed to provide the major contribution to the charge-transfer activation free energy.

Heterogeneous and homogeneous electron transfer (ET) to aromatic nitro derivatives are known to be generally rather fast,<sup>1-8</sup> particularly for dipolar aprotic solvents. However, several examples have been pointed out of relatively slow ET in nitro-organic derivatives, which have been attributed to poor delocalisation of the unpaired electron in the primary anion radical.<sup>1,9</sup> This may be due either to the aliphatic character of the moiety bound to the nitro group or to the twisting of the nitro group out of the plane of an aromatic ring, owing to the steric hindrance caused by bulky *ortho*-substituents. In both cases the low values of the ET rate constants are generally paralleled by relatively high values of the nitrogen coupling constants of the anion-radical. On the other hand, in protic media, strong solvation of the anion-radical resulting from hydrogen bonding between the solvent and the oxygen atoms of the nitro group may cause lowering of the ET rate constant by two orders of magnitude,<sup>9</sup> with respect to the values measured in aprotic solvents.

The molecular conformation can play a significant role in the thermodynamics and kinetics of ET reactions<sup>4,10</sup> and several examples have also been reported showing that structural changes can be induced by ET.<sup>11</sup>

In the course of a series of studies carried out in dipolar aprotic solvents, on proton transfer from organic molecules bearing mobile hydrogens to their basic reduction intermediates (self-protonation),<sup>12,13</sup> we have met with an example of rather slow ET to an aromatic nitro derivative such as *o*-nitrobenzoic acid, which cannot be simply rationalised in terms of steric hindrance. We report here the results of a deeper investigation on the electrochemical formation of the *o*-nitrobenzoic acid anion-radical and on the e.s.r. spectra obtained thereof. A comparison with the behaviour of the corresponding methyl ester allows some conclusions to be drawn on the kinetics and thermodynamics of heterogeneous reduction.

### Experimental

*o*-Nitrobenzoic acid (*o*-NBA) (C. Erba) was purified by crystallisation from ethanol. Methyl *o*-nitrobenzoate (*o*-NBE) (Fluka purum) was distilled at reduced pressure. *NN*-Dimethylformamide (DMF) and tetrabutylammonium perchlorate (TBAP) were purified and prepared, respectively, as previously re-

ported.<sup>14</sup> 0.1 mol dm<sup>-3</sup> TBAP-DMF solutions for measurements with *o*-NBE were further dried directly in the electrochemical cell, by repeated percolations through a column of neutral Al<sub>2</sub>O<sub>3</sub> (Merck; activity grade I), previously activated at 350 °C under vacuum. The same procedure could not be used for the acid, since the latter was deprotonated when the solvent was treated with Al<sub>2</sub>O<sub>3</sub>. In this case DMF was always distilled just before use.

The working mercury microelectrodes were prepared as previously described.<sup>14</sup> They were activated by repeatedly cycling the applied potential directly in the TBAP-DMF solutions. The surface area of the microelectrodes was determined by chronoamperometric and voltammetric measurements with anthracene, whose diffusion coefficient is known.<sup>15</sup>

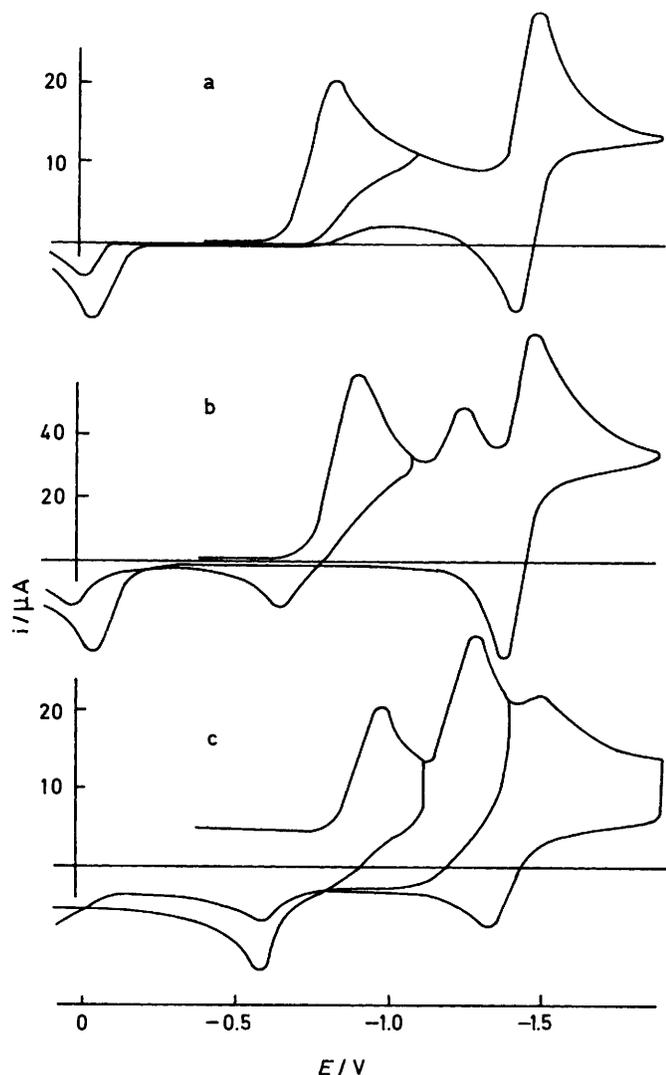
In order to get reliable values of the entropy change for the cathodic reaction, a non-isothermal cell arrangement was used.<sup>16</sup> A salt bridge, containing 0.1 mol dm<sup>-3</sup> TBAP-DMF solution, connected the cell to the reference compartment where the reference electrode<sup>14</sup> was maintained at 25 °C. The reference potential is -0.220 V *versus* s.c.e., at 25 °C, and all the reported potentials are referred to s.c.e. The cell temperature was held at a constant value within ±0.1 °C.

An EG&G apparatus formed by a 273 potentiostat-galvanostat and a 175 function generator, equipped with a Nicolet 2090 digital oscilloscope and an Amel model 862A *XY* recorder, was used for the electrochemical measurements. E.s.r. spectra were recorded at room temperature with a Varian E3 spectrometer. The working cathode for electrolyses both *intra muros* and in a separate cell was a mercury pool. Theoretical calculations and digital plotting of the spectra were performed with a PDP 11/24 computer.

### Results

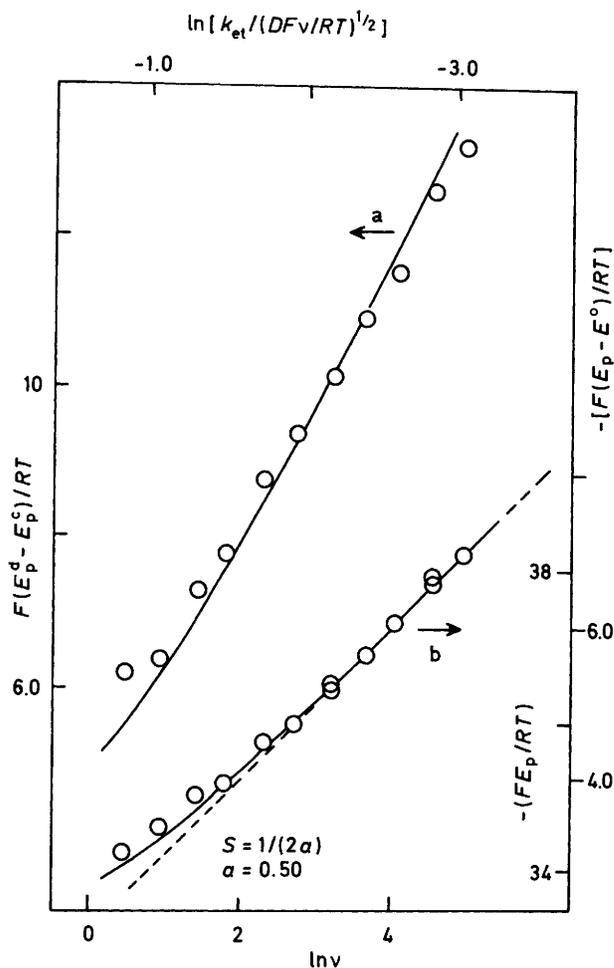
*Voltammetric Behaviour.*—The reduction of *o*-NBA in DMF gives rise to a rather complex voltammetric pattern, which is strongly dependent on the temperature *T*, the substrate concentration *c*, and the potential sweep rate *v* (see Figure 1).





**Figure 1.** Effect of temperature,  $T$ , concentration,  $c$ , and potential sweep rate,  $v$ , on the voltammetric behaviour of *o*-nitrobenzoic acid. Voltammetric conditions: a,  $T$  25 °C,  $c$   $4.4 \times 10^{-3}$  mol dm $^{-3}$ ,  $v$  0.1 V s $^{-1}$ ; b,  $T$  0 °C,  $c$   $4.4 \times 10^{-3}$  mol dm $^{-3}$ ,  $v$  5 V s $^{-1}$ ; c,  $T$  -33.9 °C,  $c$   $4.3 \times 10^{-4}$  mol dm $^{-3}$ ,  $v$  0.1 V s $^{-1}$

Exhaustive controlled-potential electrolysis at -1.00 V, requiring 0.8 electron per molecule, and product analysis indicate the stoichiometry (1) of the overall process underlying the first reduction step. In reaction (1) the substrate itself (HRNO<sub>2</sub>; R = C<sub>6</sub>H<sub>4</sub>COO) acts as a proton donor allowing the four-electron reduction of part of it to *o*-hydroxylamino-benzoic acid. This self-protonation process, analogous to that already described in detail for *p*-nitrobenzoic acid,<sup>13</sup> is fast enough to occur also in the time scale of cyclic voltammetry, at least at low  $v$  and high  $T$  and  $c$  values, as proved by the peaks attributable to the reaction products. In fact, the most positive anodic peak of Figure 1a corresponds to the oxidation of the hydroxylamino derivative to yield a nitroso intermediate, while the conjugate base of the substrate undergoes, at more negative potentials, a reversible one-electron reduction (2) to dianion radical. The presence of the associated reoxidation peak, 59 mV more positive than the cathodic one and with a unit anodic to cathodic peak current ratio, shows that (2) is a fast ET process uncomplicated by any further chemical decay.



**Figure 2.** Variation of the anodic to cathodic peak-potential difference (a, left scale) and of the cathodic peak potential (b, right internal scale) with the potential sweep rate (lower scale) for the first voltammetric peak of *o*-nitrobenzoic acid.  $T$  25 °C,  $c$   $4.0 \times 10^{-4}$  mol dm $^{-3}$ . The solid lines are the computed behaviour (see text) for the same theoretical peak-potential difference and for the theoretical overvoltage (right external scale) as a function of the kinetic parameter  $\Lambda = k_{\text{red}}^0/(fvD)^{1/2}$  ( $f = F/RT$ ). The dashed line shows the limit linear dependence of  $fE_p$  versus  $\ln v$  at high sweep rates

However, the reaction sequence giving rise to the overall process (1) is not exceedingly fast, so that the formation of the two products can be partially hindered during a voltammetric run by increasing  $v$  and/or decreasing  $T$  and  $c$  (see Figures 1b and c). At the same time an anodic component associated with the first peak and a new intermediate cathodic peak, with peak potential dependent on the sweep rates, are formed in such conditions. They correspond, respectively, to the reoxidation of the anion-radical produced in the very first step (3) of the *o*-NBA reduction and to its further reduction (4).



The large potential difference between the anodic and cathodic peaks of the first redox process indicates that the ET (3) is a relatively slow process.

Methyl substitution of the carboxylic proton of *o*-NBA, preventing the self-protonation process, entails a substantial simplification of the voltammetric pattern *o*-NBE exhibits in

**Table 1.** Electrochemical parameters

$T/^\circ\text{C}$	<i>o</i> -Nitrobenzoic acid				Methyl <i>o</i> -nitrobenzoate	
	$-E^\circ/\text{mV}^a$	$k_{\text{het}}^\circ/10^{-2} \text{ cm s}^{-1}$	$k_{\text{het,c}}^\circ/10^{-2} \text{ cm s}^{-1}$	$\alpha$	$-E^\circ/\text{mV}^a$	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$
0.0	$796 \pm 1$	$0.43 \pm 0.02$	$2.55 \pm 0.1$	0.46	$983 \pm 1$	$0.68 \pm 0.01$
25.0	$803 \pm 2$	$1.05 \pm 0.04$	$6.2 \pm 0.2$	0.50	$991 \pm 1$	
45.1	$807 \pm 2$	$2.2 \pm 0.10$	$12.3 \pm 0.5$	0.52	$999 \pm 1$	$0.965 \pm 0.015$
						$1.30 \pm 0.01$

<sup>a</sup> versus s.c.e. <sup>b</sup> Uncorrected for double-layer contribution. <sup>c</sup> With double-layer Frumkin correction.

fact two cathodic peaks (a third multi-electron cathodic step is also observed at potentials more negative than  $-2.3$  V) which correspond to the formation of the anion-radical of the substrate and its further irreversible reduction. The 1:1 peak-current ratio between the anodic and the cathodic components of the first peak, together with their peak-potential difference of 59 mV, show that the anion radical of *o*-NBE is stable and its formation is fast in the voltammetric time scale (see below).

**Determination of the ET Rate Constant.**—The strong sweep rate dependence of the first cathodic peak potential and the large potential difference between the anodic and cathodic components (Figure 2) show that ET to *o*-NBA is a relatively slow process. Although at low sweep rates the voltammetric behaviour is affected by the homogeneous decay of the anion-radical, this appears to be of no significance at the highest  $v$  values.

A linear variation of the cathodic peak potential  $E_p$  with  $\ln v$  can be observed at sufficiently high sweep rates, the actual  $v$  value depending on  $T$ . At 25 °C, for instance, the  $E_p/\ln v$  plot is linear for  $v \geq 15 \text{ V s}^{-1}$ . The corresponding slope is related to the transfer coefficient  $\alpha$ , which is ca. 0.5 and slightly dependent on  $T$  (see Table 1). For these  $\alpha$  values we have computed the voltammetric behaviour, following the theoretical treatment<sup>17,18</sup> for a species undergoing a heterogeneous one-electron exchange, with a potential-dependent rate constant according to the Butler–Volmer relation. By comparison of the computed values with the experimental results of the anodic to cathodic peak-potential difference, as a function of  $v$ , the kinetic parameter  $k_{\text{het}}^\circ/D^{\frac{1}{2}}$  can be obtained, at different temperatures. Knowing this parameter, the standard potential  $E^\circ$  can be evaluated, by comparison of the experimental  $E_p$  with the computed overvoltage  $E_p - E^\circ$ , as a function of the sweep rate (Figure 2).

Similar measurements on *o*-NBE showed that, with a sweep rate up to  $150 \text{ V s}^{-1}$ , the cathodic peak potential ( $-1.020 \pm 1 \text{ mV}$  at 25 °C) was independent of sweep rate and that the difference in the anodic and cathodic peak potentials was constant at  $59 \pm 2 \text{ mV}$ . This indicates that the ET is very fast, with a rate constant beyond the value accessible by the voltammetric technique. A lower limit for the standard rate constant can be estimated, by comparison with the theoretical behaviour, once the diffusion coefficient  $D$  is known (see below). At 25 °C, for instance, one finds  $k_{\text{het}}^\circ \geq 2 \text{ cm s}^{-1}$ .

It is worth noting that the major source of error in the evaluation of the ET rate constant from voltammetric peak potential data lays in the uncompensated ohmic drop between working and reference electrode, whose effect is quite similar to that brought about by a slow ET.<sup>18–20</sup> Since no apparent effect of this type is observed for the ester in the whole range explored, it can be confidently assumed that also the voltammetric results for *o*-NBA at the highest sweep rates are essentially determined by the slow ET.

On the other hand, since the characteristics of the first peak of the ester are determined by the diffusion process, an estimate of the diffusion coefficient can be obtained from peak current measurements, according to a relationship valid for a simple reversible ET.<sup>19</sup> The values of  $D$  thus determined at different temperatures are reported in Table 1. We have assumed that these values can give an estimate for the diffusion coefficient of the acid, probably more correct than the value obtainable from the corresponding peak current data, which are influenced in a rather complex way by the kinetics of both ET and anion-radical decay. With these values of  $D$ , the apparent standard rate constant values for the ET to *o*-NBA at different temperatures have been determined (see Table 1).

The standard rate constants and the transfer coefficients should be corrected for the double-layer contribution. Since the diffuse layer potential,  $\Phi^d$ , does not vary greatly with the electrode potential, at least at 25 °C, use was made of the experimental  $\alpha$  values. The dependence of the diffuse layer potential on the electrode potential for an interface of Hg and  $0.1 \text{ mol dm}^{-3}$  TBAP in DMF, obtained from differential capacitance data according to the Gouy–Chapman model, is only known at 25 °C. At the *o*-NBA standard potential,  $\Phi^d$  is of the order of  $-91 \text{ mV}$ , and this value was used at all temperatures. The heterogeneous ET standard rate constant were corrected according to the Frumkin model, to obtain the true values,  $k_{\text{het,c}}^\circ$  [equation (5)]. The true rate constants are also reported in Table 1. The activation energy  $E_a$ , and the pre-exponential factor  $A$ , can be estimated from the plot of  $\ln k_{\text{het,c}}^\circ$  versus  $1/T$ . They are  $25.2 \pm 0.8 \text{ kJ mol}^{-1}$  and  $(1.6 \pm 0.6) \times 10^3 \text{ cm s}^{-1}$ , respectively.

$$k_{\text{het,c}}^\circ = k_{\text{het}}^\circ \exp[-(\alpha F \Phi^d / RT)] \quad (5)$$

**E.s.r. Spectra.**—E.s.r. spectra of the paramagnetic reduction intermediates of *o*-NBA provide further support to their identification and give some indication of their configuration.

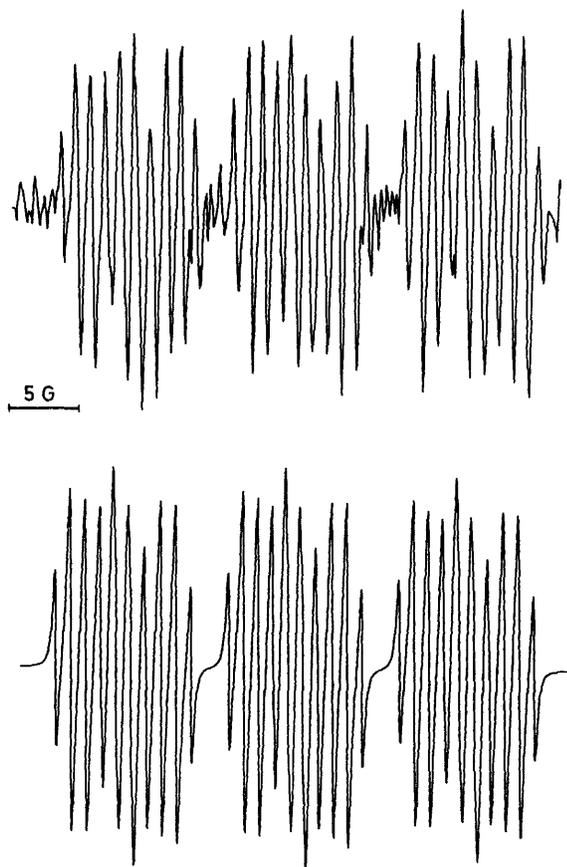
An e.s.r. spectrum attributed to the anion-radical of *o*-NBA has been already reported.<sup>21</sup> This spectrum shows a large hyperfine coupling constant for one hydrogen atom ( $a_{\text{H}}$  11.67 G) and a hyperfine splitting due to the nitrogen nucleus, which does not change when increasing amounts (up to 100%) of an hydroxylic solvent such as ethanol are added to DMF, in marked contrast to the typical behaviour of nitroaromatic anion-radicals, particularly when they are not already involved in tight ion pairs.<sup>21,22</sup> The latter fact has been interpreted as being due to the presence of an intramolecular hydrogen-bond in the anion radical, between the *o*-carboxy proton (responsible for the large  $a_{\text{H}}$ ) and the nitro group, which prevents the formation of intermolecular hydrogen-bonds with ethanol. This result was also considered as support for the assumption that the strong effect brought about by hydroxylic solvents on the hyperfine splitting of nitroaromatic anion-radicals is attributable to intermolecular hydrogen bonding.<sup>21,23</sup>

**Table 2.** Hyperfine coupling constants (in gauss) for radicals derived from *o*-nitrobenzoic acid and methyl *o*-nitrobenzoate

	$a_N$	$a_{H,p}$	$a_{H,o}$	$a_{H,m}$	$a_H^a$
Anion-radical <sup>b</sup>	12.09	3.31	3.12	1.07	0.90
Dianion-radical <sup>b</sup>	10.05	3.86	3.38	1.12	
Nitroso radical <sup>b</sup>	8.80	3.17	3.17	1.03 <sup>c</sup>	11.65
Anion-radical <sup>d</sup>	9.65	4.51	3.40	1.11 <sup>c</sup>	

<sup>a</sup> Carboxy proton. <sup>b</sup> From *o*-nitrobenzoic acid. <sup>c</sup> Two equivalent nuclei.

<sup>d</sup> From methyl *o*-nitrobenzoate.



**Figure 3.** Hand-digitised experimental (upper curve) and calculated (lower curve) e.s.r. spectrum of *o*-nitrobenzoic acid anion radical in  $0.1 \text{ mol dm}^{-3}$  TBAP-DMF solution at room temperature

However an e.s.r. spectrum coincident with that discussed above has been interpreted as due to a nitroso radical, an intermediate in the multi-electron reduction of *o*-NBA. The very large hydrogen splitting ( $a_H$  11.52 G) has been attributed to a proton forming a hydrogen-bridge between the nitrogen atom of the nitro group and the carboxylic oxygen.<sup>24</sup>

We have been able to obtain the same spectrum (see Table 2) by first carrying out extensive reduction of *o*-NBA at the potential of the first cathodic peak and then switching the potential to more positive values, where the hydroxylamino derivative previously produced is oxidised. This result confirms the attribution of the spectrum to a nitroso radical.

We have obtained a further spectrum, different both from the previous one and also from that attributed to the *o*-nitrobenzoate dianion-radical (see below), by potentiostatic reduc-

tion, *in situ*, of *o*-NBA, at the first cathodic peak potential. Although the low signal-to-noise ratio makes the interpretation uneasy, ten lines due to the hydrogen coupling can be resolved in each group of the nitrogen triplet splitting (Figure 3). According to their intensity ratio, the ten lines can be attributed to the splitting of five nuclei with  $s$  1/2, grouped in two sets of two and, respectively, three, similar but not completely equivalent atoms, with coupling constants in a *ca.* 3:1 ratio. This preliminary trial and error interpretation was further refined by fitting the hand-digitised experimental spectrum to the theoretical one (Figure 3) by means of a non-linear least-squares procedure.\* The final hyperfine coupling constants are reported in Table 2. The two largest splittings can be easily attributed to the *ortho* and *para* hydrogen atoms, while the two *meta* hydrogen atoms show nearly equal splitting. The lowest  $a_H$ , attributable to the carboxylic proton, is similar to the hyperfine splitting of the hydrogen-bonded phenolic proton in *o*-nitrophenol<sup>24,26</sup> and nitroresorcinol<sup>21</sup> anion-radicals. This indicates the formation of an intramolecular hydrogen-bond in the anion radical of *o*-NBA, which should be greatly enhanced over that of the parent molecule, owing to the negative charge localised on the nitro group of the anion-radical. This conclusion is also supported by the large  $a_N$  value, very similar to that reported for the anion-radical of *o*-nitrophenol.<sup>24,26</sup>

A much more stable and well defined e.s.r. spectrum is obtained by reduction at  $-1.70 \text{ V}$  (corresponding to the second cathodic peak of Figure 1a), yielding the *o*-nitrobenzoate dianion-radical, according to equation (2). As expected carboxylic proton splitting is absent in this case (see Table 2). The lack of an intramolecular hydrogen bond apparently causes a decrease in the hyperfine coupling constant for the nitrogen atom.

A further decrease of  $a_N$  is observed in the spectrum obtained by electrolysis at the potential of the first voltammetric peak of *o*-NBE (Table 2). This is presumably to be attributed to the lack of a second negative charge in the anion radical of the ester which, in the case of the dianion-radical, induces a greater electron density in the nitro group. The coupling constants are similar to those reported for the same anion-radical in acetonitrile.<sup>27</sup>

## Discussion

ET rate constants have been reported in the literature for a large variety of organic nitro compounds in different aprotic solvents.<sup>1-4,28-30</sup> Although the dependence of the ET data on the experimental conditions<sup>28,30</sup> allows only a rough comparison with our results, the heterogeneous ET rate constant to *o*-NBA appears exceptionally low for an aromatic nitro derivative. A closer comparison is feasible with the results obtained by Peover and Powell for a series of aliphatic and aromatic nitro compounds, in conditions similar to ours (DMF +  $0.1 \text{ mol dm}^{-3}$  TBA<sup>+</sup>, at  $30^\circ\text{C}$ ).<sup>1</sup> This shows that the value for *o*-NBA is almost coincident with that for 2-nitropropane ( $1.26 \times 10^{-2} \text{ cm s}^{-1}$ ), an aliphatic compound for which the ET process entails a large solvation free energy change, owing to the strong localisation of the charge on the nitro group of the anion-radical. The same authors have pointed out an inverse correlation between the value of the apparent ET rate constant and the  $a_N$  value. The increase of  $a_N$  in the series has been essentially attributed to a greater localisation of the unpaired electron in the nitro group. The latter may be due either to the presence of *ortho* substituents in the aromatic nitro derivatives, forcing the nitro group to rotate away from the ring plane,<sup>31</sup> or to the lack of the delocalising effect in the nitroalkanes. On the other

\* The EPR80 computer program,<sup>25</sup> on the VAX 8600 computer of Padova University, was kindly provided by Dr. M. Barzaghi.

hand, according to widely accepted theories for ET reactions,<sup>32</sup> a decrease of the ET rate constant is mainly attributable to a change of 'outer' solvent reorganisation, which is greater the higher the charge localisation in the anion-radical. It appears therefore that both effects arise from a common cause.

In the case of *o*-NBA an *ortho* effect, causing the nitro group to be twisted out of the ring plane, is not unreasonable. The lack of coplanarity has been actually proved for *o*-NBA, at least in the solid state, by structural data showing that the carboxy and nitro groups form angles of 24.1 and 54.3°, respectively, with the benzene ring.<sup>33</sup> Since only minor structural changes are generally expected in passing from the neutral molecule to the anion-radical, the large observed activation free energy change should be mainly attributed to the solvent reorganisation around the localised charge in the latter. The  $a_N$  value, larger than that of the nitrobenzene anion-radical<sup>34</sup> ( $a_N$  9.70 G), could be consistent with twisting of the nitro group out of the ring plane. However, a comparison with the ET kinetics to *o*-NBE and with the  $a_N$  value of the corresponding anion-radical, for both of which the *ortho* effect should also operate, shows that the above interpretation is far from being correct. In fact, the high value of the ET rate constant indicates that no sterically induced large solvent reorganisation energy is involved in this case. The  $a_N$  value only indicates either a small *ortho* effect, compensating the electron-withdrawing effect of the methoxycarbonyl moiety, or the absence of any substituent effect, owing to the twisting of such a group out of the ring plane.<sup>27</sup>

On the other hand, the splitting due to the carboxy proton clearly shows intramolecular hydrogen-bonding in the anion-radical of *o*-NBA, not present in the neutral parent molecule. The  $a_N$  value, higher than in the dianion-radical and in the anion-radical of *o*-NBE, can be ascribed to the presence of such a hydrogen-bond. A similarly high  $a_N$  is also evident in the two hydrogen-bonded anion radicals of *o*-nitrophenol<sup>24,26</sup> and nitroresorcinol.<sup>21</sup> An increase of  $a_N$ , together with variations of the coupling constants of other nuclei, was observed for nitroaromatic anion radicals, upon addition to the aprotic medium of protic solvents such as water or alcohols.<sup>21,22</sup> The phenomenon has been explained by an increase of the apparent electronegativity of the oxygen atoms in the nitro group, owing to the formation of hydrogen-bonded complexes with the hydroxylic solvent, which should induce a redistribution of the unpaired electron spin density.

Further support for the hypothesis of hydrogen-bond formation is provided by comparison between the standard potentials for the first ET to *o*-NBA and *o*-NBE (see Table 2) and the corresponding values for the *para* isomers.<sup>13</sup> While in the latter the two  $E^\circ$  values are close to each other, the acid ( $E_{p-NBA}^\circ$  -0.856 V) being slightly less reducible than the ester ( $E_{p-NBA}^\circ$  -0.824 V), a much larger difference, and in inverted order, is found for the *ortho* derivatives. The more negative  $E^\circ$  values for *o*-NBE, with respect to that of the *para* isomer, can be attributed to the reduced electron-withdrawing effect of the methoxycarbonyl group in the former, owing to the lack of coplanarity with the ring. This is also in line with the  $a_N$  value of the anion-radical, greater for the *ortho* (9.65 G) than for the *para* isomer (6.50 G).<sup>27</sup>

For analogous reasons, a similar  $E^\circ$  difference would be expected for the two isomeric acids. In this case, however, the reduction is easier for the *ortho* isomer, presumably because the partial delocalisation of the negative charge in the hydrogen-bonded anion radical entails a lower solvation contribution. The partial neutralisation of the negative charge is also likely to be responsible for the higher availability of the anion-radical to accept a further electron, as can be inferred from the peak potential for the reduction of the anion-radicals of the two isomers [ $(E_p)_o$  -1.35 V;  $(E_p)_p$  -1.59 V at 25 °C and  $v$  100 V s<sup>-1</sup>].

Other useful indications of the first ET process can be obtained by the temperature dependence of  $E^\circ$ , providing the  $\Delta S^\circ$  value of the electrode reaction. The electrochemical entropy mainly reflects the energetics of solvation which, for organic ion radicals, has been shown to be determined by geometrical and steric factors, by charge distribution, and by the ability of the solvent to promote short-range interactions<sup>35,36</sup> as well as by the formation of ion pairs with the supporting electrolyte.<sup>36</sup> The temperature dependence observed,  $dE^\circ/dT$ , is nearly constant in the range 0–45 °C, both for *o*-NBA and *o*-NBE, giving  $-(2.6 \pm 0.3) \times 10^{-4}$  and  $-(3.33 \pm 0.08) \times 10^{-4}$  V K<sup>-1</sup>, respectively. The corresponding values of the electrode reaction entropies are  $-25 \pm 3$  and  $-32.2 \pm 0.7$  J mol<sup>-1</sup> K<sup>-1</sup>. They are, as expected, negative, indicating that solvation is larger for the ionic ET product than for the neutral reactant molecule. The degree of order in the solvent around the anion-radical of *o*-NBA appears to be lower than for that for *o*-NBE, again indicating the formation of an intramolecular hydrogen-bonding in the former. It should be noted that both  $\Delta S^\circ$  values are less negative than those reported for nitrobenzene ( $-67$  J mol<sup>-1</sup> K<sup>-1</sup> in DMF) and for several nitroaromatics bearing electron-donating *ortho* substituents.<sup>35</sup> In fact the  $\Delta S^\circ$  value for *o*-NBE is comparable with that for dinitrobenzene ( $-28$  J mol<sup>-1</sup> K<sup>-1</sup> for *p*-dinitrobenzene in DMF and a slightly more negative value for the *ortho* isomer, as inferred from the data in acetonitrile) which have been similarly accounted for by the electron-withdrawing effect of the substituent. The smaller negative entropy change for *o*-NBA is similar to that for anthracene ( $-22.8$  J mol<sup>-1</sup> K<sup>-1</sup>),<sup>35</sup> for which the  $\pi$ -delocalised charge does not induce specific short-range solute-solvent interactions and whose behaviour can be accounted for, at least to a first approximation, by the simple Born dielectric continuum model.

All the results reported so far are in contrast with the assumption that the slow ET to *o*-NBA is caused by a large solvent reorganisation energy in the transition state, as is the case for most *ortho*-substituted nitroaromatics. There is some evidence indicating that the formation of a hydrogen-bond in the ET product, which is not present in the reactant molecule, is the main factor influencing the ET kinetics. It should be noted that a 'normal' (*i.e.* fast) ET reaction is observed for *o*-nitrophenol,<sup>12,26</sup> for which intramolecular hydrogen-bonding, giving rise to a stable six-membered ring, is present both in the reactant<sup>37</sup> and in the anion-radical.<sup>24</sup> For *o*-NBA, hydrogen-bonding in the anion-radical between the oxygen atoms of the carboxy and nitro group, resulting in a distorted seven-membered ring, entails a significant bond rearrangement, which ought to be reflected in the transition-state structure. This is in agreement with the high enthalpy contribution of the activation free energy (25.2 kJ mol<sup>-1</sup>) compared with the corresponding values for nitroresorcinol<sup>28</sup> (17.6 kJ mol<sup>-1</sup>) and for nitrobenzene<sup>5</sup> (14.6 kJ mol<sup>-1</sup>).

The 'inner' reorganisation energy for electrode reactions involving aromatic molecules is generally considered to be much smaller than the 'outer' energy, the latter often being sufficient to account for the observed ET rate constants, in terms of Marcus theory.<sup>4</sup> Although this is true when only minor structural changes are brought about by ET, it has been recently shown, by means of molecular orbital calculations, that also the 'inner' contribution may be significant.<sup>10</sup> This is likely to be the case for *o*-NBA, for which hydrogen bonding in the ET product seems to play an important role. Theoretical calculations are in progress, with a recent modification (AM1) of the NNDO semiempirical method,<sup>38</sup> to get more information on the structural modifications necessary to form an intramolecular hydrogen-bond in the anion-radical and to evaluate the 'inner' contribution associated with them.

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