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ELECTROCHEMICAL AND THERMODYNAMIC BEHAVIOUR OF OXYGENATED NITROGEN COMPOUNDS AND AROMATIC HYDROCARBONS IN NITROMETHANE, AND THE NITRATION PROCESS WITH NO_2^+ (SOLVATION PHENOMENA)

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Abstract—The electrochemical properties of oxygenated nitrogen compounds in anhydrous deoxygenated nitromethane have been studied by means of linear and cyclic voltammetry at a platinum electrode. Taking into account previous works in sulpholane, the various electrochemical couples involving nitrogen oxides at oxidation states from II to V have been identified in nitromethane, and their standard potentials have been determined at 298 K. Furthermore we have induced electrochemically the molecular association: $NO + \frac{1}{2}N_2O_4 \rightarrow N_2O_3$ (I) on a Pt electrode surface in order to reach the equilibrium constant of this reaction (I). All these findings have also allowed us to calculate the ionic dissociation constants of N_2O_3 and N_2O_4 according to $N_2O_3 \leftrightarrows NO^+ + NO_2^-$ (II) and $N_2O_4 \leftrightarrows NO_2^+ + NO_2^-$(III), respectively. It has been shown that thermodynamic data are comparable with those obtained in non-polar inert solvents and the standard potential of a couple hardly varies at all in various aprotic media if the nitrogen species involved in these chemical and electrochemical processes are solvated weakly (the solvent molecules barely intervene in these processes). On the other hand, we have undertaken the electrochemical study of aromatic hydrocarbons (ArH) in nitromethane in order to assess solvation effects on the aromatic radical cation ($ArH^{\cdot +}$) and hence to evaluate the standard potentials of $ArH/ArH^{\cdot +}$ couples. Finally, the survey of the redox process $NO_2^+ + ArH \leftrightarrows NO_2^{\cdot} + ArH^{\cdot +}$ (IV) in nitromethane has allowed us to obtain energetic and mechanistic information about the aromatic nitration with NO_2^+ and to compare it with that found in other aprotic media by reference to solvation phenomena.

INTRODUCTION

The influence of the reaction medium in condensed phases prevents the notion of a single nitration mechanism with NO_2^+ and N_2O_4 (catalysed by NO^+) due to an environment of solvation, ion pairing and other complicating factors. The solvent may play a role other than that of stabilizing ionic species in solution. For instance, solvent fluctuations are the major contributor to the reorganization energy term in the electron-transfer (ET) process involving NO_2^+ or NO^+ and arenes[1]. Theoretically there are a multitude of questions in need of answers, ranging from an explanation of the variable properties with respect to direct NO_2^+ or NO^+ attack to the possible critical role of solvation in determining the most stable form in solution. The influence of a weak solvating medium such as nitromethane minimizes solvation phenomena which alter and diversify the reactivity pattern.

We report here the electrochemical and thermodynamic properties of oxygenated nitrogen compounds and aromatic hydrocarbons in nitromethane. This study aims to provide information concerning solvation effects on the thermodynamic data in coordinating and non-coordinating solvents and their implication on the mechanism and energetics of the nitration process with NO_2^+.

EXPERIMENTAL

Chemicals

The purification of nitromethane (Fluka) has already been described[2]. Prior to use, the solvent was filtered through a dry alumina column under argon (neutral alumina was dried in a vacuum at 573 K for 1 week). Tetraethylammonium perchlorate (TEAP; Carlo Erba) was dried in a vacuum and over P_4O_{10} at 333 K for 1 week. NO_2ClO_4, $NOClO_4$, N_2O_3, N_2O_4 and $(C_2H_5)_4N^+NO_2^-$ were prepared and purified as described in refs [3–5]. Because of the dangerously explosive nature of dry NO_2ClO_4 and $NOClO_4$, it is necessary to manipulate them cautiously.

Procedures

All the apparatus employed for the voltammetric experiments has been described previously[2]. The electrochemical experiments were carried out in a thermostatted cell under argon. The ferrocene–ferricinium half-wave potential, $E_{1/2}(Fc/Fc^+)$, was chosen as the origin of the potential scale. The reference electrode Ag/Ag^+ has been described before[2, 3]. The voltammetric experiments were carried out with a platinum electrode (diameter 0.8 mm), and the auxiliary electrode was a platinum sheet of about 80 mm^2. All manipulations of materials and preparation of solutions were performed in an effective

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dry box. The water content of the reagents was controlled before use by a Karl Fischer automatic titration.

RESULTS AND DISCUSSION

Electro-oxidation of nitrite

The electrochemical properties of nitrite dissolved in anhydrous and deoxygenated nitromethane have been studied by means of linear and cyclic voltammetry at a platinum electrode. We showed previously that the nitrite ion undergoes two consecutive oxidation steps[5]:

$$2NO_2^- \leftrightarrows NO + NO_3^- + e^- \qquad (1)$$

$$NO + NO_3^- \leftrightarrows N_2O_4 + e^-. \qquad (2)$$

Reactions (1) and (2) are found to be reversible and quasi-reversible charge transfers, respectively, in sulpholane[5]. Furthermore, an extensive study of the first anodic wave indicated that nitrogen dioxide and its dimer occur as intermediates according to:

$$\text{Scheme I} \begin{cases} NO_2^- \leftrightarrows NO_2^{\cdot} + e^- & (3) \\ NO_2^{\cdot} \leftrightarrows \tfrac{1}{2}N_2O_4 & (4) \\ \tfrac{1}{2}N_2O_4 + NO_2^- \leftrightarrows NO + NO_3^- & (5) \end{cases}$$

The sum (3)+(4)+(5) gives the overall reaction (1). The cyclic and rotating-disc voltammograms obtained for the first oxidation step of the NO_2^- species in nitromethane are shown in Figs 1 and 2. At slow sweep rates ($v \leq 0.1$ V s^{-1}), the process appears irreversible due to the generation of non-electroactive species (NO and NO_3^-) on the Pt electrode surface at these potentials (Fig. 1A). However, at high sweep rates ($v \geq 0.2$ V s^{-1}) it appears as a weak cathodic peak on the cyclic voltammograms resulting from the intervention of couple (3) (Fig. 1B). The kinetic constants of the chemical reactions (4) and (5) following the electron-transfer (3) are large. In order to establish the reversibility of systems (1), we have studied the anodic E–i curve (Fig. 2). If $[NO]=[NO_3^-]=0$, the Nernst equation applied to couple (1) is given by:

$$E = E^{\circ}(1) + (RT/F)\ln[k_{NO_2^-}^2/k_{NO}\cdot k_{NO_3^-})] + (RT/F)\ln[i^2/(i_{NO_2^-}-i)^2]. \qquad (6)$$

The coefficients of proportionality, defined by $k = i_l/[C]$, are $k_{NO_2^-}$, k_{NO} and $k_{NO_3^-}$ for NO_2^-, NO and NO_3^- compounds, respectively. We obtained a linear E *vs* $\log[i^2/(i_{NO_2^-}-i)^2]$ plot with an average slope of 58.5 ± 1.0 mV, which is close enough to the theoretical value: $2.303(RT/F)$ (Fig. 2). Assuming that the diffusion coefficients for the NO_2^-, NO and NO_3^- species are equal, we can write $k = k_{NO_2^-} \simeq k_{NO} \simeq k_{NO_3^-}$. Under this condition, the half-wave potential defined by

$$E_{1/2}(1) = E^{\circ}(1) + (RT/F)\ln[k_{NO_2^-}^2/(k_{NO}\cdot k_{NO_3^-})]$$
$$= 0.082 \pm 0.008 \text{ V}$$

can be assimilated to the standard potential of couple (1), $E^{\circ}(1)$.

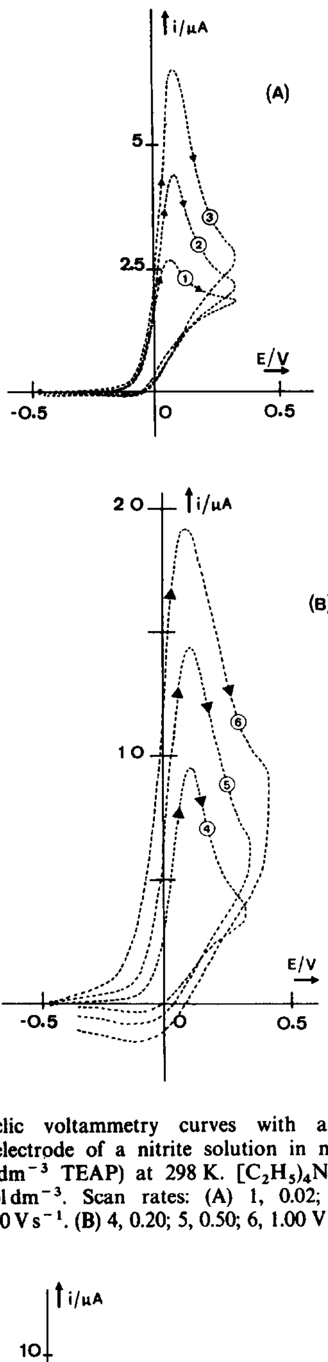

Fig. 1. Cyclic voltammetry curves with a stationary platinum electrode of a nitrite solution in nitromethane (+0.1 mol dm^{-3} TEAP) at 298 K. $[C_2H_5)_4NNO_2] = 1.26 \times 10^{-2}$ mol dm^{-3}. Scan rates: (A) 1, 0.02; 2, 0.05; 3, 0.10 V s^{-1}. (B) 4, 0.20; 5, 0.50; 6, 1.00 V s^{-1}.

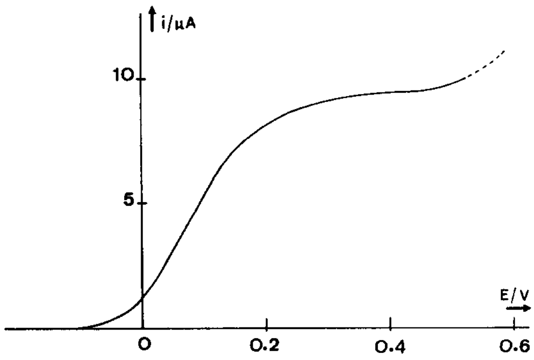

Fig. 2. Linear voltammetry curve with a platinum rotating-disc electrode of a nitrite solution in nitromethane (+0.1 mol dm^{-3} TEAP) at 298 K. $[(C_2H_5)_4NNO_2] = 1.26 \times 10^{-2}$ mol dm^{-3}. Rotation rate of the Pt electrode: 20.9 rps.

Electroreduction of NO^+ *alone and in the presence of* N_2O_4

It is now well known that the electroreduction of NO^+ occurs according to[6]:

$$NO^+ + e^- \leftrightarrows NO. \qquad (7)$$

This system is very sensitive to oxygen at trace levels in solution due to the side reaction: $NO_{elect.} + \frac{1}{2}O_2 \rightarrow NO_2^{\cdot} \leftrightarrows \frac{1}{2}N_2O_4$[6]. The cyclic and rotating-disc voltammograms (at the Pt electrode) in anhydrous and deoxygenated nitromethane are shown in Figs 3 and 4. NO^+ exhibits a reduction E–i wave at $E_{1/2}(7) = +0.88$ V *vs* $E_{1/2}(Fc/Fc^+)$ independent of its concentration (Fig. 3). The cyclic voltammogram shows the apparent reversibility of the electrode system (Fig. 4). If [NO] = 0, the Nernst equation applied to couple (7) is:

$$E = E^\circ(7) + (RT/F)\ln(k_{NO}/k_{NO^+}) +$$

$$(RT/F)\ln[(i - i_{NO^+})/(-i)].$$

The plot of E *vs* $\log[(i - i_{NO^+})/(-i)]$ is a straight line with a slope equal to 67 ± 2 mV and an intercept $E_{int.} = +880$ mV depending on the standard potential of couple (7), $E^\circ(7)$. Assuming that the diffusion coefficients for NO *and* NO^+ *are equal* $k_{NO} \simeq k_{NO^+}$),the value of $E_{int.}$ can be approximated to the standard potential $E^\circ(7)$.

From the ionic dissociation constant of N_2O_4 into NO^+ and NO_3^- ($K^i_{N_2O_4} = [NO^+][NO_3^-]/[N_2O_4] = 6.3 \times 10^{-10}$ mol dm^{-3} at 298 K in nitromethane [7]) it is possible to evaluate the standard potential of the following couple

$$N_2O_4 + e^- \leftrightarrows NO + NO_3^- \qquad (8)$$

from the equation

$$E^\circ(8) = E^\circ(7) + (RT/F)\ln K^i_{N_2O_4}. \qquad (9)$$

We found $E^\circ(8) = +0.330 \pm 0.010$ V *vs* $E_{1/2}(Fc/Fc^+)$. The standard potentials for couples (3) and (10)

$$2NO_2^- \leftrightarrows N_2O_4 + 2e^- \qquad (10)$$

can be calculated from the values of $E^\circ(1)$, $E^\circ(7)$, $E^\circ(8)$, $K^i_{N_2O_4}$ and the molecular dissociation constant of N_2O_4 into $NO_2^{\cdot}$ ($K^h_{N_2O_4} = [NO_2]^2/[N_2O_4] = 1.5 \times 10^{-4}$ mol dm^{-3} at 298 K in nitromethane [2]):

$$E^\circ(3) = [E^\circ(1) + E^\circ(7)]/2$$

$$+ (RT/2F)\ln[K^i_{N_2O_4})/(K^h_{N_2O_4})]$$

$$= +0.320 \pm 0.010 \text{ V} \, vs E_{1/2}(Fc/Fc^+)$$

and

$$E^\circ(10) = [E^\circ(1) + E^\circ(8)]/2 =$$

$$+0.205 \pm 0.010 \text{ V } vs$$

$$E_{1/2}(Fc/Fc^+).$$

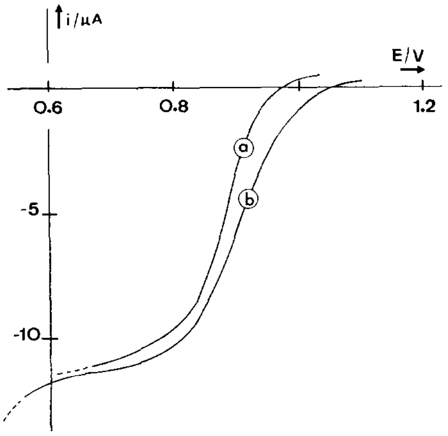

Fig. 3. Linear voltammetry curves with a platinum rotating-disc electrode of a nitrosonium solution and an $NO^+ + N_2O_4$ mixture in nitromethane (+0.1 mol dm^{-3} TEAP) at 298 K. [$NOC1O_4$] = 8.68 × 10^{-3} mol dm^{-3}. [N_2O_4] = 0 (a) and 2.15 × 10^{-2} mol dm^{-3} (b). Rotation rate of the Pt electrode: 62.8 rps.

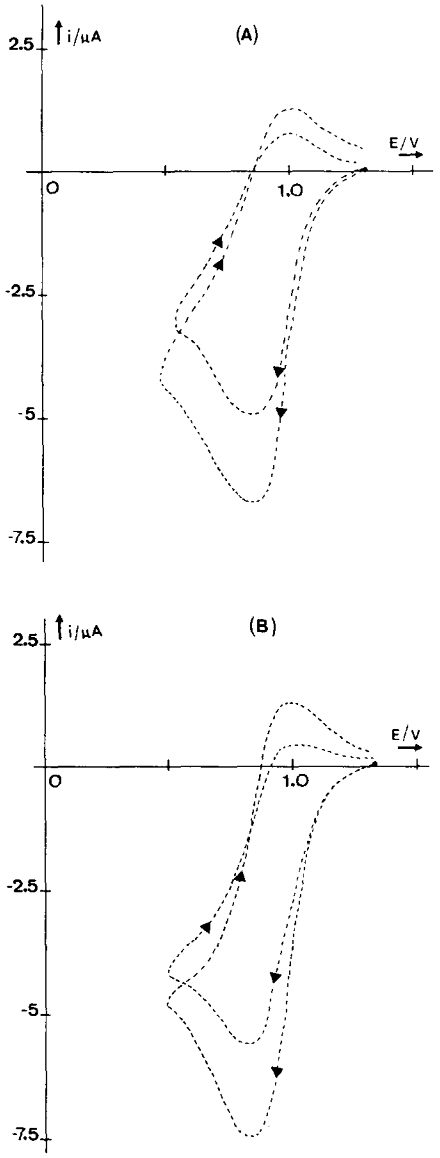

Fig. 4. Cylic voltammetry curves with a stationary platinum electrode of a nitrosonium solution and an $NO^+ + N_2O_4$ mixture in nitromethane (+0.1 mol dm^{-3} TEAP) at 298 K. [$NOClO_4$] = 8.68 × 10^{-3} mol dm^{-3}. [N_2O_4] = 0 (A) and 2.15 × 10^{-2} mol dm^{-3} (B). Scan rates: 0.05 and 0.10 V s^{-1}.

As shown in Fig. 3b, the cathodic E–i curve obtained for an $NO^+ + N_2O_4$ mixture exhibits a positive shift with reference to this one, corresponding to an NO^+ solution. This phenomenon has been ascribed to a chemical reaction following the electron transfer step according to[6, 7]:

$$NO^+ + e^- \leftrightarrows NO \qquad (7)$$

$$NO + [NO_2^{\cdot} \leftrightarrows \tfrac{1}{2}N_2O_4] \leftrightarrows N_2O_3. \qquad (11)$$

The cyclic voltammogram of the oxidation wave of N_2O_3 is very similar to those found with $NO^+ + N_2O_4$ mixtures (Fig. 5) and shows an apparent reversibility. In order to sustain this result and to gain more information concerning reaction (11), we have undertaken the study of the cathodic E–i curve obtained with an $N_2O_4 + NO^+$ mixture. If $[N_2O_3] = 0$, the Nernst equation applied to the overall process

$$NO^+ + \tfrac{1}{2}N_2O_4 + e^- \leftrightarrows N_2O_3 \qquad (12)$$

may be written as follows

$$E = E^\circ(12) + (RT/F)\ln[k_{N_2O_3}/(k_{NO^+})(k_{N_2O_4})^{1/2}]$$
$$+ (RT/F)\ln\{(i - i_{NO^+})(i - i_{N_2O_4})^{1/2}/(-i)\} \qquad (13)$$

where $k_{N_2'O_3}$, k_{NO^+} and $k_{N_2O_4}$ are the coefficients of proportionality for N_2O_3, NO^+ and N_2O_4, respectively. Assuming that the diffusion coefficients of N_2O_3 and NO^+ are equal, the coefficient for N_2O_4 is given by $k_{N_2O_4} \simeq 2k_{N_2O_3} \simeq 2k_{NO^+} = 2k$. We found a linear E *vs* log $\{i - i_{NO^+})(i - i_{N_2O_4})^{1/2}/(-i)\}$plot with a slope close enough to $2.303RT/F$: $\leqq 79$ mV(if $\omega \leqq 62.8$ rps) depending upon the rotating rate, ω, of the Pt electrode. Indeed, process (12) was found to be more reversible when ω decreases. This phenomenon has been ascribed to the occurrence of the kinetics of molecular reaction (11)[7] induced on the Pt electrode surface. From this result, we have then attempted to evaluate the standard potential of couple (12) using the relationship:

$$E_{1/2}(12) = E^\circ(12) + (RT/F)\ln\big[[N_2O_4] - [NO^+]/4\big]^{1/2} \qquad (14)$$

where $E_{1/2}(12)$ is the half-wave potential of the E–i curve obtained with a known mixture of NO^+ and N_2O_4. We obtained $E^\circ(12) = 0.955 \pm 0.010$ V *vs*$E_{1/2}$(Fc/Fc$^+$) by taking several $NO^+ + N_2O_4$ mixtures with different $[N_2O_4]/[NO^+]$ ratios from ½ to 3. On the other hand, $E^\circ(12)$ may also be written:

$$E^\circ(12 = E^\circ(7) - (RT/F)\ln K^{m}_{N_2O_3}. \qquad (15)$$

Thereby, the equilibrium constant $K^{m}_{N_2O_3}$ corresponding to the molecular dissociation

$$N_2O_3 \leftrightarrows NO + \tfrac{1}{2}N_2O_4 \qquad (16)$$

has been calculated: $k^{m}_{N_2O_3} = (5.6 \pm 2.6) \times 10^{-2}\ \mathrm{mol^{1/2}\,dm^{-3/2}}$ in nitromethane at 298 K. From the homolytic dissociation constant of N_2O_4, we can also evaluate the equilibrium constant, $K^{m'}_{N_2O_3}$, for the reaction

$$N_2O_3 \leftrightarrows NO + NO_2^{\cdot}. \qquad (17)$$

$K^{m'}_{N_2O_3} = (6.8 \pm 1.0) \times 10^{-4}\ \mathrm{mol\,dm^{-3}}$ at 298 K in nitromethane.

We have then attempted to obtain the ionic dissociation constant, $K^{i}_{N_2O_3}$, of N_2O_3 as $N_2O_3 \leftrightarrows NO^+$

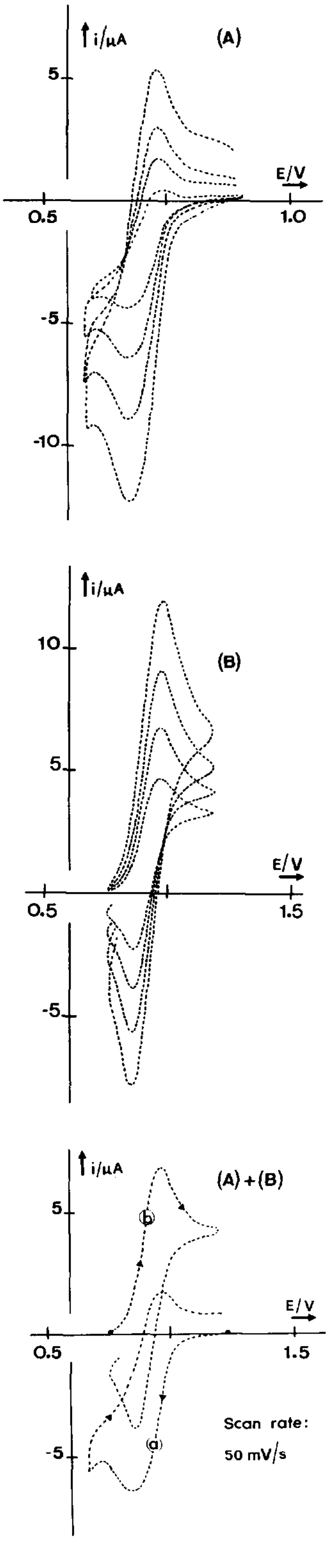

Fig. 5. Cyclic voltammetry curves with a stationary platinum electrode of a dinitrogen trioxide solution and an $NO^+ + N_2O_4$ (in excess) mixture in nitromethane (+0.1 mol dm^{-3} TEAP) at 298 K. (A) $[NOClO_4] = 8.7 \times 10^{-3}$ mol dm^{-3} , and N_2O_4 in excess: $[N_2O_4] \simeq 8.0 \times 10^{-2}$ mol dm^{-3}. (B) $[N_2O_3] \simeq 10^{-2}$ mol dm^{-3}. Scan rates: 0.02, 0.05, 0.10 and 0.20 V s^{-1}.

$+NO_2^-$. The ionic formation of N_2O_3 results from the redox reaction

$$NO^+ + e^- \leftrightarrows NO \qquad (7)$$

$$NO_2^- \leftrightarrows \tfrac{1}{2}N_2O_4 + e^- \qquad (10)$$

followed by the molecular association

$$NO + \tfrac{1}{2}N_2O_4 \leftrightarrows N_2O_3. \qquad (16)$$

Hence, $K^{i}_{N_2O_3}$ can be calculated from the equation

$$\log K^{i}_{N_2O_3} = [E°(10) - E°(7)]F/(2.303\,RT) + \log K^{m}_{N_2O_3}.$$

We found $K^{i}_{N_2O_3} = (1.3 \pm 0.4) \times 10^{-13}\ \mathrm{mol\,dm^{-3}}$ at 298 K in nitromethane.

Electro-oxidation of nitrogen dioxide

The rotating-disc voltammograms of N_2O_4 dissolved in anhydrous and deoxygenated nitromethane are shown in Figs 6 and 7. The shape of the anodic wave exhibits a dramatic change with temperature. Indeed the height of the anodic wave increases strongly and its half-wave potential is shifted dramatically to lower potentials as the temperature increases. In addition, the peak potentials (E^{a}_{p}, E^{c}_{p}) of the cyclic voltammograms obtained with N_2O_4 solutions are close enough to those corresponding to the reduction of NO_2^+ (Figs 7 and 8). As suggested previously[2], these phenomena can be attributed to the occurrence of the homolytic dissociation on N_2O_4

$$\text{Scheme II}\left\{\begin{array}{ll} N_2O_4 \underset{k_4}{\overset{k_{-4}}{\leftrightarrows}} 2NO_2^{\cdot} & (4) \\ 2NO_2^{\cdot} \leftrightarrows 2NO_2^+ + 2e^- & (18) \end{array}\right.$$

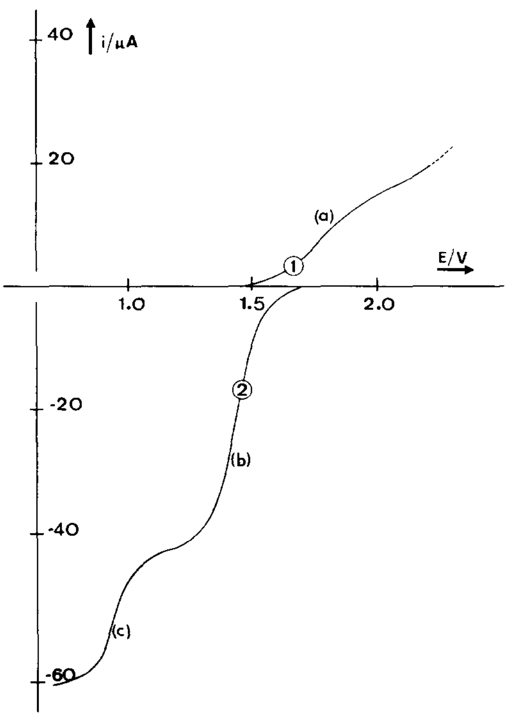

Fig. 7. Linear voltammetry curves with a platinum rotating-disc electrode of an N_2O_4 solution and a nitryl solution in nitromethane (+0.1 mol dm^{-3} TEAP) at 298 K. (1) $[N_2O_4] = 1.05 \times 10^{-2}$ mol dm^{-3}; (2) $[NO_2ClO_4] \simeq 1.10 \times 10^{-2}$ mol dm^{-3}. Wave (a): oxidation of nitrogen dioxide resulting from the monomerization $N_2O_4 \rightarrow 2NO_2^{\cdot}$. Wave (b): reduction of nitronium ion according to $2NO_2^+ + 2e^- \leftrightarrows 2NO_2^{\cdot} \leftrightarrows N_2O_4$. Wave (c): reduction of nitrosonium ions provided both by the $NOClO_4$ salt present as an impurity in the NO_2ClO_4 salt, and by the reduction of NO_2^+ in the presence of $HClO_4$ (resulting from the hydrolysis of NO_2^+), as mentioned previously[4]. Rotation rate of the Pt electrode: 62.8 rps.

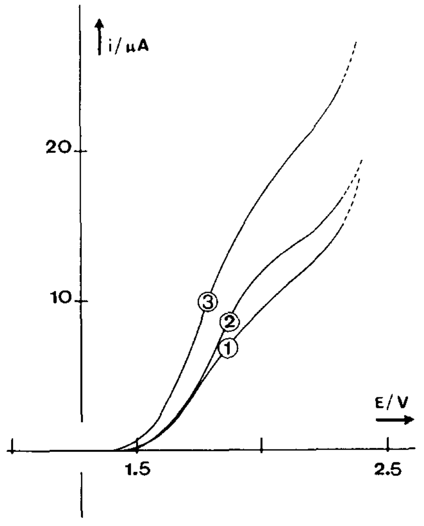

Fig. 6. Linear voltammetry curves with a platinum rotating-disc electrode of a dinitrogen tetroxide solution in nitromethane (+0.1 mol dm^{-3} TEAP) at various temperatures. $[N_2O_4] = 1.07 \times 10^{-2}$ mol dm^{-3}. $T = 295$ K (1), 299 K (2) and 303 K (3). Rotation rate of the Pt electrode: 62.8 rps.

where N_2O_4 is considered to be a non-electroactive species at these potentials. A general mathematical formulation for scheme II has already been described[2, 8, 9]. At high sweep rates ($v \geq 0.2\ \mathrm{V\,s^{-1}}$) the electrochemical system is kinetically controlled in CV, and the peak height does not depend on v. The measured CV current becomes independent of the kinetics of ET, and the $E-i$ curves of cyclic voltammetry are like polarographic waves (Fig. 9). The CV potential is related to a dimensionless parameter ξ^+ [8] as follows

$$E = E°(18) + (RT/F)\xi^+ + (RT/2F)\ln(4RT/3F) + (RT/4F)\ln K^{h}_{N_2O_4} + (RT/4F)\ln[N_2O_4] + (RT/2F)\ln k_{-4} - (RT/2F)\ln v \qquad (19)$$

where $[N_2O_4]$ is the overall concentration of N_2O_4, and k_{-4} is the rate constant for the dimerization of nitrogen dioxide. With the known values of $K^{h}_{N_2O_4}$, k_{-4}, $[N_2O_4]$ and ξ^+ ($\xi^+ = +0.13$ at the half-plateau current), the standard potential of the $NO_2^+/NO_2^{\cdot}$ couple can be evaluated: $E°(18) = 1.620 \pm 0.020$ V *vs* $E_{1/2}(Fc/Fc^+)$. Conversely, for very weak values of the potential scan rate ($v \leq 0.01\ \mathrm{V\,s^{-1}}$), the CV potential (depending on the time)E *vs* ξ^* (a dimensionless

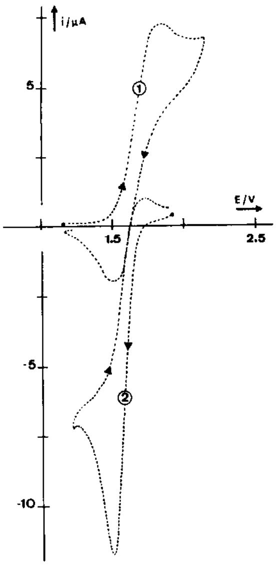

Fig. 8. Cyclic voltammetry curves with a stationary platinum electrode of an N_2O_4 solution and a nitryl solution in nitromethane (+0.1 mol dm^{-3} TEAP) at 303 K. (1) $[N_2O_4] \simeq 9.0 \times 10^{-3}$ mol dm^{-3}; (2) $[NO_2ClO_4] \simeq 1.4 \times 10^{-2}$ mol dm^{-3}. Scan rate: 0.02 V s^{-1}.

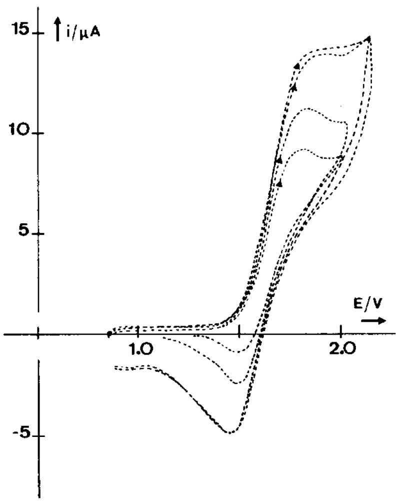

Fig. 9. Cyclic voltammetry curves with a stationary platinum electrode of an N_2O_4 solution in nitromethane (+0.1 mol dm^{-3} TEAP) at 298 K. $[N_2O_4] \simeq 1.0 \times 10^{-2}$ mol dm^{-3}. Scan rates: 0.05, 0.10, 0.20 and 0.50 V s^{-1}.

parameter) according to[8]

$$E = E^\circ(18) + (RT/F)\xi^* - (RT/2F)\ln K^{h}_{N_2O_4} + (RT/2F)\ln[N_2O_4]. \qquad (20)$$

The value of ξ^* for the half-peak potential, $E_p^{1/2}$, is $\xi^* = -0.40$. We found $E^\circ(18) = 1.625 + 0.020$ V *vs* $E_{1/2}(Fc/Fc^+)$. This value is in good agreement with that obtained above. The standard potential of the couple

$$NO_2^+ + e^- \leftrightarrows \tfrac{1}{2}N_2O_4 \qquad (21)$$

can also be determined from the relationship

$$E^\circ(21) = E^\circ(18) - (RT/2F)\ln K^{h}_{N_2O_4} = 1.730 \pm 0.020 \text{ V}.$$

The ionic dissociation of N_2O_4

$$N_2O_4 \leftrightarrows NO_2^+ + NO_2^- \qquad (22)$$

may be considered as a disproportionation equilibrium

$$\tfrac{1}{2}N_2O_4 \leftrightarrows NO_2^+ + e^- \qquad (21)$$

$$\tfrac{1}{2}N_2O_4 + e^- \leftrightarrows NO_2^- \qquad (10)$$

The equilibrium constant for reaction (22) can then be evaluated by the equation

$$\log K^{ii}_{N_2O_4} = [E^\circ(10) - E^\circ(21)]F/(2.303\, RT).$$

The value of $\log K^{ii}_{N_2O_4}$ was found to be -25.4 ± 1.5 at 298 K in nitromethane.

All the results are reported in Table 1 and compared with those obtained in other solvents. Consequently, compared with a non-donar solvent such as CCl_4 or liquid N_2O_4, the molecular dissociation of the N_2O_4 and N_2O_3 species are relatively close in nitromethane but less extensive in a donor solvent such as acetonitrile, propylene carbonate or sulpholane. It is worth noting that the values of the standard potentials can depend strongly on solvation phenomena if the species involved in the corresponding couples are highly electron accepting such as NO^+ and NO_2^+, whereas if the nitrogen species are solvated weakly such as NO_3^-, NO_2^-, NO and NO_2[7, 10], the solvent molecules barely intervene in the electrochemical process and thereby the value of the standard potential of a couple such as (1) or (3) does not vary significantly whatever the solvent used (Table 1). All these findings suggest that the solvating properties of nitromethane are weak.

On account of the highly oxidizing behaviour of the NO_2^+ ion in nitromethane, it is now interesting to examine its action on aromatic hydrocarbons despite the low solubility of nitryl salts in this solvent[7].

Nitration of aromatics with NO_2^+ *in nitromethane*

A direct comparison of the ionization potentials (I_p) of aromatics (ArH) with the anodic peak potentials (E_p^a) of the $ArH^{\cdot+}/ArH$ couple allows solvation effects to be assessed[11–13]. As mentioned previously[14], the variation of anodic peak potential (measured at a constant sweep rate of 0.1 V s^{-1}) obtained under irreversible CV conditions in nitromethane has been studied as a function of I_p for various aromatics. The line in the graph describes the relationship

$$E_p^a = 0.70\,(I_p) - 4.48 \qquad (23)$$

where E_p^a is given in volts *vs* $E_{1/2}(Fc/Fc^+)$, and I_p is given in electron volts. Equation (23) is close enough to that found previously by Kochi *et al.*[13] in acetonitrile: (after correction) $E_p^a = 0.704\,(I_p) - 4.327$ V *vs* $E_{1/2}(Fc/Fc^+)$ or $E_p^a = 0.704\,(I_p) - 3.627$ V *vs* normal hydrogen electrode (*nhe*), with $E(nhe) = E_{1/2}(Fc/Fc^+) + 0.70$ V. Taking into account the difference in free energy associated with the solvation changes for the reaction $ArH \leftrightarrows ArH^{\cdot+} + e^-$, defined by

$$\Delta G_s^\circ = (G_s^\circ - G_g^\circ)_{ArH^{\cdot+}} - (G_s^\circ - G_g^\circ)_{ArH} \qquad (24)$$

with s: solvent and g: gas,

Table 1. Electrochemical and thermodynamic data for reactions involving oxygenated nitrogen compounds in nitromethane, and comparison with results obtained in other organic solvents

Electrochemical couple	Standard potential[†] E°/V Nitromethane	 Sulpholane[2, 5, 6]
$2NO_2^- \leftrightarrows NO + NO_3^- + e^-$	$+0.082 \pm 0.008$	$+0.070$
$2NO_2^- \leftrightarrows N_2O_4 + 2e^-$	$+0.205 \pm 0.010$	$+0.175$
$NO_2 + e^- \leftrightarrows NO_2^-$	$+0.320 \pm 0.010$	$+0.320$
$N_2O_4 + e^- \leftrightarrows NO + NO_3^-$	$+0.330 \pm 0.010$	$+0.280$
$NO^+ + e^- \leftrightarrows NO$	$+0.880 \pm 0.010$	$+0.715$
$NO^+ + \frac{1}{2}N_2O_4 \leftrightarrows N_2O_3$	$\pm 0.955 \pm 0.010$	$+0.850$
$NO_2^+ + e^- \leftrightarrows NO_2^{\cdot}$	$+1.620 \pm 0.020$	$+1.35$
$2NO_2^+ + 2e^- \leftrightarrows N_2O_4$	$+1.730 \pm 0.020$	$+1.50$

Chemical reaction	Equilibrium constant ($\log K$) at 298 K in nitromethane	 in various solvents (see refs [2, 5–7, 24–27])
$N_2O_4 \leftrightarrows NO^+ + NO_3^-$	-9.2[7]	-7.2(TMS);[‡] -7.3(PC)
$N_2O_4 \leftrightarrows NO_2^+ + NO_2^-$	-25.4 ± 1.5	-22.0(TMS)[‡]
$N_2O_4 \leftrightarrows 2NO_2^{\cdot}$	-3.82[2]	-4.85(TMS); -4.73(PC); -3.75(CCl_4)
$N_2O_3 \leftrightarrows NO^+ + NO_2^-$	-12.89 ± 0.12	-11.2(TMS);‡ -12.6 (liquid N_2O_3 at low *T*)
$N_2O_3 \leftrightarrows NO + \frac{1}{2}N_2O_4$	-1.25 ± 0.25	-2.25(TMS); -1.00(CCl_4); -1.72 (water); -1.83(AN); -1.60 (toluene)
$N_2O_3 \leftrightarrows NO + NO_2^{\cdot}$	-3.2 ± 1.0	-4.8(TMS); -4.1(AN); -2.9(CCl_4)
$NO^+ + NO_2^- \leftrightarrows NO + NO_2^{\cdot}$	$+9.3$	$+6.6$(TMS)[‡]
$2NO_2^- + N_2O_4 \leftrightarrows 2NO + 2NO_3^-$	$+4.1 \pm 0.3$	$+3.6$(TMS)[‡]

Abbreviations: AN, acetonitrile; PC, propylene carbonate; TMS, tetrahydrothiophene-1,1-dioxide or sulpholane.

† *Versus* the half-wave potential of a ferrocene solution.

‡ Values determined at 303 K.

and the reorganization energy of $ArH^{\cdot+}$ as

$$\Delta G_r^\circ = G_g^\circ(ArH^{\cdot+}) - G_g^\circ(ArH^{+*}) \tag{25}$$

the standard oxidation potential of $ArH^{\cdot+}/ArH$ may be expressed as

$$E^\circ(ArH^{\cdot+}/ArH) = I_p + (\Delta G_r^\circ + \Delta G_s^\circ)/F + C_{ste}. \tag{26}$$

For the series of arenes under consideration, the sum $\Delta G_r^\circ + \Delta G_s^\circ$ varies according to[13]

$$\Delta G_r^\circ + \Delta G_s^\circ = m_s F(I_p) + B \quad -1 < m_s < 0 \tag{27}$$

where B and m_s (a parameter attributed to solvation properties of the solvent) are constant.

Hence, equation (26) becomes

$$E^\circ(ArH^{\cdot+}/ArH) = (1 + m_s)I_p + B. \tag{28}$$

The electron transfer $ArH \rightarrow ArH^{\cdot+} + e^-$ was previously considered as a rapid, reversible pre-equilibrium followed by the chemical reaction $ArH^{\cdot+} \xrightarrow{k}$ side-products in aprotic media[12, 13] (where k is the kinetic constant). Therefore, the irreversible CV voltammograms obtained for the aromatic hydrocarbons at a constant sweep rate (0.1 $V\,s^{-1}$) reflect the kinetics of the follow-up reaction. As pointed out by Nadjo and Savéant[15], the anodic peak potential arising from this EC process is given by

$$E_p^a = E^\circ(ArH^{\cdot+}/ArH) - (RT/F)\ln(kRT/Fv) + C_{ste}.$$

Thereby, the variation of the anodic peak potential can be written as

$$\Delta E_p^a = \Delta E^\circ(ArH^{\cdot+}/ArH) - RT/F(\Delta \ln k)$$

where v is a constant sweep rate. The kinetic term $\Delta \ln k$ in this last expression was considered as a scattering factor, $\pm \delta E$, in the assessment of the E_p^a potential[13]. Accordingly E_p^a can be directly related to E° with a slope close to 1

$$E_p^a = E^\circ \pm \delta E. \tag{29}$$

The combination of the relationships in equations (28) and (29) leads to the correlation of the irreversible E_p^a with the vertical I_p as follows (with NM: nitromethane)

$$E_p^a = (1 + m_{NM})I_p + B \pm \delta E. \tag{30}$$

Comparing equation (30) with equation (23), the value of m_{NM} can be deduced: $m_{NM} = -0.30$, which is close to that obtained in acetonitrile, AN ($m_{AN} = -0.296$)[13]. The decrease of ($\Delta G_r^\circ - \Delta G_s^\circ$) is related to the structural changes of increasing size of the arene. Such a phenomenon indicates that the deviation of the slope (E_p^a/I_p) from unity represents variations of mainly ΔG_s°[13]. Hence, solvation phenomena on an aromatic and its radical cation in nitromethane are similar to those observed in acetonitrile. According to Marcus theory[16–18], the outer-sphere (solvent) reorganization energy depends upon the static dielectric constant (D) and the refractive index (η). Under these conditions, the correlation of the standard oxidation potentials of the aromatic hydrocarbons in trifluoroacetic acid ($D = 39.5$ and $\eta = 1.2850$) with the anodic peak potentials obtained from the irreversible cyclic voltammograms in acetonitrile ($D = 37.5$ and $\eta = 1.3441$)[13]

$$E^\circ(\mathrm{ArH}^{\cdot +}/\mathrm{ArH}) = 1.01\ E_p^a - 0.001\ \mathrm{V} \qquad (31)$$

is still valid in nitromethane ($D = 35.9$ *and* $\eta = 1.3817$). The values of the standard potentials of some aromatics used in this work to study the nitration process with NO_2^+ in nitromethane are reported in Table 2 and compared to those found in other organic solvents[1, 12, 13, 19, 20]. Hence the equilibrium constant, $K(32)$, for the ET

$$NO_2^+ + \mathrm{ArH} \leftrightarrows NO_2^{\cdot} + \mathrm{ArH}^{\cdot +} \qquad (32)$$

with a free energy difference, $\Delta G^\circ(32)$, can be determined in nitromethane by means of the equation

$$\log K(32) = [E^\circ(18) - E^\circ(\mathrm{ArH}/\mathrm{ArH}^{\cdot +})]F/(2.303\ RT)$$

$$\Delta G^\circ(32) = -RT \ln K(32).$$

The results are reported in Table 3 and compared with those obtained previously in acetonitrile and sulpholane. It can be concluded that the NO_2^+ species is found to be more suitable for the nitration of aromatics (even those not easily oxidizable) because of the greater oxidizing behaviour of nitronium ions in nitromethane.

The activation free energy, $\Delta G^*(32)$, for the ET process (32) is given by the Marcus theory[21–23]

$$\Delta G^*(32) = (\lambda/4)[1 + \Delta G^\circ(32)/\lambda]^2 \qquad (33)$$

where λ is the total reorganization energy. The effect of nitromethane is assumed to decrease the activation energy due to an increase of $K(32)$, with reference to phenomena observed in acetonitrile[19, 20]. But, as suggested by Eberson and Radner[19, 20], outer-sphere ET is generally prohibited for kinetic reasons, with the exception of highly polycyclic and very electron-rich systems, due to the very large reorganization energy of the $NO_2^+/NO_2^{\cdot}$ couple[19, 20]. Hence, even if $K(32)$ is larger than in sulpholane or acetonitrile, the interaction of NO_2^+ with an aromatic should still lead to an association step to give a σ or Wheland intermediate according to an inner-sphere ET mechanism.

On the other hand, Schmitt *et al.*[29] showed that NO_2^+ does not nitrate aromatics to give a σ or Wheland intermediate, ArHNO_2^+, in the gas phase but instead reacts by either O^+ or ET. However, when a mixture ArH/Bs/NO_2 (where Bs is a basic solvent such as pyridine) was ionized, rapid proton transfer to Bs was observed from the product of the reaction between $\mathrm{ArH}^{\cdot +}$ and $NO_2^{\cdot}$[29]

$$\mathrm{ArHNO}_2^+ + \mathrm{Bs} \rightarrow \mathrm{ArNO}_2 + \mathrm{HB}_s^+.$$

In condensed media, the occurrence of aromatic nitration also depends upon deprotonation phenomena induced, in part, by the donor character of the solvent used, and the presence of basic ions such as ClO_4^- and NO_3^- (which can be generated in solution through the

Table 2. Standard potentials, $E^\circ(\mathrm{ArH}^{\cdot +}/\mathrm{ArH})$, of some aromatics determined in organic media

Aromatic compounds	I_p/eV	Standard potential, $E^\circ(\mathrm{ArH}^{\cdot +}/\mathrm{ArH})$/V†		
		Acetonitrile‡ (and/or trifluoroacetic acid) [1, 12, 13, 19, 20]	Sulpholane[28]	Nitromethane§
Anthracene	7.40	0.91	0.86	0.71
Naphthalene	8.12	1.38	1.32	1.22
Phenanthrene	8.10	1.37	1.33	1.20
Mesitylene	8.40	1.65–1.56	1.56	1.41
p-Xylene	8.44	1.60	1.57	1.44
Toluene	8.81	1.94–1.82	1.86	1.71

† *Versus* the half-wave potential of a ferrocene solution, $E_{1/2}(\mathrm{Fc}/\mathrm{Fc}^+)$.

‡ The values of $E^\circ(\mathrm{ArH}^{\cdot +}/\mathrm{ArH})$ determined previously *vs* E(*nhe*) are expressed in this table with reference to $E_{1/2}(\mathrm{Fc}/\mathrm{Fc}^+)$ by means of the equation: $E_{1/2}(\mathrm{Fc}/\mathrm{Fc}^+) = E(nhe) - 0.70$ V.

§ This work.

Table 3. Equilibrium constant, $K(32)$, and standard free energy, $\Delta G^\circ(32)$, corresponding to the reaction $NO_2^+ + \mathrm{ArH} \leftrightarrows NO_2^{\cdot} + \mathrm{ArH}^{\cdot +}$ (32) for various aromatic hydrocarbons in some aprotic solvents

Aromatic compound	I_p/eV	Nitromethane		Sulpholane[28]		Acetonitrile[19, 20]	
		log $K(32)$	$\Delta G^\circ(32)$/ kJ mole^{-1}	log $K(32)$	$\Delta G^\circ(32)$/ kJ mole^{-1}	log $K(32)$	$\Delta G^\circ(32)$/ kJ mole^{-1}
Anthracene	7.40	+15.2	−87.2	+8.3	−48.3	−0.8	+4.6
Naphthalene	8.12	+6.8	−38.8	+0.5	−2.9	−8.67	+49.8
Phenanthrene	8.10	+7.0	−40.2	+0.3	−1.9	—	—
Mesitylene	8.40	+3.4	−19.6	−3.5	+20.3	−15.2	+87.5
p-Xylene	8.44	+2.9	−16.8	−3.7	+21.3	—	—
Toluene	8.81	−1.4	+8.1	−8.5	+49.3	−17.6	+100.9

ionic dissociation of N_2O_4 into NO^+ and NO_3^-)[30, 31]

$$(NO_2^+, ClO_4^-) + ArH \rightarrow ArNO_2 + HClO_4 \quad (34)$$

$$(NO_2^+, ClO_4^-) + N_2O_4 + ArH \rightarrow ArNO_2 + (NO^+, ClO_4^-) + HNO_3. \quad (35)$$

Indeed, it has been shown that $HClO_4$ and above all HNO_3 are weakly dissociated in aprotic media: the acidity constants for $HClO_4$ and HNO_3 are equal to 3 and 16 in sulpholane at 303 K[30–32] and 7.4 and 20.2 in nitromethane at 298 K (A. Boughriet and M. Wartel, unpublished work).

To summarize, as suggested previously in the gas phase[29], the deprotonation of the σ-complex in aprotic media seems similarly to play a crucial role to yield nitro compounds, in connection with the highly oxidizing characteristics of nitronium ions on the aromatic ring in sulpholane, propylene carbonate[7] and especially in nitromethane (see Table 3).

CONCLUSION

The electrochemical properties of oxygenated nitrogen compounds have been studied in nitromethane at 298 K by means of cyclic and linear voltammetry at a platinum electrode. It has been possible to determine the ionic and molecular dissociation constants of N_2O_3 and N_2O_4. Since the neutral nitrogen species are weakly solvated in nitromethane, the thermodynamic values found are in reasonably good agreement with those determined previously in non-polar, inert solvents. The weak solvating properties of nitromethane also explain the low ionic dissociations of N_2O_4 and N_2O_3 in comparison with those obtained in sulpholane or propylene carbonate. Likewise, if the nitrogen species involved in an electrochemical couple are barely affected by solvation phenomena (such as NO, NO_2, NO_2^- or NO_3^-), the standard potential values remain nearly constant in all the aprotic solvents used.

This work has been extended to the study of the electro-oxidation of aromatic (ArH) into aromatic radical cation ($ArH^{\cdot +}$) in order to evaluate the standard oxidation potential of $ArH^{\cdot +}/ArH$. We have subsequently undertaken the study of the aromatic nitration process $NO_2^+ + ArH \rightarrow ArNO_2 + H^+$. This problem has been addressed by the survey of the redox system $NO_2^+ + ArH \leftrightarrows NO_2^{\cdot} + ArH^{\cdot +}$. The equilibrium constant for this reaction is found to be much higher than in sulpholane and particularly acetonitrile, due to the highly oxidizing properties of NO_2^+. However, the nitration process should proceed, in most cases, according to an inner-ET mechanism. Indeed, the very large reorganization energy of the $NO_2^+/NO_2^{\cdot}$ couple prevents the nitronium ion from acting as a reagent for non-bonded ET. The generation of a σ-complex, $ArHNO_2^+$, is followed by its deprotonation either owing to the ability of this intermediate to accept electron donation from the basic solvent or under the action of basic compounds dissolved in the medium. This deprotonation occurs as a key step enabling the formation of nitro compounds in condensed media as well as in the gas phase (if this contains gaseous molecules of basic solvents such as pyridine).

REFERENCES

1. L. Eberson, *Adv. Phys. org. Chem.* **18,** 79 (1982).
2. A. Boughriet, M. Wartel, J. C. Fischer and C. Bremard, *J. electroanal. Chem.* **190,** 103 (1985).
3. M. Wartel, A. Boughriet and J. C. Fischer, *Anal. Chim. Acta* **110,** 211 (1979).
4. J. C. Fischer, A. Boughriet and M. Wartel, *Talanta* **28,** 233 (1981).
5. A. Boughriet, J. C. Fischer, G. Leman and M. Wartel, *Bull. Soc. Chim. Fr.* **1,** 8 (1985).
6. A. Boughriet, M. Wartel, J. C. Fischer and Y. Auger, *J. electroanal. Chem.* **186,** 201 (1985) and references therein.
7. A. Boughriet, A. Coumaré, J. C. Fischer and M. Wartel, *J. electroanal. Chem.* **200,** 217 (1986).
8. J. M. Savéant and E. Vianello, *Electrochim. Acta* **12,** 1545 (1967).
9. J. Koutecky and V. Levich, *Zh. Fiz. Klim.* **32,** 1565 (1958).
10. A. Boughriet and M. Wartel, *J. electroanal. Chem.* **251,** 127 (1988).
11. B. Case, *Reactions of Molecules at Electrodes* (Edited by N. S. Hush), p. 25. John Wiley, New York (1964).
12. V. D. Parker, *J. Am. chem. Soc.* **98,** 98 (1976).
13. J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman and J. K. Kochi, *J. Am, chem. Soc.* **106,** 3968 (1984) and references therein.
14. A. Boughriet and M. Wartel, *Chem. Commun.*, in press.
15. L. Nadjo and J.-M. Savéant, *J. electroanal. Chem.* **48,** 113 (1973).
16. R. A. Marcus, *J. Chem. Phys.* **24,** 4966 (1956).
17. R. A. Marcus, *J. Chem. Phys.* **43,** 679 (1965).
18. R. A. Marcus, *J. phys. Chem.* **72,** 891 (1968).
19. L. Eberson and F. Radner, *Acta Chem. Scand.* **38**B, 861 (1984).
20. L. Eberson and F. Radner, *Acc. Chem. Res.* **20,** 53 (1987).
21. R. A. Marcus, *Annu. Rev. phys. Chem.* **15,** 155 (1964).
22. R. A. Marcus, *Special Topics in Electrochemistry* (Edited by P. A. Rock) p. 161. Elsevier, Amsterdam (1977).
23. R. A. Marcus, *Faraday Discuss. Chem. Soc.* **74,** 7 (1982).
24. T. F. Redmond and B. B. Wayland, *J. phys. Chem.* **72,** 1626 (1968).
25. A. W. Shaw and A. J. Vosper, *J. chem. Soc. A* 1592 (1971).
26. M. Grätzel, S. Taniguchi and A. Henglein, *Ber. Bunsenges. phys. Chem.* **74,** 488 (1970).
27. A. W. Shaw and A. J. Vosper, *J. chem. Soc., Dalton Trans.* 2172 (1974).
28. A. Boughriet and M. Wartel, *J. electroanal. Chem.* **262,** 183 (1989).
29. R. J. Schmitt, S. E. Buttrill Jr. and D. S. Ross, *J. Am. chem. Soc.* **106,** 926 (1984).
30. A. Boughriet and M. Wartel, *Talanta* **35,** 205 (1988).
31. A. Boughriet, C. Bremard and M. Wartel, *Electrochim. Acta* **33,** 701 (1988).
32. J. F. Coetzee and R. J. Bertozzi, *Analyt. Chem.* **45,** 1064 (1973).