Electrochemical and Thermodynamic Properties of Oxygenated Nitrogen Compounds and Aromatics in Nitromethane. Application to the Energetic Aspects of the Nitration Process *via* Inner-sphere and/or Outer-sphere Electron-transfer Mechanisms
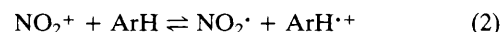
Abdel Boughriet* and Michel Wartel

Laboratoire de Chimie Analytique et Marine, Bât C8, Université des Sciences et Techniques de Lille-Flandres-Artois, 59655 Villeneuve d'Ascq Cédex, France

The electrochemical and thermodynamic behaviour of oxygenated nitrogen compounds and aromatics has been studied in nitromethane (under weak solvation conditions) in order to provide energetic and mechanistic information concerning aromatic nitration comparable to that from gas-phase studies.

Important undefined aspects of the nitration mechanism in organic solvents and in the gas phase remain the focus of active interest.[1—6] The notion of a single nitration mechanism is inapplicable in the condensed phase due to the influence of the reaction medium, *e.g.* solvation and ion-pairing effects.[1—6] An effective approach to minimising these difficulties, and thus progressing towards a general theory of aromatic nitration directly comparable with theoretical results obtained in the gas phase, is the extension of our recent studies in tetrahydrothiophene 1,1-dioxide (sulpholane)[7,8] [D.N. (the donor number of the solvent as established by Gutmann *et al.*[9]) = 14.8] to nitration phenomena in less basic solvent such as nitromethane (D.N. = 2.7[9]). The activation free energy, $\Delta G^{\ddagger}$, for electron transfer (ET) is given by the Marcus equation (1),[10] where ΔG° is the standard free energy change corresponding to the ET reaction (2) and λ is the total

$$\Delta G^{\ddagger} = (\lambda/4)(1 + \Delta G^{\circ}/\lambda)^2 \tag{1}$$

$$NO_2^+ + ArH \rightleftharpoons NO_2^{\boldsymbol{\cdot}} + ArH^{\boldsymbol{\cdot}+} \tag{2}$$
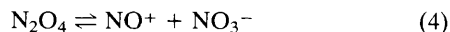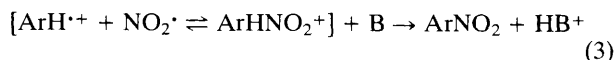
reorganization energy.[1,11] The quantitative evaluation of the feasibility of electron transfer in such a situation requires the standard redox potentials, E°, of both $NO_2^+/NO_2^{\boldsymbol{\cdot}}$ and $ArH^{\boldsymbol{\cdot}+}/ArH$. By combining cyclic and linear voltammetry and e.s.r. spectroscopy, E° ($NO_2^+/NO_2^{\boldsymbol{\cdot}}$) has been determined in nitromethane (Table 1), as for tetrahydrothiophene 1,1-dioxide.[12] Furthermore, as suggested previously,[13] the anodic peak potential (E_p) measured at a standard sweep rate can be correlated to both the vertical ionization potential (I_p) of the same aromatic hydrocarbons in the gas phase [$E_p = 0.70$ (I_p)

Table 1. Electrochemical and thermodynamic properties of oxygenated nitrogen compounds in nitromethane at 298 K.[a]

Electrochemical couple	Standard potential E°/V[b]	Chemical reaction	Equilibrium constant (log K) (298 K) MeNO₂	Equilibrium constant (log K) (298 K) Sulph.[c]
$2NO_2^- \rightleftharpoons NO + NO_3^- + e^-$	0.082 ± 0.008	$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$	-9.2	-7.2[d]
$2NO_2^- \rightleftharpoons N_2O_4 + 2e^-$	0.205 ± 0.010	$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^-$	-25.4 ± 1.5	-22.0[d]
$NO_2^{\boldsymbol{\cdot}} + e^- \rightleftharpoons NO_2^-$	0.320 ± 0.010	$N_2O_4 \rightleftharpoons 2NO_2^{\boldsymbol{\cdot}}$	-3.82	-5.03
$N_2O_4 + e^- \rightleftharpoons NO + NO_3^-$	0.330 ± 0.010	$N_2O_3 \rightleftharpoons NO^+ + NO_2^-$	-12.89 ± 0.40	-11.2[d]
$NO^+ + e^- \rightleftharpoons NO$	0.880 ± 0.010	$N_2O_3 \rightleftharpoons NO + \frac{1}{2}N_2O_4$	-1.25 ± 0.25	-2.25
$NO^+ + \frac{1}{2}N_2O_4 + e^- \rightleftharpoons N_2O_3$	0.955 ± 0.010	$N_2O_3 \rightleftharpoons NO + NO_2^{\boldsymbol{\cdot}}$	-3.2 ± 1.0	-4.8
$NO_2^+ + e^- \rightleftharpoons NO_2^{\boldsymbol{\cdot}}$	1.620 ± 0.020	$NO^+ + NO_2^- \rightleftharpoons NO + NO_2^{\boldsymbol{\cdot}}$	$+9.3$	6.6[d]
$2NO_2^+ + 2e^- \rightleftharpoons N_2O_4$	1.730 ± 0.020	$2NO_2^- + N_2O_4 \rightleftharpoons 2NO + 2NO_3^-$	$+4.1$	3.6[d]
$AnthrH \rightleftharpoons AnthrH^{\boldsymbol{\cdot}+} + e^-$	0.780 ± 0.050	$NO_2^+ + AnthrH \rightleftharpoons NO_2^{\boldsymbol{\cdot}} + AnthrH^{\boldsymbol{\cdot}+}$	$+14.0$	$+7.5$;[d] -0.8[e]
$NaphtH \rightleftharpoons NaphtH^{\boldsymbol{\cdot}+} + e^-$	1.215 ± 0.050	$NO_2^+ + NaphtH \rightleftharpoons NO_2^{\boldsymbol{\cdot}} + NaphtH^{\boldsymbol{\cdot}+}$	$+6.75$	$+0.8$;[d] -8.67[e]

[a] *Abbreviations:* Sulph., tetrahydrothiophene 1,1-dioxide (sulpholane); NaphtH, naphthalene; AnthrH, anthracene. [b] *Vs.* the half-wave potential of a ferrocene solution. [c] Refs. 7, 8, and 17. [d] K Determined at 303 K. [e] In acetonitrile, refs. 1 and 3.

— 4.48 V *vs.* the half-wave potential of a ferrocene (Fc) solution, $E_{1/2}(Fc/Fc^+)]$ and the standard oxidation potentials, $E°(ArH^{·+}/ArH)$, determined in trifluoroacetic acid. These correlations afford a prediction of the standard oxidation potential of various aromatics in nitromethane. Such a correlation derives from the well-established mechanism for the electrochemical (EC) oxidation of ArH which is controlled by the rates of the follow-up reactions.[13] The radical cation formed probably undergoes deprotonation by the basic solvent, reaction (3),[14,15] or by a strong base such as NO_3^- [provided by the ionic dissociation of N_2O_4 added in solution, reaction (4)] to form the very weak acid HNO_3, $pK_a \geqslant 16$.[16]

$$[ArH^{·+} + NO_2^· \rightleftharpoons ArHNO_2^+] + B \rightarrow ArNO_2 + HB^+ \tag{3}$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \tag{4}$$

The mechanism of the aromatic nitration with N_2O_4 and/or N_2O_3 catalysed by NO^+ has also been studied using linear and cyclic voltammetry and e.s.r. spectroscopy (Table 1), taking into account the thermodynamical and electrochemical properties of oxygenated nitrogen compounds dissolved in nitromethane. It should be noted that, on account of the weakly solvation properties of nitromethane, the NO_2^+ and NO^+ species are found to be much more powerful oxidizing agents in nitromethane than in dihydrothiophene 1,1-dioxide, propylene carbonate, and particularly acetonitrile (Table 1). The activation energy for the nitration reaction (2) in nitromethane has been calculated by means of equation (1), taking into account the Gibbs energy, equation (5), and the

$$\Delta G° = F[E°(ArH^{·+}/ArH) - E°(NO_2^+/NO_2)] \tag{5}$$

reorganization energies of the following couples: $ArH^{·+}/ArH$, $\lambda \simeq +42$ kJ mol^{-1};[1] and $NO_2^+/NO_2^·$, $\lambda = +506$ kJ mol^{-1} (with $\lambda = \lambda_i + \lambda_o$; the inner- and outer-sphere reorganizational energies λ_i and λ_o respectively were obtained using the classical Marcus expression for λ_o and Kharkats' ellipsoidal model for λ_i[1,11]). The value of $\Delta G^{\ddagger}$ found in nitromethane is weaker than those determined in acetonitrile[1] or tetrahydrothiophene 1,1-dioxide.[19] However, it is still too high to consider the nitration process as an outer-sphere ET. This sustains our experimental results concerning the highly nitrating characteristics of NO_2^+ on aromatics found previously by us[18] in nitromethane (and as already suggested by Olah and co-workers[20,21]) despite the low solubility of nitryl salts in this medium.[19,22,23] Hence, the interaction of NO_2^+ or $NO^+ + N_2O_4$ mixtures with aromatics occurs *via* an associa-

tion–dissociation mechanism or *via* an inner-sphere ET mechanism.

References

1 L. Eberson and F. Radner, *Acta Chem. Scand., Ser. B*, 1984, **38**, 861.
2 R. J. Schmitt, S. E. Buttrill, Jr., and D. R. Ross, *J. Am. Chem. Soc.*, 1984, **106**, 926.
3 L. Eberson and F. Radner, *Acc. Chem. Res.*, 1987, **20**, 53.
4 M. Attinà, F. Cacace, and M. Yañez, *J. Am. Chem. Soc.*, 1987, **109**, 5092.
5 S. Sankararaman, W. A. Haney, and J. K. Kochi, *J. Am. Chem. Soc.*, 1987, **109**, 5235.
6 J. T. Gleghorn and G. Torossian, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1303.
7 A. Boughriet, C. Bremard, and M. Wartel, *J. Electroanal. Chem.*, 1987, **225**, 125.
8 A. Boughriet, C. Bremard, and M. Wartel, *New J. Chem.*, 1987, **11**, 245.
9 U. Mayer and V. Gutmann, *Struct. Bonding (Berlin)*, 1972, **12**, 113; V. Gutmann, *Chem. Technol.*, 1977, 255.
10 R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155; 'Special Topics in Electrochemistry,' ed. P. A. Rock, Elsevier, Amsterdam, 1977, p. 161; Faraday Discuss. Chem. Soc., 1982, **74**, 7.
11 L. Eberson, *Adv. Phys. Org. Chem.*, 1982, **18**, 79.
12 A. Boughriet, M. Wartel, J. C. Fischer, and C. Bremard, *J. Electroanal. Chem.*, 1985, **190**, 103.
13 J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman, and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3968, and references therein.
14 C. J. Schelesener, C. Amatore, and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 7472.
15 F. G. Bordwell and M. J. Bausch, *J. Am. Chem. Soc.*, 1986, **108**, 2473.
16 A. Boughriet and M. Wartel, *Talanta*, 1988, **35**, 205.
17 A. Boughriet, C. Bremard, and M. Wartel, *Electrochimica Acta*, 1988, **33**, 701.
18 A. Boughriet and M. Wartel, *J. Electroanal. Chem.*, in the press.
19 A. Boughriet, A. Coumaré, J. C. Fischer, and M. Wartel, *J. Electronanal. Chem.*, 1986, **200**, 217.
20 G. A. Olah, H. C. Lin, J. A. Olah, and S. C. Narang, *Proc. Natl. Acad. Sci. U.S.A.*, 1978, **75**, 1045.
21 G. A. Olah, S. C. Narang, J. A. Olah, and K. Lammertsma, *Proc. Natl. Acad. Sci. U.S.A.*, 1982, **79**, 4487.
22 J. C. Bardin, Ph.D. Thesis, Paris VI, 1972.
23 G. A. Olah and S. I. Kuhn, 'Friedel and Related Reactions. Acylation and Related Reactions,' vol. 3, part II, Interscience, New York, 1964, p. 1393.