CHEMICAL AND ELECTROCHEMICAL ACTIVATION OF THE NITRATION OF NAPHTHALENE BY N₂O₃ IN APROTIC MEDIA

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Abstract—The chemically or electrochemically activated nitration by N_2O_3 has been studied in sulfolane using Raman spectroscopy, electrochemical techniques and gas chromatography. The mechanistic aspects of this reaction are discussed, taking into account the various equilibria occurring in the N_2O_3 solutions and the electrochemical and kinetic properties of oxygenated nitrogen compounds in aprotic media. Thus, whatever be the nature of the catalytic procursor used, it has been shown that the promotion of the naphthalene nitration by N_2O_3 proceeds from an electrophilic attack of NO^+ concerted with N_2O_4 which is formed by the molecular dissociation of N_2O_3 .

INTRODUCTION

Recently[1-3], we reported our results on the nitration of naphthalene by N_2O_4 and these accounts described the chemical and electrochemical activation of the nitration reaction in aprotic media. The results are in good agreement with a catalytic process involving $NO^+[1-3]$. The N(III) species are claimed to be catalysts for the nitration of aromatics by nitrogen oxides at higher oxidation states[4]. N_2O_3 is a well-known nitrosating agent and possesses a poor nitrating efficiency[5]. N_2O_3 has been scarcely used for nitrations, nevertheless some aspects of the activation of the nitration of at Lewis acid such as $BF_3[5]$.

The present work was undertaken in order to bring more information about the mechanistic aspects of the activation of N_2O_3 by chemical and electrochemical means towards nitration reaction. The nitration of naphthalene by N_2O_3 in sulfolane (tetrahydrothiophene 1,1-dioxide) was used as a test for the nitrating efficiency of the chemical and electrochemical activation of N_2O_3 . The knowledge of the different equilibria which occur in the N_2O_3 solutions electrolysed anodically has allowed us to understand the electrocatalysis of naphthalene nitration by N_2O_3 . The results are discussed and interpreted from the kinetic and thermodynamic constant values of the equilibria between oxygenated nitrogen compounds and the electrochemical properties of these species in sulfolane.

EXPERIMENTAL

Chemicals

Sulfolane (Merck) was purified as previously described[6]. Prior to use, the solvent was filtered through a dry alumina column under argon (neutral alumina dried in vacuum at 573 K during a week). The supporting electrolyte, tetraethylammonium perchlorate (TEAP), (Carlo Erba) was dried *in vacuo* at 333 K over P_4O_{10} during a month. The preparative procedures for N_2O_3 , N_2O_4 , nitric acid and NOClO₄ were similar to those described elsewhere[7–9]. Prior to use, AgClO₄ was dried *in vacuo* at 333 K during a week. Anhydrous perchloric acid was obtained from the reaction between dry HCl and AgClO₄ in sulfolane at room temperature as follows:

$$AgClO_4 + HCl \rightarrow AgCl\downarrow + HClO_4$$
.

Instrumentation

Controlled potential electrolysis experiments were coulometrically monitored by coupling the potentiostat to a Tacussel IG 5 N digital integrator. A conventional three-electrode cell with a working volume of approximatively 0.03 dm³ was used during these experiments. The working electrode was a platinum gauze and the counterelectrode was a platinum sheet separated from the working electrode compartment via a fine porosity fritted disk. After each electrolysis, the nitration experiments were conducted in a dry box containing a nitrogen atmosphere.

Product identification and analysis

Products arising from nitration experiments were analysed using a Gildel 3000 gas chromatograph, equipped with a flame ionization detector. Gas chromatographic analyses were performed using a Hewlett-Packard Model 3380A. Pyrex column was packed with 5% OV-17 on Chrom. W HP D.M.C.S. These chromatographic analyses were operated over a temperature range of 423-483 K with a nitrogen carrier gas.

The Raman spectra were recorded by means of a Dilor R.T. 30 Raman Spectrometer. The tubes containing the products were sealed before use.

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THERMODYNAMIC, KINETIC AND ELECTROCHEMICAL PROPERTIES OF OXYGENATED NITROGEN COMPOUNDS IN SULFOLANE

In order to interpret the nitration reactions in sulfolane, we have summarized in this paragraph the principal results recently published concerning the chemical equilibria and electrochemical properties of N_2O_3 and N_2O_4 in sulfolane. We have also considered the chemical equilibria between the oxygenated nitrogen species involved in many side reactions encountered in aromatic nitration in anhydrous and deoxygenated sulfolane. The distribution of the different nitrogen species generated in HClO₄-N₂O₃ mixtures is exhibited in Fig. 1, taking into account the equilibrium constants listed in Table 1. In addition, the knowledge of the pK_A values of HClO₄, HNO₃ and HNO₂ is necessary [12, 15, 16]. The kinetic constant values of reaction (3) have been evaluated previously[17]:

$$NO + \frac{1}{2}N_2O_4 \frac{k_f}{\vec{k}_b}N_2O_3$$
(3)

with $k_f = 1.35 \times 10^3 \text{ dm}^{3/2} \text{ mole}^{-1/2} \text{ s}^{-1}$ and $k_b = 8.9 \text{ s}^{-1}$ in sulfolane at 303 K[17].

The electrochemical data for the electroactive species involved in the present study are summarized in Table 1.

RESULTS

The nitrating efficiency of N_2O_4 , HNO_3 and N_2O_3 towards naphthalene in sulfolane at room temperature has been compared in Table 2. The yield is calculated from $[ArNO_2]/[ArH]$ ratio. The nitrating activities of



Fig. 1. Distribution of the species generated by dissolving N_2O_3 and $HClO_4$ in sulfolane at 303 K. Initial concentration of N_2O_3 : 0.21 mol dm⁻³.

the nitrogen compounds are poor and decrease in the order N_2O_4 , HNO₃, N_2O_3 .

Chemical activation of the nitration of naphthalene by N_2O_3

The addition of small quantities of NOClO₄ to a mixture N_2O_3 + naphthalene brought about a rapid

Table 1. Chemical and electrochemical properties of N_2O_3 and N_2O_4 in sulfolane at 303 K. (a) vs The half-wave potential of a ferrocene solution in TEAP 0.1 moldm⁻³. (b) $E_{1/2}$ Determined for a known concentration of electroactive species ($\sim 10^{-2} \text{ mol dm}^{-3}$). (c) Equilibrium constants calculated from the pK_A acidities of HClO₄ and HNO₃ or HNO₂ equal to 3.0, 16.0 and 20.6, respectively[12, 15, 16]

Equation () Chemical reaction	Equilibrium constan	at	Ref
1	$N_7O_3 \Rightarrow NO^+ + NO_7^-$	6.3×10^{-12}		10
2	$N_2O_3 \Rightarrow NO + NO_2$	2.5×10^{-5}		10
3	$N_2O_3 \rightleftharpoons NO' + \frac{1}{2}N_2O_4$	6.6×10^{-3}		10
4c	$N_{1}O_{1} + HClO_{4} \neq HNO_{1} + NO^{+} + ClO_{4}^{-}$	$2.5 \times 10^{+6}$		10, 12
5	$N_2O_4 \approx NO^+ + NO_3^-$	7.1×10^{-8}		9
6	$N_2O_4 \neq NO_7^+ + NO_7^-$	10-22		11
7	$N_2 O_4 \neq 2 NO_2$	1.4×10^{-5}		11
8c	$N_{2}O_{4} + HClO_{4} \approx HNO_{3} + NO^{+} + ClO_{4}^{-}$	$6.3 \times 10^{+5}$		9.12
9c	$N_2O_4 + HClO_4 \Rightarrow HNO_2 + NO_2^+ + ClO_4^-$	4.0×10^{-5}		11, 12
Equation () Electrochemical couple		Standard potentialhalf-wave potential $E^{\circ}()^{a}/V$ $E_{1/2}^{b}/V$		Ref.
10	$N_2O_4 \rightleftharpoons NO^+ + \frac{1}{2}N_2O_4 + e^-$	+ 0.85	~ + 0.81	10
11	NaphtH \neq NaphtH ⁺ + e ⁻		+ 1.26	13, 14, 15
12	$NO \neq NO^+ + e^-$	+ 0.715	~ 0.715	10
13	$N_2O_4 \neq 2NO_2^+ + 2e^-$	+ 1.50	~ + 1.63	11
14	$NO_3 \neq NO_3^+ + e^-$	+ 1.35		11
18	$NO_2 + N_2O_4 + e^- \neq N_2O_3 + NO_3^-$	+ 0.56	+ 0.58	15, 18
19	$2N_2O_3 + e^- \neq 3NO + NO_3^-$)		
20	$N_2O_4 + e^- \approx NO + NO_3^-$	5	~ + 0.08	15, 18
21	$\frac{1}{2}N_2O_4 + H(NO_3)_2 + e^- \approx HNO_2 + NO_3$	J		

	Concentrations		(%) yield of nitronaphthalene ($\alpha + \beta$)				Isomer
Nitrating agent	of solutes (mol dm ⁻³)	after 10 mn	after 20 mn	after 30 mn	after 40 mn	after 60 mn	α/β after 60 mn
HNO,	$[HNO_1] = [Naph] = 0.30$	< 1.0	~ 1.0	1.5	2.0	2.5	
N ₂ O	$[N_2O_4] = [Naph] = 0.33$	2.5	4.5	6.0	7.5	9.0	19
N_2O_3	$[N_2O_3] = [Naph] = 0.32$	~ 0.5	~ 1.0	~1.5	1.5	2.0	17
	$[N_2O_3] = [Naph] = 0.17$						
	$[NO^+] = 0$	< 1	≤1	~ 1	~ 1.5	2	17
N_2O_3	$[N_2O_3] = [Naph] = 0.17$						
+	$[NO^+] = 2.5 \times 10^{-3}$	4	8	13	16	21	17
NOClO₄	$[N_2O_3] = [Naph] = 0.17$						
	$[NO^+] = 9.4 \times 10^{-3}$	8	16	22	27	34	17
	$[N_2O_3] = [Naph] = 0.17$						
	$[NO^+] = 18.0 \times 10^{-3}$	11	19	27	32	40	17
	$[N_2O_3] = [Naph] = 0.17$						
	$[NO^+] = 30.0 \times 10^{-3}$	19	29	35	40	48	18
	$[N_1O_1] = [Naph] = 0.20$						
	$[H^+] = 3.1 \times 10^{-3}$	5	9	15	18	22	17
N_2O_3	$[N_2 \tilde{O}_3] = [Naph] = 0.20$						
	$[H^+] = 5.0 \times 10^{-3}$	7	12	18	20	26	17
+							
HClO₄	$[N_2O_3] = [Naph] = 0.20$						
	$[H^+] = 10.0 \times 10^{-3}$	9	16	21	25	32	17-18

Table 2. Nitration of naphthalene by HNO₃, N_2O_4 and N_2O_3 in anhydrous and deoxygenated sulfolane at room temperature. Catalysis of the naphthalene nitration by NOClO₄ and HClO₄

nitration. The nitration of naphthalene by N_2O_3 in sulfolane catalysed by NOClO₄ was analysed by gas chromatography (Table 2), electrochemical technique, and Raman spectroscopy. During the course of the reaction, the height of the reduction wave on the voltammogram, corresponding to NO⁺ remains constant, as well as the intensity of the Raman band at 2285 cm⁻¹ assigned to $v(N \equiv 0)^+$.

The rate of formation of nitronaphthalenes (α and β) increases with the NO⁺ concentration and demonstrates the catalytic role of NO⁺.

The gas chromatography analysis of the isomer ratio α/β (Table 2) gives a similar value in all the experiments (17.5 ± 0.5) . During the course of the reaction, HNO₂ is clearly observed by its reduction wave, located at $E_{1/2} = -1.4$ V on the voltammograms[7]. The other byproduct of the nitration HNO₃ was not detected in the mixture. Another probable product, NO, was not observed by its oxidation wave at $E_{1/2} = +0.72$ V [10], because of its low solubility in sulfolane. From these results, the following stoichiometry of the nitration of naphthalene by N₂O₃ can be pointed out:

NaphtH + $2N_2O_3 \rightarrow NaphtNO_2 + HNO_2 + 2NO.(15)$

The addition of aliquots of strong acid such as anhydrous HClO₄ to a N₂O₃-naphthalene mixture, brought about a rapid nitration, Table 2. The reaction between N₂O₃ and naphthalene catalysed by HClO₄ is analysed by the same experimental techniques as NO⁺ catalysis. The main experimental features are analogous to those described in the former paragraph. During the course of the nitration, the height of the reduction wave at E = +0.77 V corresponding to NO⁺ [10] and the intensity of the Raman band at 2285 cm⁻¹ remain constant. When the catalysed nitration by HClO₄ is surveyed by linear voltammetry, the *i*-E patterns are analogous to those obtained with NO⁺ catalyst. From these results, it is tempting to assume that the catalytic precursors NOClO₄ and HClO₄ generate the same nitration products through the same pathway. The active species NO⁺ is generated according to the ionic dissociation of N₂O₃ (equation (1), Table 1):

$$\mathrm{HClO}_4 + \mathrm{N}_2\mathrm{O}_3 \rightleftharpoons \mathrm{NO}^+ + \mathrm{ClO}_4^- + \mathrm{HNO}_2. \quad (4)$$

Figure 1 gives the relative concentration of the species generated in N_2O_3 -HClO₄ mixtures, and the quantity of NO⁺ formed through reaction (4) is then closed to that of HClO₄. Then the nitration goes to completion according to the stoichiometic reaction (15).

In order to examine the electrocatalysis of the naphthalene nitration by N_2O_3 , we have firstly studied the electrochemical behaviour of N_2O_3 in sulfolane.

Electrooxidation of N_2O_3 in sulfolane

The rotating-disc voltammograms (at the Pt electrode) of N_2O_3 dissolved in anhydrous and deoxygenated sulfolane containing 0.1 mol dm⁻³ TEAP (tetraethylammonium perchlorate) are shown in Fig. 2. N₂O₃ exhibits an oxidation wave (wave A of Fig. 2) at $E_{1/2}(10) \simeq +0.81$ V vs $E_{1/2}(Fc/Fc^{+})$ with $N_2O_3 = 5.8$ mmol dm⁻³ and corresponding to [10]:

$$N_2O_3 \rightleftharpoons NO^+ + \frac{1}{2}N_2O_4 + e^-.$$
 (10)

The cyclic voltammogram of the oxidation wave of N_2O_3 (Fig. 3) is very similar to that found with a NO⁺ + N_2O_4 mixture, and shows the apparent reversibility of the electrode system, Figs 3 and 4. It is worth noting that the cathodic E-i curves obtained for NO⁺ + N_2O_4 mixtures exhibit positive shift with reference to this one corresponding to a NO⁺ solution, NO⁺ + $e^- \Rightarrow$ NO (12). Because of the weak solubility of NO

(a)

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i (μΔ)

0.5

formed through the low molecular decomposition of N_2O_3 and the effect of water at trace levels in the medium, $[H_2O] < 10^{-3} \text{ mol dm}^{-3}$ (the water content is determined by the Karl Fischer method before addition of N_2O_3), the following chemical equilibria:

$$2N_2O_3 \approx 2NO + N_2O_4 \tag{3}$$

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2$$
 (16)

$$HNO_{1} + N_{2}O_{4} \rightleftharpoons N_{2}O_{3} + HNO_{3}$$
(17)

also occur in sulfolane. It should be noted that the residual anodic current, $i_{res.}$, on the cyclic voltammogram of a NO⁺ + N₂O₄ mixture (Fig. 4) results from the small amounts of N₂O₃ generated by the side-reactions (16) and (17) due to the water at trace levels in the sulfolane. Knowledge of the electroactive properties of N₂O₄, HNO₃ and HNO₂ has allowed us to ascribe waves *B*, *B'*, *C* and *D* of Fig. 2 to the following processes[18].

• wave
$$B' NO_2 + N_2O_4 + e^- \approx N_2O_3 + NO_3^-$$
 (18)

wave B

$$2N_2O_3 \neq 2NO + N_2O_4 \tag{3}$$

$$2N_2O_3 + e^- \approx 3NO + NO_3^-$$
(19)

$$N_2O_4 + e \approx NO + NO_3$$
 (20)

$$\left(\frac{1}{2}N_2O_4 + H(NO_3)_2^- + e^- \rightleftharpoons HNO_2 + 2NO_3^-\right)$$
(21)

The three couples act to broaden the current-potential curve.





Fig. 3. Cyclic voltammograms at a Pt electrode of a solution of 5.9 mmol dm⁻³ N₂O₃ in sulfolane containing 0.1 mol dm⁻³ TEAP at several scan rates: 0.01, 0.02, 0.05, 0.10 Vs^{-1} (vs $E_{1/2}(Fc/Fc^+)$).

Fig. 4. Cyclic voltammetric curves with a stationary platinum electrode of N_2O_3 and a $NO^+ + N_2O_4$ mixture in sulfolane at 303 K. Supporting electrolyte: $[(C_2H_3)_4NClO_4] = 0.1 \mod 4m^{-3}$. (a) $[N_2O_3] = 5.8 \mod 4m^{-3}$; (b) $[NO^+] = 5.2 \mod 4m^{-3}$ and $[N_2O_4] = 5.5 \mod 4m^{-3}$. Scan rate: 10 mV s⁻¹.

• wave
$$C = H(NO_3)_2^- + e^- \neq \frac{1}{2}H_2 + 2NO_3^-$$
 (22)

• wave
$$D = HNO_2 + e^- \rightleftharpoons \frac{1}{2}H_2 + NO_2^-$$
 (23)

Controlled potential electrolysis at an applied potential of 1.0 V vs $E_{1/2}$ of the Fc/Fc^+ system was performed on solutions of N₂O₃ in sulfolane. The wave corresponding to the reduction of NO⁺ in the presence of N₂O₄ (wave F of Fig. 2):

$$NO^{+} + \frac{1}{2}N_{2}O_{4} + e^{-} \Rightarrow N_{2}O_{3}$$
 (10)

appears on the E-i curves at $E_{1/2}(10) \simeq +0.77$ V vs $E_{1/2}(Fc/Fc^+)$. The height of this wave is function of the amount of charge passed through the solution. Curve F of Fig. 2 corresponds to a charge of 0.1 mol of electrons per mol of N₂O₃. We can notice that the shape of the linear voltammogram, waves A + F of Fig. 2, obtained after electrolysis of a N₂O₃ solution shows that process (10) appears reversible.

Electrocatalysis of the $N_2O_3\mbox{-naphthalene}$ nitration in sulfolane

Controlled potential electrolysis at an applied potential of + 1.0 V vs $E_{1/2}$ of Fc/Fc^+ system was performed on solution of N₂O₃ in sulfolane. The potential used for these experiments was sufficient to oxidise N₂O₃ according to equation (10). Naphthalene was added to electrolysed solutions in separate experiments after the applied potential was discontinued. A rapid nitration occurs and the yield and α/β isomer ratio of nitronaphthalenes were monitored as a function of time and amount of charge passed. The results are listed in Table 3. The nitration rate appears closely associated with the charge passed through the N₂O₃ solution. N₂O₃ is oxidised anodically according to:

$$N_2O_3 \rightleftharpoons NO^+ + \frac{1}{2}N_2O_4 + e \tag{10}$$

The electrogenerated NO⁺ species is easily detected by cyclic voltammetry or by Raman scattering. Hence when the nitration reaction is surveyed by electrochemical means, the *i*-*E* patterns are analogous to those obtained with NO⁺ and H⁺ catalytic precursors and the nitration goes to completion according to the stoichiometric reaction (15). On the other hand, the electrocatalytic nitration of naphthalene by N₂O₃ can also be performed in a solution containing both naphthalene and N₂O₃. The yield and α/β isomer ratio of nitronaphthalenes are similar to those obtained in separate experiments (Table 3).

If the nitration rate is closely associated with the charge passed through the solution, the nitration of naphthalene goes to completion even with a small amount of charge passed.

DISCUSSION

The results of the chemical and electrochemical activation of the nitration of naphthalene by N₂O₃ are in good agreement with one catalytic pathway through the NO⁺ active species, regardless of the catalytic precursors. NO⁺ can be introduced or generated in situ by chemical or electrochemical means. It is not reasonable to invoke another active species such as NO_2^+ , taking into account the low concentration of this powerful nitrating agent (Fig. 1). The NO⁺ catalysis of the nitration of naphthalene by N_2O_4 has been extensively investigated in aprotic media[1-3, 19]. As proposed recently[1-3, 19], NO⁺ alone cannot be the attacking species, and is assumed that electrophilic attack of NO⁺ is concerted with $N_2O_4[1-3]$. Such a mechanism is unlike the NO⁺ catalysed nitration of naphthalene by N_2O_3 . It is more reasonable to invoke the homolytic dissociation of N_2O_3 through:

$$N_2O_3 \stackrel{k_2}{\rightleftharpoons} NO + NO_2 \tag{2}$$

$$NO_2 \stackrel{k_7}{\underset{k_{-7}}{\stackrel{\pm}{\rightarrow}}} \frac{1}{2}N_2O_4 \tag{7}$$

hence:

The concentration of the N_2O_4 species is notable in N_2O_3 -sulfolane solution, Fig. 1, and the kinetic constant of N_2O_4 formation[3] is sufficiently high[17] not to limit kinetically the nitration rate. In such conditions, the catalytic nitration pathways of naph-thalene by N_2O_3 can be written as proposed earlier for nitration by N_2O_4 [1-3]:

 $N_2O_3 \stackrel{k_b}{\underset{k_f}{\rightleftharpoons}} NO + \frac{1}{2}N_2O_4$

$$2N_2O_3 \rightleftharpoons 2NO + N_2O_4 \tag{3}$$

NaphtNO₂ +
$$N_2O_3$$
 + H⁺ (24)

$$H^+ + N_2O_3 \rightarrow HNO_2 + NO^+$$
 (4)

$$\int \mathbf{H}^+ + \mathbf{N}_2 \mathbf{O}_4 \to \mathbf{H} \mathbf{N} \mathbf{O}_3 + \mathbf{N} \mathbf{O}^+ \tag{8}$$

$$r \left(HNO_3 + N_2O_3 \rightleftharpoons N_2O_4 + HNO_2 \right)$$
(17)

NaphtH +
$$2N_2O_3 \rightarrow NaphtNO_2 + 2NO + HNO_2$$
(15)

Table 3. Electrocatalyzed nitration at E = +1.00 V of naphthalene by N₂O₃ in anhydrous and deoxygenated sulfolane at 298 K. [N₂O₃] = [Naph] = 0.32 mol dm⁻³. (a) vs The half-wave potential of the ferrocene-ferricinium system in TEAP 0.1 mol dm⁻³. (b) Calculated for 1 mol of electron per mol of N₂O₃.

0

	Charge	(%) yield of nitronaphthalenes($\alpha + \beta$)					Isomer
Electrolysis mediun	passed (%) ^b	after 10 mn	after 20 mn	after 30 mn	after 40 mn	after 60 mn	ratio α/β after 60 mr
	0	~ 0.5	~ 1.0	~ 1.5	1.5	2.0	16-17
N_2O_3 in Sulfolane	1.7	6	11	15	19	25	17
	2.6	8	15	20	24	31	17
	4.3	12	22	27	32	38	16

(13)

The nitration of naphthalene by N_2O_3 has been undertaken in this work under argon to prevent side reactions with oxygen. It should be noted that under oxygen, the rate and the yields of nitronaphthalenes (α and β) are greater than those obtained under argon. The present work demonstrates that N_2O_3 reacts as a mixture of NO and N_2O_4 , and under oxygen the non nitrating species NO is converted by molecular oxygen into nitrating species N_2O_4 through: $2NO + O_2$ $\rightarrow N_2O_4(25)$. The optimization of the catalytic nitration is not the purpose of this work. However, it is obvious that under O_2 and N_2O_3 pressures the formation rate and the yields of nitronaphthalenes are promoted.

The poor nitrating efficiency of N_2O_3 can be increased by chemical and electrochemical means, and the activation of the nitration reaction occurs through the same catalytic process than that invoked in nitration via $N_2O_4[1-3]$.

REFERENCES

- 1. A. Boughriet, J. C. Fischer, M. Wartel and C. Bremard, Nouv. J. Chim. 9, 651 (1985).
- A. Boughriet, C. Bremard and M. Wartel, Nouv. J. Chim. 11, 245 (1987).
- 3. A. Boughriet, C. Bremard and M. Wartel, J. electroanal. Chem. 225, 125 (1987).
- (a) D. S. Ross, G. P. Hum and W. G. Blucker, J. Chem. Soc., Chem. Commun., 532 (1980).
 (b) L. Main, R. B.

Moodie and K. Schofield, J. Chem. Soc., Chem. Commun., 48 (1982). (c) R. S. Ross, K. D. Moran and R. Malhotra, J. Org. Chem. 48, 2118 (1983). (d) B. Milligan, J. Org. Chem. 48, 1495 (1983).

- 5. G. A. Olah and S. J. Kuhn, Friedel-Crafts and Related Reaction, Vol III, Part. 2, Interscience, New York (1964).
- P. Pierens, Y. Auger, J. C. Fischer and M. Wartel, Can. J. Chem. 53, 2989 (1975).
- 7. A. Boughriet, J. C. Fischer, G. Leman and M. Wartel, Bull. Soc. Chim. France 1, 8 (1985).
- 8. J. C. Fischer, A. Boughriet and M. Wartel, *Talanta* 28, 233 (1981).
- 9. M. Wartel, A. Boughriet and J. C. Fischer, Anal. Chim. Acta 110, 211 (1979).
- 10. A. Boughriet, M. Wartel, J. C. Fischer and Y. Auger, J. electroanal. Chem. 186, 201 (1985).
- 11. A. Boughriet, M. Wartel, C. Bremard and J. C. Fischer, J. electroanal. Chem. 190, 103 (1985).
- 12. A. Boughriet and M. Wartel, *Talanta*, (accepted for publication).
- L. Eberson, L. Johnson and F. Radner, Acta Chem. Scand. B32, 749 (1978).
- J. M. Achord and C. L. Hussey, J. Electrochem. 123(12), 2556 (1981).
- 15. A. Boughriet, Thesis, Lille, France (1984).
- J. F. Coetzee and R. J. Bertozzi, Anal. Chem. 45, 1064 (1973).
- 17. A. Boughriet, C. Coumare, J. C. Fischer and M. Wartel, J. electroanal. Chem. 200, 217 (1986).
- A. Boughrict, M. Wartel and J. C. Fischer, *Talanta* 33, 385 (1986).
- (a) L. Eberson and F. Radner, Acta Chem. Scand. B39, 343 (1985) (b) L. Eberson and F. Radner, Acta Chem. Scand. B39, 357 (1985).