Journal of Organometallic Chemistry, 268 (1984) 63–72
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DIRECT, INDIRECT AND ASSISTED ELECTROOXIDATION OF BENZENETRICARBONYLCHROMIUM DERIVATIVES. A COMPARATIVE STUDY IN ACETONITRILE AND IN *N*,*N*-DIMETHYLFORMAMIDE

CHANTAL DEGRAND and ANNE RADECKI-SUDRE

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au C.N.R.S. (LA 33), Faculté des Sciences, 6 boulevard Gabriel 21100 Dijon (France)

(Received November 28th, 1983)

Summary

The direct, indirect and assisted electrooxidations of benzenetricarbonylchromium (Bct) moieties were investigated in acetonitrile (MeCN) and at a glassy carbon anode. These results were compared with the results previously obtained in *N*,*N*-dimethylformamide (DMF). In the case of benzenetricarbonylchromium (**1**), the anodic oxidation was a 2-electron process in MeCN, with formation of a chromium(II) species, whereas three electrons were transferred in DMF where a chromium(III) species was generated. The indirect electrooxidation of **1** by catalysts was less efficient in MeCN than in DMF. Similarly, the assisted electrooxidation of the Bct moiety in molecules which contained both a Bct group and a redox system capable of serving as a catalyst, was less efficient in MeCN than in DMF. A ligand substitution in the intermediate Bct^+ cation by a molecule of solvent was suggested to occur in both catalytic and assisted oxidation processes. It would account for the lower efficiency in MeCN.

Introduction

The electrooxidation of (arene)tricarbonylchromium complexes in solvents of low nucleophilicity such as methylene chloride [1] and trifluoroacetic acid (TFAA) [2] proceeds according to a reversible one-electron process. Complexes that possess steric bulk around the aromatic ring also give stable cations in propylene carbonate [3,4] and acetonitrile (MeCN) [5]. Conversely, in *N*,*N*-dimethylformamide (DMF) and MeCN, the electrooxidation of benzenetricarbonylchromium, BctH, **1** and its monosubstituted derivatives BctX, is complicated by rapid follow-up reactions which result in overall multielectron processes [5,6]. In both solvents, destruction of the complexes occurs [5,6]. Ikeshoji and Parker have shown that in MeCN and at a platinum electrode the electrooxidation of **1** corresponds to a 2-electron process and that the cation initially electro-generated decomposes by a mechanism of the ECE_h

type (E_h indicates a second homogeneous electron transfer) [5]. The first order rate constant is 2500 s^{-1} at 25 °C. A chromium(II) species, benzene and carbon monoxide are generated. In DMF, a 3-electron process is observed, along with the formation of a chromium(III) species [6]. The decomposition of the initially electrogenerated cation is so fast that the electrooxidation can be carried out indirectly [6] by homogeneous redox catalysis [7]. In this solvent, an assisted electrooxidation of Bct moieties is observed in the case of mixed compounds which contain both a Bct group and a reversible redox system A capable of serving as a catalyst [6,8]. A condition to be fulfilled is that electrons can be delocalized between the Bct and A groups (induced oxidation). We have shown that the Fc/Fc^+ and TTF^{2+}/TTF^+ redox systems can work as catalysts; Fc^+ and TTF^+ are, respectively, the ferricinium and the tetrathiafulvalene cations [6,8].

The indirect and assisted electrooxidation of a Bct group in the presence of a redox system A in solution (redox catalysis) or bound in a mixed molecule (induced oxidation) has been thought to occur in DMF according to eqs. 1–4 [6,8]. Although the involvement of the solvent does not appear in this mechanism, it can interfere in the global reactions 3 and 4 which summarize a series of cleavage reactions and electron transfers.

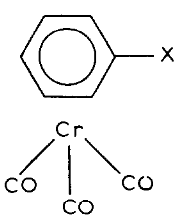
$$A \overset{-e}{\rightleftharpoons} A^+ \qquad (1)$$

$$A^{+\cdot} + C_6H_5XCr(CO)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A + [C_6H_5XCr(CO)_3]^+ \qquad (2)$$

$$[C_6H_5XCr(CO)_3]^+ \xrightarrow{k} C_6H_5X + Cr^I + 3CO \qquad (3)$$

$$Cr^I \xrightarrow{-2e} Cr^{III} \qquad (4)$$

Investigated below are the indirect electrooxidation of **1** and the assisted electrooxidation of the derivatives **2**–**9** in acetonitrile (MeCN) and at a glassy carbon anode. The potential catalyst is a Fc group in compounds **2**–**7** and a TTF group in the chalcones **8** and **9**.



(**1**: X = H;
2: X = CH=CHFc;
3: X = Fc;
4: X = COFc;
5: X = $CH_2CH(OH)Fc$;
6. X = CH_2COFc;
7: X = CH_2Fc,
8: X = $C(CH_3)$=CHCOTTF;
9: X = COCH=$C(CH_3)$TTF)

The results are obtained by voltammetry at a stationary disc electrode (SDE), cyclic voltammetry at a rotating disc electrode (RDE) and coulometry. They are compared with the results previously obtained in DMF [6,8]. As shown below, both indirect and assisted electrooxidations are less efficient in MeCN than in DMF. These results will be discussed in the context of a ligand substitution by the solvent of the intermediate Bct^+ cation.

At a Pt RDE, the behaviour in MeCN of **3** and **7** has been described previously [9]. For both compounds, the oxidation wave of the Fc group precedes the anodic wave of the Bct group. The Fc and Bct waves have a similar height in the case of **3**, whereas the Bct wave is about twice as high as the Fc wave in the case of **7**. No oxidation mechanism was proposed in ref. 9.

Experimental

Compounds **2**–**11**, which have already been utilized in refs. 6, 8 and 10, were kindly provided by Prof. Besançon.

The carbon electrode was a disc made of a rod of V 25 Carbone Lorraine glassy carbon sealed in glass tubing. Its diameter was 3 mm. Reproducible measurements were obtained when the electrode was cleaned as follows. Between each experiment the electrode was washed with water, polished on alumina (alumine Escil A3, average dimension of the grains 0.5 μm), and washed again with water and acetone.

Voltammograms at the RDE were obtained with a three electrode Tacussel–Tipol. Cyclic voltammograms at the SDE were obtained with a Tacussel UAP 4 unit and a GSTP function generator, and were recorded on an Ifelec 2025 C X–Y recorder. An Amel 552 potentiostat and a Tacussel IG 5-N integrator were used in the coulometry. All the potentials were refered to the aqueous saturated calomel electrode (SCE). As supporting electrolyte 0.1 *M* Bu_4NPF_6 was employed. All the experiments were performed under an argon atmosphere.

Results and discussion

At a RDE, fouling of the electrode, i.e. decrease in the limiting currents and shifts of the waves during repetitive scannings, or even during the first scan, occurred in some cases. Figure 1 shows the influence of the potential scan rate v on the shape of the voltammogram obtained in MeCN in the case of **5**. Fouling could be diminished by either increasing v or lowering the concentration. To achieve reproducible results at a RDE or a SDE, a careful cleaning of the electrode was necessary between each measurement.

Benzenetricarbonylchromium (1)

At the RDE, the oxidation of **1** occurred with $E_{1/2}$ 0.72 V; the anodic wave was ill-defined (Fig. 2) and fouling of the electrode was observed. A comparison of the

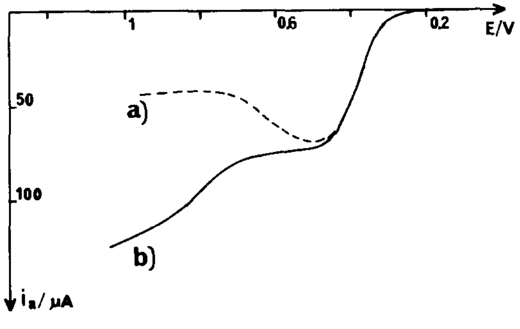


Fig. 1. Influence of the potential scan rate v on the shape of the voltammograms at a RDE in MeCN of **5** (1.0 m*M*). The potential scan rate is (a) 10 mV s^{-1}, (b) 25 mV s^{-1}. The angular velocity ω is 210 s^{-1}.

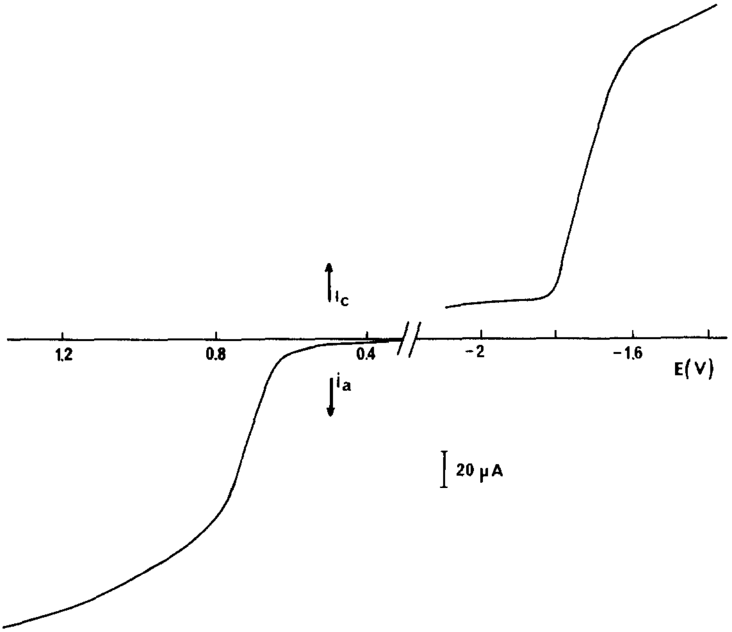


Fig. 2. Cathodic and anodic waves in MeCN at a RDE of **1** (1.0 mM). The angular velocity is 105 s^{-1}.

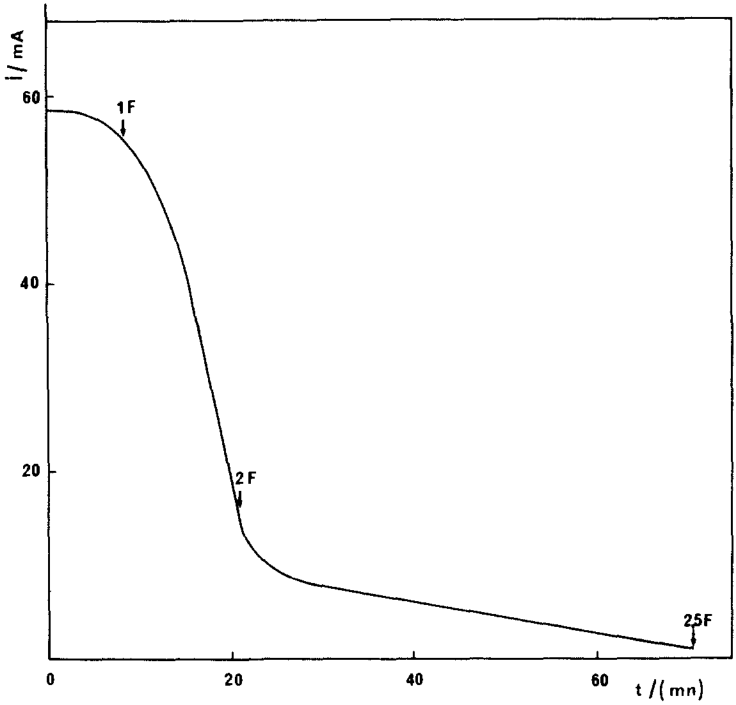


Fig. 3. Faradaic current vs. electrolysis time during the coulometry of **1** (4.3 mM). The applied potential is 0.9 V.

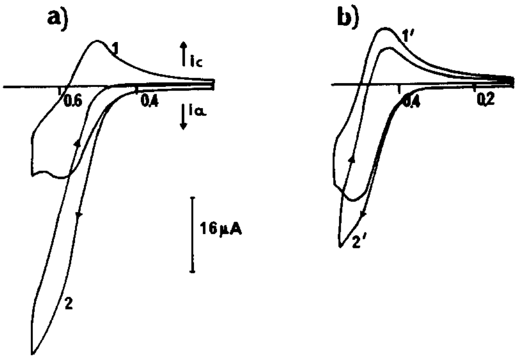
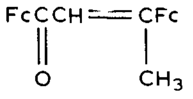


Fig. 4. Modifications of the cyclic voltammograms of catalyst **10** (1.0 m*M*) upon addition of **1** (2.0 m*M*) in (a) DMF, (b) MeCN. Curves 1 and 1′ correspond to the catalyst alone; curves 2 and 2′ are obtained in the presence of **1**. The scan rate is 90 mV s^{-1}.

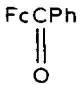
height of the anodic wave of **1** with the height of its reduction wave, which corresponds to a 2-electron process [11], led to the conclusion that two electrons were involved in the oxidation mechanism. In agreement with the results obtained at a platinum electrode [5], a chromium(III) species was therefore generated. The cyclic voltammograms at the SDE were found to be totally irreversible when the scan rate v ranged from 0.02 to 2 V s^{-1}.

In the coulometry, 2.5 electrons per molecule were transferred; the corresponding faradaic current vs. time curve presented a tailing (Fig. 3). It again suggested a transfer of two electrons accompanied by the formation of an electroinactive chromium(II) species which was slowly transformed, leading to some species which were electroactive at the applied potential. No further investigation was performed to elucidate this transformation process.

The electrooxidation of **1** could be performed indirectly by homogeneous redox catalysis. However, in MeCN, the catalysis was much less efficient than in DMF, as it is shown in Fig. 4 which compares, in DMF and MeCN, the first oxidation peak of the diferrocenyl chalcone **10** in the presence of **1**. In MeCN, a very small increase of the anodic current of **10** occurred when **1** was added. The wave separation $\Delta E_{1/2}$ between the catalyst **10** and the substrate **1**, remained effectively the same in both solvents. Indeed, the half-wave potential of **10** (first oxidation wave) was 0.57 V in DMF and 0.47 V in MeCN whereas the oxidation wave of **1** was observed with $E_{1/2}$ 0.83 V in DMF [6] and 0.72 V in MeCN (see above). Therefore, the low efficiency of the catalysis in MeCN could not be related to a larger value of $\Delta E_{1/2}$ between **1** and **10** in this solvent than in DMF. A series of catalysts was oxidised in the presence of **1**. As expected in the context of a redox catalysis [7], an increase of the catalytic current was observed as the waves of **1** and of the catalysts approached each other.


$\mathrm{FcC(=O)CH{=}C(CH_3)Fc}$

(10)


$\mathrm{FcC(=O)Ph}$

(11)

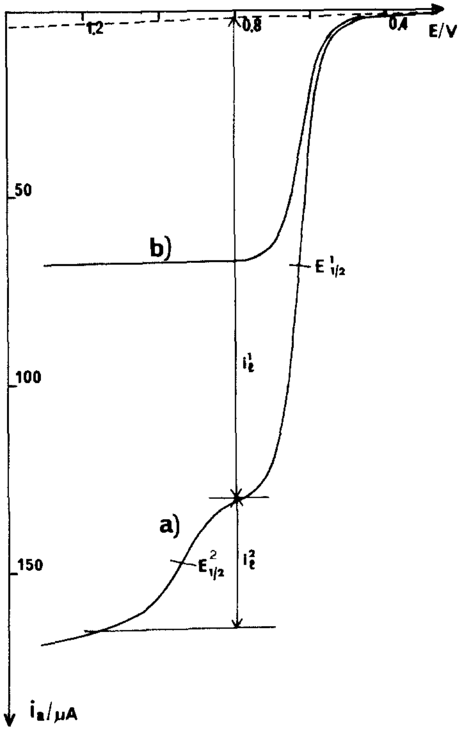


Fig. 5. Voltammograms at a RDE in MeCN of (a) **4** (1.0 mM), (b) **11** (1.0 mM). The angular velocity ω is 105 s^{-1}.

*Mixed benzenetricarbonylchromium and ferrocene compounds (**2–7**)*

The electrooxidation of these compounds was similar in MeCN and DMF. It occurred in two steps (Fig. 5) except in the case of **6**, where a single anodic wave was observed. The characteristics of the anodic waves A and B obtained in MeCN and at a RDE are summarized in Table 1.

As in our preceding study in DMF [8], we define n_1 and n_2 as the apparent number of electrons involved in each step, in MeCN. The ferrocenyl derivative **11**,

TABLE 1

CHARACTERISTICS OF THE ANODIC WAVES A AND B OF **2–7** AND OF THE OXIDATION WAVE OF **11** IN MeCN [a]

Compound	10^3c° (M)	$E^1_{1/2}$ (V)	$10^3 i^1_l c^{\circ\,-1}$ (A M^{-1})	$E^2_{1/2}$ (V)	$10^3 i^2_l c^{\circ\,-1}$ (A M^{-1})
2	0.5	0.42	70	0.77	85
3	0.25	0.48	68	0.84	76
4	1	0.63	128	0.95	32
5	0.5	0.40	58	0.80	68
6	1	0.62	150	–	–
7	0.5	0.41	55	0.80	44
11	1	0.62	64		

[a] The angular velocity is 105 s^{-1}.

which is the parent of compound **4**, was chosen as reference for $n = 1$ (Fig. 5). Such a choice led to apparent values of n_1 and n_2 which could be lower than the real values because **11** probably diffused faster than the more bulky complexes **2–7**. Furthermore, the occurrence of fouling phenomena, mainly at the potentials of wave B, could decrease the heights of the waves and therefore the values of n_1 and n_2. The apparent values obtained in MeCN for n_1 and n_2 are given in Table 2, which indicates also the values previously obtained in DMF. The values of the wave separation $\Delta E_{1/2}$ between waves A and B also appear in this table. From the comparative results in Table 2, four conclusions could be drawn.

(1) Changing the solvent did not modify the values of $\Delta E_{1/2}$.

(2) The behaviour of **2–7** was qualitatively the same in both solvents. More than one electron was transferred in the first oxidation step of **2–4** in which the electrons could be delocalized between the Bct and Fc groups. Hence, for these compounds, a partial induced oxidation of the Bct group by the Fc^+ moiety occurred at the potentials of wave A in both solvents. At a platinum electrode, the observed similar heights of waves A and B of **3** (Fig. 2 of ref. 9) can now be clearly understood in the context of a partially induced oxidation mechanism. In the case of **5**, where the Bct and Fc groups were remote and no conjugation existed between them, their oxidation proceeded independently of each other and $n_1 = 1$. In the case of **6**, the close proximity of the waves A and B, due to the electron-withdrawing effect of the carbonyl group adjacent to the Fc moiety, led to the appearance of a single wave. For **7**, no assisted oxidation was observed in MeCN whereas some electronic intramolecular exchange was thought to occur in DMF [8]. For this compound, the exceptionaly low values of $n_1 + n_2$ in Table 2 can certainly be related to fouling phenomena.

(3) Although the apparent values of $n_1 + n_2$ in MeCN did not reach 3 (2.5 in the best case), they could account for an overall 3-electron process, with formation of a chromium(II) species.

(4) In the case of **2–4**, where a partially induced oxidation was observed, the catalytic efficiency was lower in MeCN than in DMF. Taking into account that the oxidation of the Bct group was a 2-electron process in MeCN and a 3-electron process in DMF, the ratios $(n_1 - 1)/2$ and $(n_1 - 1)/3$ gave the catalytic efficiency, CAT, in MeCN and DMF, respectively. From the results of Table 2, the following

TABLE 2

CHARACTERISTICS OF THE ANODIC WAVES A AND B OF 2–7. COMPARATIVE RESULTS IN MeCN AND IN DMF

Compound	MeCN [a]					DMF [b]				
	10^3c^0 (M)	n_1 [c]	n_2 [c]	$n_1 + n_2$	$\Delta E_{1/2}$ (V)	10^3c^0 (M)	n_1 [c]	n_2 [c]	$n_1 + n_2$	$\Delta E_{1/2}$ (V)
2	0.5	1.09	1.33	2.42	0.35	1	1.25	2.17	3.42	0.34
3	0.25	1.06	1.19	2.25	0.36	0.14	1.94	0.64	2.58	0.35
4	1	2.00	0.50	2.50	0.32	1	2.97	0.17	3.15	0.32
5	0.5	0.91	1.06	2.05	0.40	1	0.97	2.00	2.97	0.36
6	1	2.34	–	2.34	–	1	2.89	–	2.89	–
7	0.5	0.86	0.69	1.55	0.39	0.5	1.17	2.22	3.41	0.39

[a] Fouling of the electrode occurs. [b] From ref. 8. [c] Compound **11** is chosen as reference for $n = 1$.

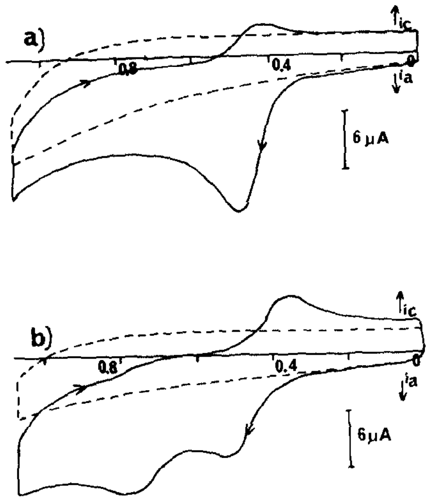


Fig. 6. Cyclic voltammograms at a SDE of **3** (0.25 mM) in (a) DMF, (b) MeCN. The potential scan rate is 86 mV s^{-1}. The dashed line corresponds to the voltammograms acquired in the presence of the supporting electrolyte alone.

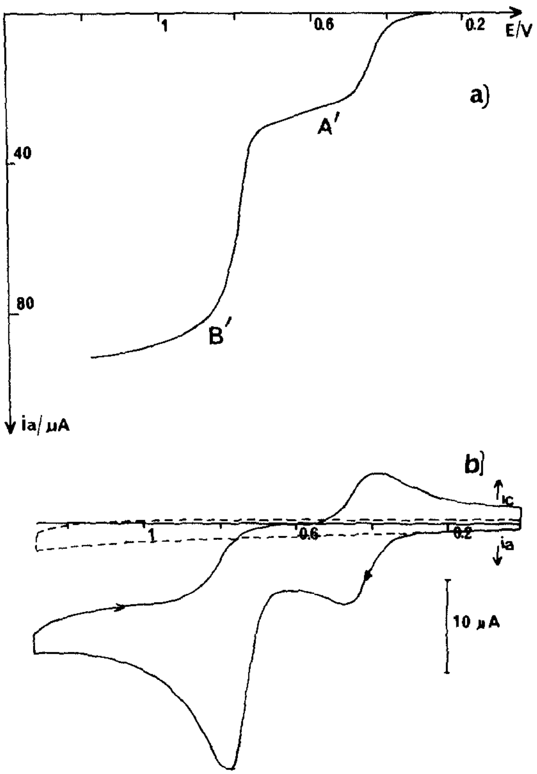


Fig. 7. Voltammograms in MeCN of **9** (0.5 mM) at (a) a RDE (ω 105 s^{-1}), (b) a SDE (v 54 mV s^{-1}). The dashed line corresponds to the voltammogram acquired in the presence of the supporting electrolyte alone.

values of CAT were obtained in MeCN for **2**, **3** and **4**: 0.045, 0.03 and 0.50. The corresponding values in DMF were: 0.08, 0.31 and 0.66. Cyclic voltammetry at the SDE led to the same conclusion. In Fig. 6a, the presence of a single oxidation peak indicates a total induced oxidation of **3** in DMF at the potentials of wave A, whereas it was only partial in MeCN (Fig. 6b).

*Mixed chalcones **8** and **9***

At a RDE, two waves A′ and B′ were observed in MeCN (Fig. 7a); in cyclic voltammetry at a SDE, a reversible peak system was associated with wave A′ (Fig. 7b). This behaviour differed from the behaviour in DMF where three waves A, B and C were observed (cf. Fig. 3 of ref. 6) which were related to the oxidation of the TTF, TTF^+ and the Bct units contained in the chalcones. At the potentials of wave B, a partial induced oxidation of the Bct group occurred [6]. In MeCN, the electrooxidation of the TTF^+ and Bct units occurred simultaneously (wave B′); in other words, the oxidation potentials of the TTF^+ moeities were more positive in MeCN than in DMF. This anodic shift in MeCN was in agreement with a stronger solvation of the TTF^{2+} dicationic species by DMF, whose donor number DN is 26.6 [12], than by MeCN (DN = 14.1 [12]). The higher the value of DN, the more negative is the standard potential of cationic redox systems [12]. In conclusion, the appearance of a single wave B′ in MeCN resulted from a closer proximity of the waves of the TTF^+ cation and of the Bct group, along with a possible induced oxidation.

In order to account for the above results, which show that the indirect electrooxidation of **1** and the induced oxidation of **2**–**4** are less efficient in MeCN than in DMF, we suggest that the slow chemical step in the global reaction 3 would be a ligand exchange with the solvent, according to eq. 5. Since DMF is a better nucleophile than MeCN (see the discussion above for the case of the chalcones **8** and **9**), a faster ligand exchange 5 would occur in DMF than in MeCN. A higher value of the rate constant k in DMF would explain a higher efficiency of the catalytic or induced process in this solvent. In solvents of low nucleophilicity such as TFAA, a ligand exchange is unfavored and the electro-generated cations are very stable [2]. The new cationic species thus generated would decompose after further electron transfers. Ikeshoji and Parker [5] suggested that the chromium-containing species resulting from the decomposition in MeCN of $MCr(CO)_3{}^+$ (M = substituted toluene) still contained CO and existed with $BF_4{}^-$ or MeCN as ligand. The supporting electrolyte was 0.1 M Bu_4NPF_6.

$$[C_6H_5XCr(CO)_3]^+ \xrightarrow[+L]{k} [C_6H_5XCr(CO)_2L]^+ + CO \qquad (5)$$

(L = DMF or MeCN)

Ligand exchange in metal carbonyls by an electrode-mediated process has been extensively investigated [13]. Facile substitution of ligands in anodically-generated 17-electron metal carbonyl derivatives by added nucleophiles has been shown to occur [13]. Electrochemical substitution of a carbonyl group by a phosphorous ligand in arenechromium tricarbonyl complexes has been reported recently [14].

Acknowledgements

We thank Prof. Besançon for providing samples of the compounds **1**–**11**. We are very grateful to Prof. V.D. Parker for copies of manuscripts prior to publication, and for helpful comments.

References

1 M.K. Lloyd, J.A. McCleverty, J.A. Connor and E.M. Jones, J. Chem. Soc., Dalton Trans., (1973) 1768.
2 S.N. Milligan, I. Tucker and R.D. Rieke, Inorg. Chem., 22 (1983) 987.
3 R.D. Rieke, S.N. Milligan, I Tucker, K.A. Dowler and B.R. Willeford, J. Organomet. Chem., 218 (1981) C25.
4 R.D. Rieke, I. Tucker, S.N. Milligan, R.B. Willeford, L.J. Radonovich and M.W. Eyring, Organometallics, 1 (1982) 938.
5 T. Ikeshoji and V.D. Parker, Acta Chem. Scand., Ser. B, in press.
6 C. Degrand, A. Radecki-Sudre and J. Besançon, Organometallics, 1 (1982) 1311.
7 C.P. Andrieux, J.M. Dumas-Bouchiat and J.M. Saveant, J. Electroanal., 87 (1978) 39; ibid., 113 (1980) 1.
8 C. Degrand, J. Besançon and A. Radecki-Sudre, J Electroanal. Chem., 160 (1984) 199.
9 S.P. Gubin and V.S. Khandkarova, J. Organomet. Chem., 22 (1970) 449.
10 J. Besançon, A. Radecki-Sudre, C. Degrand and J. Tirouflet, C. R. Acad. Sci., Paris, 293 (1981) 365
11 R.E. Dessy, F.E. Stary, R.B. King and M. Waldrop, J. Am. Chem. Soc., 88 (1966) 471.
12 V. Guttmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum Press, New York, 1978, pp. 121–131.
13 J.W. Hershberger, C. Amatore and J.K. Kochi, J. Organomet. Chem., 250 (1983) 345, and ref. therein.
14 M.G. Peterleitner, M.V. Tolstaya, V.V. Krivykh, L.I. Denisovitch and M.I. Rybinskaya, J. Organomet. Chem., 254 (1983) 313.