REACTION OF AROMATIC RADICAL CATIONS WITH $RuCl_3·3H_2O$

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Received November 18, 1999
Accepted March 14, 2000

Presented at the 32nd Heyrovský Discussion on Organic Electrochemistry, Třešť, June 6–10, 1999. (This work is dedicated to Professor Herbert Schumann from TU Berlin on the occasion of his 65th birthday).

Interactions of $RuCl_3·3H_2O$ with radical cations of aromatic ethers, 1,4-di-*tert*-butyl-2,5-dimethoxybenzene, 3,5-di-*tert*-butyl-1,2-dimethoxybenzene and 2-*tert*-butyl-1,4-dimethoxybenzene, and with aromatic amines, 2,4,6-tri-*tert*-butylaniline and *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine, were observed by voltammetry. ESR and UV spectroscopies were used for the study of the the first two ethers. The effect of $RuCl_3·3H_2O$ was also examined by controlled potential electrolysis.

Key words: Electrooxidation; Electrocatalysis; Oxidations; Radical cations; Ruthenium chloride; Benzoquinones; Ethers; Anilines.

The first step in electrooxidation of many organic aromatic compounds is the formation of radical cations by single electron transfer[1] (ET). Since many competing pathways are available for further reactions of radical cations[2,3], seeking possibilities of controlling selectivity with catalysts is an important objective. With very reactive radical cations and fast, consecutive reactions, the first step may become indistinguishable from further irreversible ET or chemical steps[4]. Aromatic compounds that can be oxidized to relatively stable radical cations, provide a useful niche for mechanistic and synthetic information on catalysis by the study of distinct oxidation steps.

Ruthenium chloride trihydrate, $RuCl_3·3H_2O$, has been described in previous publications as a possible catalyst for electrooxidation of water[5]. It was also used for electrooxygenation of aromatic hydrocarbons such as naphthalene and 2-methylnaphthalene to 1,4-naphthoquinone and to 2-methyl-1,4-naphthoquinone[6]. Water is the obvious source of oxygen and

$RuCl_3 \cdot 3H_2O$ enhances the selectivity and rate of quinone formation. Linear sweep voltammetry shows two irreversible oxidation steps for naphthalene and 2-methylnaphthalene[6]. In the presence of $RuCl_3 \cdot 3H_2O$, the second oxidation step is shifted towards a lower oxidation potential by 120 ± 20 mV, with a small increase in the peak current whereas the first oxidation potential remains conspicuously unaffected[6]. It was proposed that this pattern in voltammetry reflects formation of an intermediate complex of the aromatic radical cation with $RuCl_3 \cdot 3H_2O$ and that such complex provides a clue to the linkage between organic oxidation and oxygenation with water[7]. However, in the absence of further examples, other explanations such as possible effects on overpotential of the water units coordinated in $RuCl_3 \cdot 3H_2O$, could not be ruled out. Both oxidation steps of naphthalene and 2-methylnaphthalene are irreversible and their radical cations react fast with water. When water concentration in acetonitrile increases, say to 0.1 mol l^{-1}, the two oxidation waves tend to converge. All this limits the value of comparing microscale current–potential data obtained in dry acetonitrile with macroscale electrolysis in wet acetonitrile. The present study has been extended to include compounds that yield stable radical cations displaying a reversible redox behaviour indicated by voltammetry and a separate second oxidation step. The compounds studied were: 1,4-di-*tert*-butyl-2,5-dimethoxybenzene (**1**), 3,5-di-*tert*-butyl-1,2-dimethoxybenzene (**2**), 2-*tert*-butyl-1,4-dimethoxybenzene (**3**), 2,4,6-tri-*tert*-butylaniline (**4**), *N*,*N*,*N′*,*N′*-tetramethyl-1,4-phenylenediamine (**5**). The role of $RuCl_3 \cdot 3H_2O$ was tested by voltammetry with compounds **1**–**5**, by simultaneous electrochemical ESR (SEESR) and UV-VIS spectroscopy with **1** and **2**. The relevance of these observations to preparative electrolysis has been examined.

EXPERIMENTAL

Materials

Acetonitrile (Mallinckrodt analytical, maximum 0.03% H_2O, $16.7 \cdot 10^{-3}$ mol l^{-1}) was used as supplied. Tetrabutylammonium perchlorate (TBAP), tetrabutylammonium hexafluoroborate (TBAH, Fluka), silver perfluoroborate (Fluka), sodium hydride, methyl iodide, ruthenium chloride trihydrate (Aldrich, Johnson Matthey), 2,4,6-tri-*tert*-butylaniline (**4**), *N*,*N*,*N′*,*N′*-tetramethyl-1,4-phenylenediamine (**5**), 3,5-di-*tert*-butylpyrocatechol, 3,5-di-*tert*-butyl-1,2-benzoquinone (**7**) and 2-*tert*-butylhydroquinone (**10**), were used as received from Aldrich, BDH, or Fluka. The preparation of **1** and **6** has been described[8].

3,5-Di-tert-butyl-1,2-dimethoxybenzene (**2**) was prepared by methylation of 3,5-di-*tert*-butylpyrocatechol with sodium hydride followed by methyl iodide according to Matsuura *et. al.*[9]. The crude yellow oil obtained was purified by chromatography over silica gel with 40% chloroform in petroleum ether and crystallized from dichloromethane. The final product is colourless with m.p. 53 °C (yield ≈50%). GC-MS, *m/z* (%): 250 (40), 236 (18), 235 (100), 164 (11), 57 (14). ^{1}H NMR, δ (ppm): 1.31 (9 s); 1.39 (9 s); 3.87 (6 s); 6.83 (1 d, *J* = 2.4 Hz); 6.91 (1 d, *J* = 2.4 Hz).

2-tert-Butyl-1,4-dimethoxybenzene (**3**) was prepared by the reaction of 2-*tert*-butylhydroquinone with dimethyl sulfate in accord with Kharasch *et. al.*[10]. Alternatively, 2-*tert*-butylhydroquinone (2 g) in dry dimethyl sulfoxide (25 ml) was added over 5 min to NaH (1 g) in dry dimethyl sulfoxide (50 ml) and stirred for 30 min to yield a brown slurry. Methyl iodide (2 g) in dimethyl sulfoxide (50 ml) was slowly added. Products, a brown solution and a white precipitate, were cooled, hydrolyzed and extracted with ether. The ether extract was washed and dried over $MgSO_4$. Evaporation and chromatography as above or evaporation and distillation yields **3** as an oil, b.p. 240 °C/50 mm, yield ≈60%. GC-MS, *m/z* (%): 195 (4), 194 (60), 180 (15), 179 (100), 164 (45), 151 (35), 149 (15), 121 (15), 91 (16), 77 (14). ^{1}H NMR, δ (ppm): 1.43 (9 s); 3.84 (3 s); 3.83 (3 s); 6.75 (1, 2 × d), 6.85 (1, d); 6.97 (1 d, *J*(ab) = 0.03, *J*(ac) = 0.01). (H_a, H_b, and H_c protons at positions 6, 5 and 3, respectively).

N-(3-tert-butyl-4,5-dimethoxyphenyl)acetamide (**8**) was found among products of electrolysis of **2** at 2.2 V. It was separated by chromatography on silica gel 60 with $CHCl_3$–petroleum ether and was identified by GC-MS only. GC-MS, *m/z* (%): 251 (5), 226 (14), 225 (100), 224 (10), 223 (58), 210 (6), 133 (3).

2-tert-Butyl-1,4-benzoquinone (**9**) was prepared by reaction of 2-*tert*-butylhydroquinone (3 g), in ice cool concentrated H_2SO_4 (10 ml) with an aqueous solution of $K_2Cr_2O_7$ (8 g), that was added dropwise. The mixture was allowed to react for 15 min and terminated with 5 ml of methanol; then water was added and the product extracted with ether (yield 80%). GC-MS, *m/z* (%): 166 (15), 164 (60), 151 (39), 149 (100), 121 (63), 93 (35), 77 (42). ^{1}H NMR, δ (ppm): 1.28 (9 s); 6.59 (1 s); 6.66 (2 s).

Voltammetry was performed under Ar using EG&G Princeton Applied Research Versastat in a three-electrode cell with Pt tip (2 mm^2) as a working electrode, Pt plate (1 cm^2) as a counter electrode and Ag|AgCl|3 M KCl as a reference (0.1 mm Ag foil, Sigma). Pt electrodes were cleaned with concentrated HNO_3, washed successively with triple-distilled water, H_2SO_4 and finally with water again. Background currents were checked after each washing. Concentration of tetrabutylammonium perchlorate (TBAP) was 0.1 mol l^{-1} in acetonitrile and that of ruthenium salt was 3 mmol l^{-1}. Tests were conducted in 50 ml of CH_3CN solutions (<16.7 mM H_2O), using scan rates from 50 to 1 000 mV s^{-1}. The influence of water was examined for compounds **2** and **3** at 10^{-3} M concentrations in 20 ml of CH_3CN solutions (<16.7 mM H_2O). One series was without ruthenium salt, another series with 10^{-4} M $RuCl_3 \cdot 3H_2O$.

Control Tests

The reproducibility was checked by repeated voltammetric measurements with materials, electrolytes and solvents from various sources. Electrodes were checked for possible effects of invisible coating by voltammetric test of pairs of anodes A and B. Anodes in group A were freshly cleaned between voltammetric measurements whereas those in group B were used continuously without any treatment. Electrolysis was then performed with the two sets of electrodes, in the presence or absence of $RuCl_3$, at 1.0, 1.5, 1.8 and 2.0 V, for the duration of 5 min each, a time long enough to cover any voltammetric test. Subsequently, CV scans were performed at 50 mV s^{-1} from 0.0 to 2.8 V. From 0.0 to 2.45 V, no changes or differences were detected between electrodes of groups A and B. No surface effects have been detected in tests where compounds **1** and **2** were present. The build-up of an anodic wave was observed at 2.49 V with all electrodes. (The potential range relevant in this work is <2.2 V). With **3**, visible coating appeared on the surface and two broad irreversible reduction waves at 0.8 and 0.3 V were recorded.

Controlled potential electrolysis (CPE) was run on an EG&G Princeton Applied Research Potentiostat model 362, under Ar, at 26 ± 1 °C, in a three-electrode cell with Pt plates (300 mm^2) as a working and counter electrodes. The volume of solution was 50 ml. The reference electrode was a silver foil dipped in 0.1 M $AgBF_4$ in CH_3CN, in a glass tube with a sintered-glass tip. The reference electrode was freshly prepared and calibrated against Ag|AgCl. Its potential was +400 mV relative to Ag|AgCl and +600 mV relative to standard hydrogen electrode (SHE). Products were isolated by addition of 50 ml water and extraction with $CHCl_3$. After drying, chromatography was carried out on Dowex 50W X2-200 with 50% CH_3CN–H_2O as an eluent which removes electrolyte residues. The extract was analyzed by GC-MS and TLC. Chromatography with $CHCl_3$ over alumina was used to isolate material for NMR analysis. The Dowex 50W X2-200 column was prepared by washing in triple-distilled water (TDW). The resin was regenerated by washing with 10% $HClO_4$.

Controlled Potential Electrolysis of **2**

From stock solutions of **2**, 50 ml samples were prepared in pairs, one of them containing 0.1 mM $RuCl_3 \cdot 3H_2O$. Samples were electrolyzed at the same temperature. Samples were prepared in CH_3CN containing <16.7 mM or 11.1 M H_2O with 0.1 M TBAP and concentration of **2** 1.0 mmol l^{-1}. Electrolysis was performed at three constant potentials 1.1, 1.5 and 1.9 V *vs* 0.1 M Ag|0.1 M $AgBF_4$, *i.e.* at 1.4, 1.8, 2.2 V *vs* Ag|AgCl (*cf.* CV tests in Fig. 9). Electrolysis in presence of $RuCl_3 \cdot 3H_2O$ was run for 2 h an average current density of ≈4 μA mm^{-2} ($12 \cdot 10^{-9}$ F s^{-1}). Aliquots of 50 μl were analyzed in 10 min intervals by HPLC equipped with a UV detector (245 nm) and a reverse-phase C18 column with acetonitrile–water or methanol–water as solvents. HPLC injections were of pre-set to 20 μl. Initial reaction rates (for the first ten coulombs) of **2** and of formation of **7** are given in Fig. 9.

Controlled Potential Electrolysis of **3**

Electrolysis was performed at 1.75 V (Ag|AgCl) (Fig. 3b) in 50 ml of CH_3CN solutions (16.7 mM H_2O) containing 30 mM **3**, 0.1 M TBAP and in CH_3CN–H_2O (11.1 mol l^{-1}) solutions with and without 5 mM $RuCl_3 \cdot 3H_2O$ until a charge of 600–800 °C passed. In CH_3CN with water concentration less than 16.7 mol l^{-1}, some 2-*tert*-butyl-1,4-benzoquinone (**9**) and 2-*tert*-butylhydroquinone (**10**) formed but reaction was very slow. When $RuCl_3$ was present, only two isomeric chlorination products, two isomers of 2-*tert*-butyl-1,4-dimethoxychlorobenzene, **11** and **12** were formed[11]. In a CH_3CN–H_2O mixture (11.1 M H_2O), formation of **9** and **10** was predominant, and the rate of formation of **9** is doubled when $RuCl_3$ is present. In some cases, black coating was formed on the electrodes under prolonged CPE.

Simultaneous Electrochemical ESR (SEESR)

In the SEESR method electrochemical analysis is performed in a cell mounted inside the cavity of an ESR spectrometer. The SEESR method and instrument used here has been already described in ref.[12]. Conditions of specific SEESR tests are described in the captions to Figs 5–7.

UV-VIS Measurement of Radical Cation $1^{+\bullet}$

A 50 ml solution of 1.0 M **1** in CH_3CN with 0.1 M TBAP was electrolyzed for 10 min at 2.9 mA (a charge of 1.8 C). The maximum concentration of $[\mathbf{1}]^{+\bullet}$ is therefore $1.8 \cdot 10^{-5}$ mol l^{-1}. A green colour of the radical cation appears in solution. An aliquot of 2 ml was transferred to quartz cuvettes containing 0.1 ml CH_3CN or 0.1 ml CH_3CN with 0.25 mM $RuCl_3{\cdot}3H_2O$ and examined using a Kontron UV 930 spectrophotometer. The sample transfer required less than 2 min. The absorbance was recorded at 463 nm for $[\mathbf{1}]^{+\bullet}$ to obtain the decay curve.

RESULTS AND DISCUSSION

Compounds **1**–**5** were studied by voltammetry in commercial dry acetonitrile (0.3 % H_2O). In all figures, potential sweep started from zero to positive potential (oxidation) and back. All compounds show a sequence of two oxidation steps. The first is a single-electron transfer (ET) forming a radical cation, reversible at scan rates of 30–1 000 mV s^{-1}. The second step represents further irreversible oxidation for compounds **1**–**4** as shown in Figs 1a (ref.[8]), 2a and 3. An exception was found for compound **5** where the second step is reversible as well[13] (Fig. 4). The relation of the first reversible step to the formation of radical cations is indicated for **1** and **2** by appearance of an ESR signal (Figs 5 and 6) while the second transition is ESR-silent. A similar status has been established elsewhere for compounds **4** (ref.[14]) and **5** (ref.[13]).

Compounds **1**–**4** show a shift of the second transition in presence of $RuCl_3{\cdot}3H_2O$. The first CV is not affected by $RuCl_3{\cdot}3H_2O$ as it is shown in Figs 1–3. Similar behaviour was found for naphthalene and 2-methylnaphthalene having irreversible CV. Except for **4** and **5**, the potential shift is between 100 and 140 mV towards less positive potentials. In the case of compound **4**, the shift is to more positive potentials whereas with **5**, the second peak potential is not shifted at all. Its peak current decreases while both transitions remain reversible (Fig. 4). Clearly, in all the cases, the effect can be attributed to the second oxidation stage rather than to the starting material. For **1** and **2**, it is clearly shown by CV, SEESR and by UV spectrum of **1** that a radical cation forms in the first oxidation step (Figs 5 and 6). When potential steps were applied in the SEESR experiment of values of the first oxidation step (1.2 V for **1** and 1.4 V for **2**), half-life times were measured from the intensity of the ESR signal. Values of $\tau_{1/2}$ in dry acetonitrile are 1 800 s for **1** and 300 s for **2**. Both values are reduced in the presence of $RuCl_3{\cdot}3H_2O$ by a factor of 3–4. The decay of **2** shown in Fig. 7 is 3.7 times faster in the presence of ruthenium chloride. In cases of **1** and **2**, the presence of $RuCl_3{\cdot}3H_2O$ does not alter the shape of the ESR signal of cation radicals and there is no new signal detected between 0.0–2.2 V. This implies charge transfer between $[ArH]^{+\bullet}$ and $RuCl_3 \cdot 3H_2O$. This differs from the reported behaviour of $[\mathbf{4}]^{+\bullet}$ where an added base produces the deprotonated radical with consequent display of a different ESR signal[14] but this is expected since **4** has available protons.

In CV and SEESR experiments $RuCl_3 \cdot 3H_2O$ is added at the beginning and therefore it is already partly oxidized at potentials above 1.4 V as concluded from the voltammetry of $RuCl_3 \cdot 3H_2O$. In order to test the effect of non-oxidized $RuCl_3 \cdot 3H_2O$, the ruthenium salt was added to prepared solu-

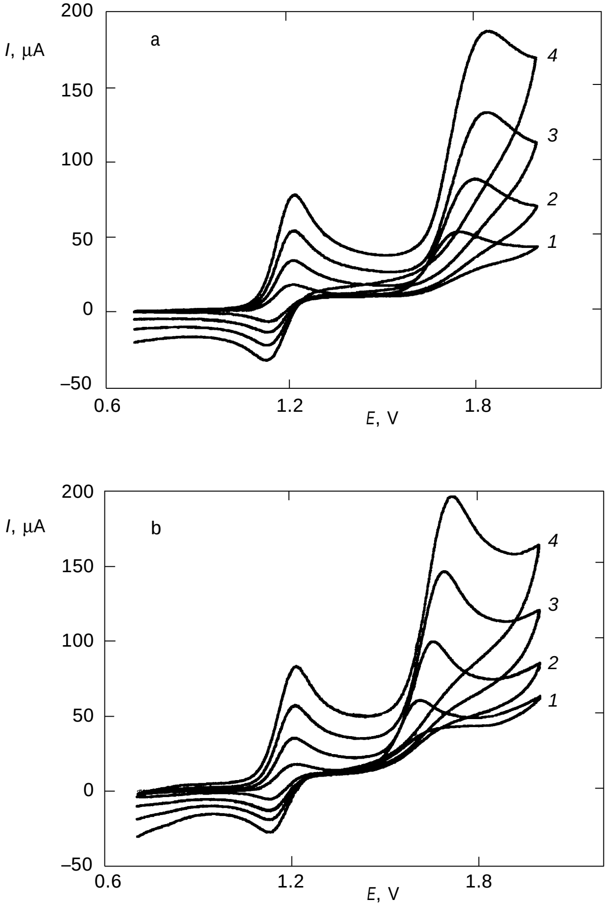


FIG. 1

CV of 1.0 mM 1,4-di-*tert*-butyl-2,5-dimethoxybenzene (**1**) in CH_3CN with 0.1 M TBAP; $v = 50$ (*1*), 200 (*2*), 500 (*3*), 1 000 (*4*) mV s^{-1}; at 28(±2) °C; Pt electrodes; reference Ag|AgCl|KCl (sat). a: In absence of $RuCl_3 \cdot 3H_2O$, b: in presence of 1.8 mM $RuCl_3 \cdot 3H_2O$

tions of radical cation. The particularly stable $[\mathbf{1}]^{+\bullet}$ (ref.[15]) shows absorption at λ_{max} = 463 nm. It was electrogenerated from solutions of compound **1**, aliquots of the oxidized solution were transferred to quartz cuvettes and the absorption spectra monitored. If required, $RuCl_3 \cdot 3H_2O$ was added only at that stage. The value of $\tau_{1/2}$ for **1** was 1 243 s. As **1** is not produced *in situ*, the estimated $\tau_{1/2}$ from UV-VIS absorption experiments is less accurate than the value of 1 800 s obtained from ESR. In a representative UV-VIS test, the

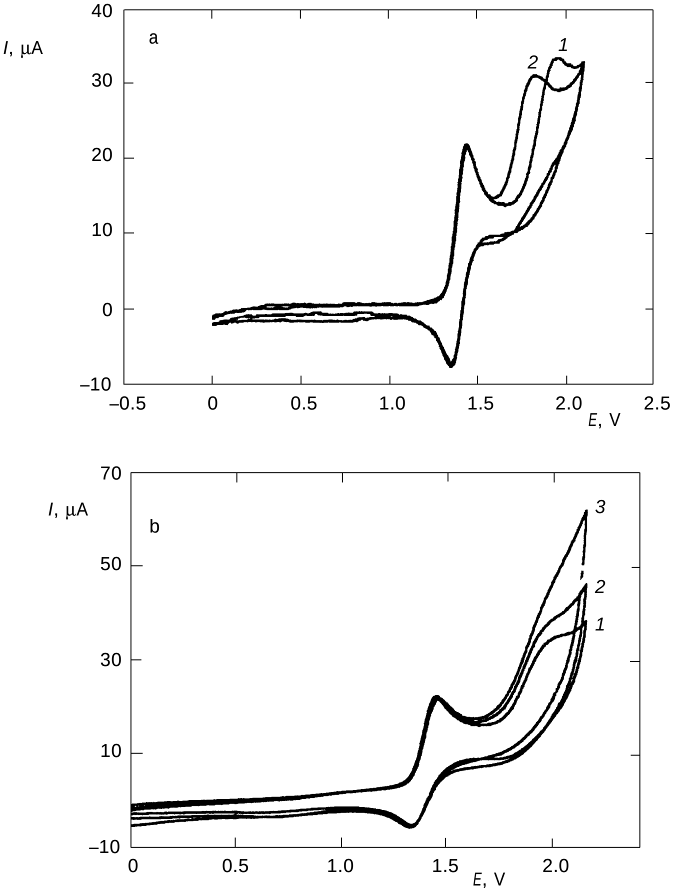


FIG. 2

CV of 10^{-3} M 3,5-di-*tert*-butyl-1,2-dimethoxybenzene (**2**) in CH_3CN with 1.0 M TBAP, at 28(±2) °C, Pt electrodes, reference Ag|AgCl|KCl (sat) in solutions. a CH_3CN contains 0.03% H_2O (16.7 mM H_2O), v = 50 mV s^{-1}. In absence of $RuCl_3 \cdot 3H_2O$ (*1*), in presence of 1.8 mM $RuCl_3 \cdot 3H_2O$ (*2*). b 20 ml CH_3CN with 0.1 M TBAP, v = 100 mV s^{-1}, 22(±2) °C, in absence of $RuCl_3 \cdot 3H_2O$, at various concentrations of water: 22 (*1*), 122.7 (*2*), 176.7 (*3*) mM H_2O

decay of $[\mathbf{1}]^{+\bullet}$ was 3.5 faster in the presence of $12.5 \cdot 10^{-6}$ M $RuCl_3 \cdot 3H_2O$ (Fig. 8). The initial concentration of $[1]^{+\bullet}$ does not exceed $1.8 \cdot 10^{-5}$ mol l^{-1}. The value of $\tau_{1/2} = 1\,243 \pm 10$ with a first-order rate constant for the decay, $k = 6 \cdot 10^{-3}$ s^{-1}, was reduced to $\tau_{1/2} = 347$ s, $k = 19 \cdot 10^{-3}$ s^{-1} in presence of $RuCl_3 \cdot 3H_2O$.

The effect of water on the redox behaviour was tested for two reasons. First, to determine the influence of water content in $RuCl_3 \cdot 3H_2O$ on

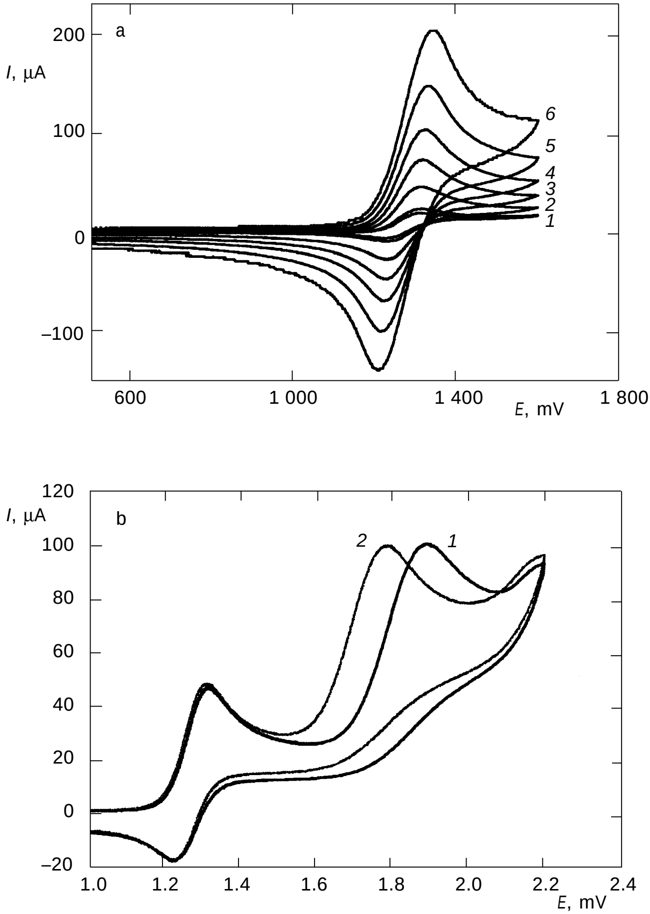


FIG. 3

CV of 10^{-3} M 2-*tert*-butyl-1,4-dimethoxybenzene (**3**) in CH_3CN with 0.1 M TBAP, at 28(±2) °C, Pt electrodes, reference Ag|AgCl|KCl (sat). a First oxidation, v = 50 (*1*), 100 (*2*), 200 (*3*), 300 (*4*), 500 (*5*), 1 000 (*6*) mV s^{-1}; b full oxidation range at 500 mV s^{-1}: in absence of $RuCl_3 \cdot 3H_2O$ (*1*), in presence of 1.8 mM $RuCl_3 \cdot 3H_2O$ (*2*) voltammetry and, second, to judge the relevance of comparing voltammetry with electrolysis. Acetonitrile is the preferred medium for voltammetry whereas effective electrolysis often requires the presence of water. The effect of water on voltammetry of **1**–**3** was investigated for water concentrations ranging from 0.017 mmol l^{-1} (in commercial-grade dry acetonitrile) to 1.1 mol l^{-1} (Fig. 2b). Concentrations of water up to 0.5 mol l^{-1} do not affect the first reversible transition. In the range of 0.5–1.0 mol l^{-1}, water causes gradual loss of reversibility of the first oxidation step. As far as the second oxidation step is concerned, the effect of water differs from that caused by the ruthenium salt in three ways: The potential shift is significantly smaller. Approximately 240 mM water is required to cause a shift of the same magnitude as caused by 1 mM $RuCl_3 \cdot 3H_2O$ (*i.e.* 3 mM water in $RuCl_3 \cdot 3H_2O$). The effect of the ruthenium compound is 80 times larger. The CV curve of the second transition changes shape. The I_p^{ox} of the second step, not detected above $170 \cdot 10^{-3}$ M water, merges with the background at the window limit. In contrast, $RuCl_3 \cdot 3H_2O$ causes a 100 mV shift without loss of distinction of the second oxidation peak, over scan rates of 50–500 mV s^{-1} (Figs 1–3). For the concentration of aromatic compound about 0.1 mol l^{-1}, the potential shift caused by $RuCl_3 \cdot 3H_2O$ reaches its maximum at concentrations below 3 mmol l^{-1} whereas the effect of water is continuous over a wider range. Obviously, the influence of $RuCl_3 \cdot 3H_2O$ is of a different nature than that of water.

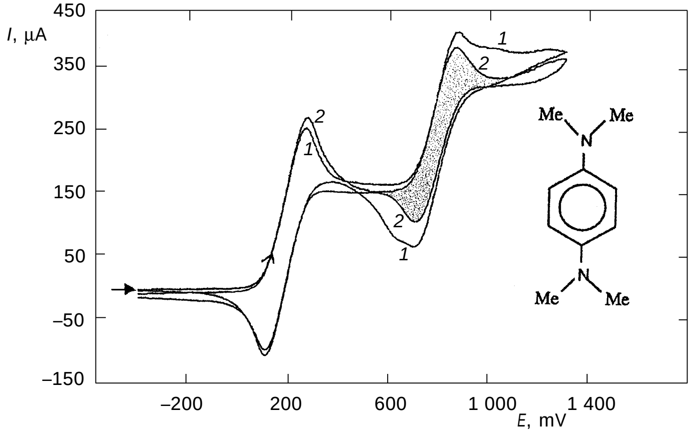


FIG. 4
CV of 10^{-3} M *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine (**5**) in CH_3CN with 0.1 M TBAP, v = 200 mV s^{-1}, at 28(±2) °C, Pt electrodes, reference Ag|AgCl|KCl (sat). In absence of $RuCl_3 \cdot 3H_2O$ (*1*), in presence of 1.8 mM $RuCl_3 \cdot 3H_2O$ (*2*). Voltammogram of the second oxidation step in presence of ruthenium salts is marked by shading

The effect of water in the presence of 1 mM $RuCl_3 \cdot 3H_2O$ is similar up to a point. The added water (150 mmol l^{-1}) shifts the potential of the second oxidation step. The first oxidation curves of **2** and **3** remain reversible or

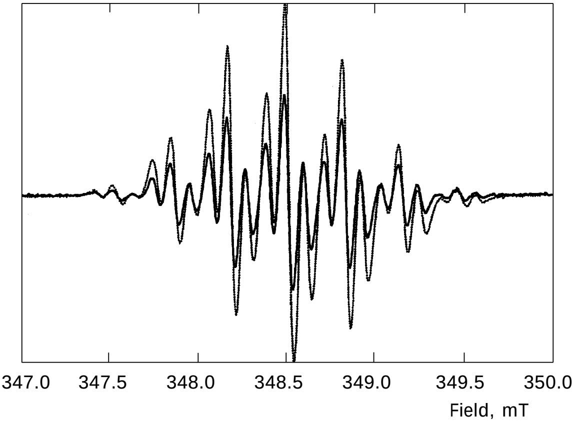


FIG. 5
SEESR; first-derivative ESR spectrum of the radical cation of $5 \cdot 10^{-3}$ M 1,4-di-*tert*-butyl-2,5-dimethoxybenzene in CH_3CN with 0.1 M TBAH, [**1**]$^{+\bullet}$ generated by electrolysis *in situ* at a Pt electrode; $g = 2.0031$, $a(^1H) = 0.322$ mT (6 H), $a(^1H) = 0.100$ mT (2 H), solid line experimental, dotted line simulated

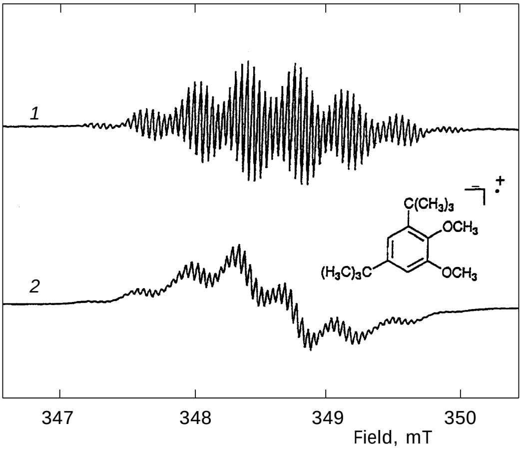


FIG. 6
SEESR; first-derivative of *in situ* ESR spectrum obtained during electrolysis at 20(±1) °C (Pt electrode) in CH_3CN containing 0.1 M TBAP and 3,5-di-*tert*-butyl-1,2-dimethoxybenzene (**2**) of concentrations: (*1*) 5, (*2*) 30 mmol l^{-1}. The modulation amplitude is 0.02 mT and modulation frequency 50 kHz; $g = 2.0032(\pm 0.0001)$

slightly distorted up to 1.4 M water. When the water concentration exceeded 1.4 mol l^{-1}, both transitions gradually converged; this was observed for compounds **2** and **3** only. Compound **1**, on the other hand, is catalytically oxidized in presence of both water and ruthenium salt at water concentration above 0.2 mol l^{-1}. Here a complicated multistep oxidation takes place and **1** is oxidized to **6** (ref.[8]).

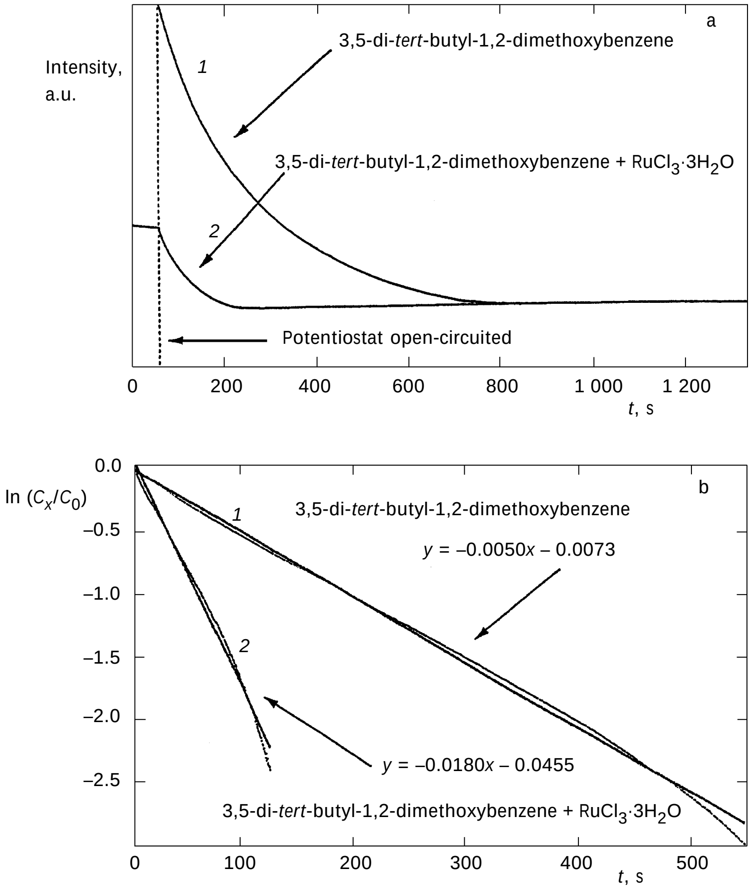


FIG. 7

Time development of the ESR signal at open circuit conditions following the oxidative electrolysis of **2** (30 mmol l^{-1}) with 0.1 M TBAP, at 20 °C. In absence of $RuCl_3 \cdot 3H_2O$ (*1*), in presence of 5 mM $RuCl_3 \cdot 3H_2O$ (*2*), modulation amplitude 1 mT (a). The relation of ln (C_x/C_0) (where C_0 is the ESR signal intensity at $t = 0$ and C_x is the signal intensity at time t) plotted *vs* t (s) (b). Data from Fig. 7a

The possibility that potential shifts in voltammetric curves can be caused by adsorption[16], here by $[ArH]^{+\bullet}_{ads}$, has to be considered. In present experiments, adsorption cannot be detected either visually or by voltammetry. In a series of voltammetric and electrolysis experiments, clean electrodes were compared with electrodes used repeatedly without cleaning. There were no evidence of coating or any differences in voltammograms measured both in acetonitrile or acetonitrile–water solutions. Furthermore, the peak current at the potential shifted by an influence of $RuCl_3 \cdot 3H_2O$ fits with diffusion control criteria, *i.e.*, it is linear with $v^{1/2}$ and shows no saturation level even with small (1 mm^2) electrodes. At high scan rates, it shows the same IR potential drop as the unshifted wave. The exception was observed when solutions of compound **3** were electrolyzed. Electrode coating appears during electrolysis in the presence of $RuCl_3 \cdot 3H_2O$ and seems to be associated with chlorination. With compound **3**, chlorination is a very effective reaction at low concentrations of chloride[11]. This complication was not observed with **1** and **2**.

A similar shift of the second oxidation wave of compounds **2** and **3** was observed in the presence of $Ru(CH_3CN)_3Cl_3$ (ref.[17]). On the other hand, no shift was found in oxidation of compounds **1**–**3** in the presence of tris(acetylacetonato)ruthenium, $Ru(acac)_3$.

The initial oxidation rates in CPE at the shifted potential were considered rather than optimum yields of specific products. In accord with the CV

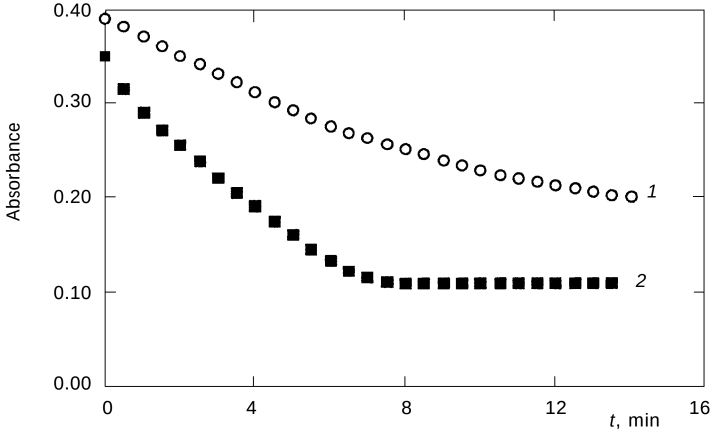


FIG. 8
Time dependence of the absorbance at 463 nm for $[\mathbf{1}]^{+\bullet}$ in CH_3CN with 1.0 M TBAP, at 20 °C. In absence of $RuCl_3 \cdot 3H_2O$ (*1*), in presence of 1.8 mM $RuCl_3 \cdot 3H_2O$ (*2*)

study, CPE of **2** was performed at three predetermined potentials, 1.4, 1.8 and 2.2 V (Ag|AgCl|KCl as a reference, *cf.* Fig. 2). Experiments in the presence and absence of $RuCl_3 \cdot 3H_2O$ were compared under identical conditions and products 3,5-di-*tert*-butyl-1,2-benzoquinone (**7**) and *N*-(3-*tert*-butyl-4,5-dimethoxyphenyl)acetamide (**8**) were identified (Scheme 1). Figures 9a and 9b display reaction rates of **2** and formation of **7** at different potentials in dry acetonitrile (16.7 mM H_2O). In the non-catalyzed process, consumption of **2** increases gradually and the rate of formation of **7** decreases regularly with increasing potential. In the presence of $RuCl_3 \cdot 3H_2O$, consumption of **2** increases similarly, but the rate of formation of **7** is particularly accelerated with a maximum value around 1.8 V (Fig. 9). The current efficiency for **7** is also exceptionally high at 1.8 V: 20% without $RuCl_3 \cdot 3H_2O$ and 50% in its presence. The production of **7** induced by $RuCl_3 \cdot 3H_2O$ at 1.8 V is outstanding. The rate in this case is only doubled but the effect depends on the exact value of potential selected for electrolysis (*cf.* Fig. 2a). Voltammetry indicates that a larger effect is possible. Formation of **7** slows down again at more positive potentials starting from 2.2 V where compound **8** becomes an important product.

To form quinones, the positions at the methoxy groups are attacked and the *tert*-butyl groups remain intact. At more positive potentials the reaction with acetonitrile becomes significant. This is altogether a different reaction whereby the methoxy groups remain intact and a *tert*-butyl group is re-

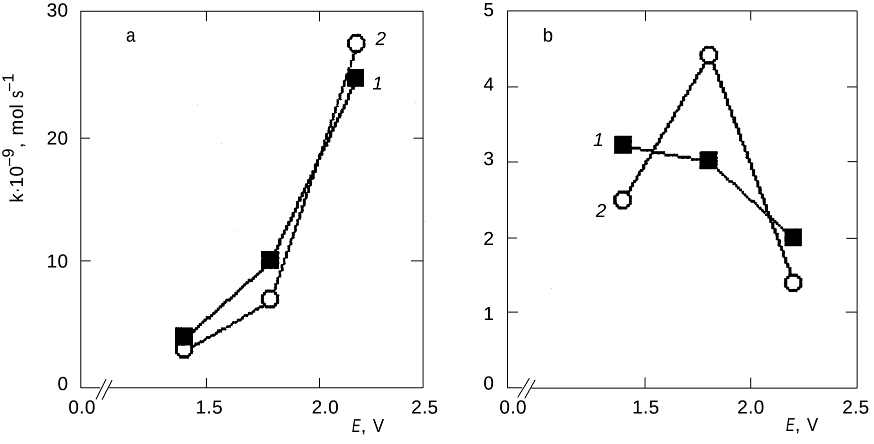
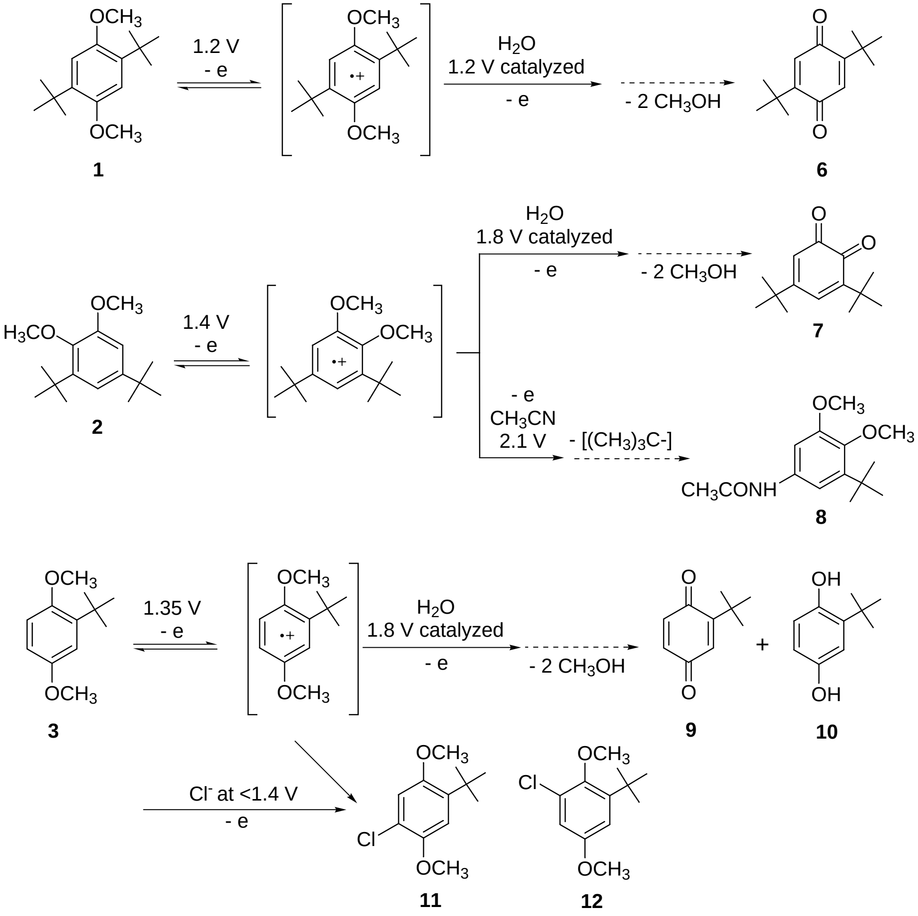


FIG. 9

Initial rates of oxidation of compound **2** (a); initial rates of formation of quinone **7** at 1.4, 1.8 and 2.2 V *vs* Ag|AgCl, at 28(±2) °C, Pt electrodes (b). In absence of $RuCl_3 \cdot 3H_2O$ (*1*), in presence of $RuCl_3 \cdot 3H_2O$ (*2*) placed. Also the aromatic molecule is oxidized beyond the level of radical cation. The competition between water and acetonitrile was noted in other cases depending either on the applied potential[18] or on the electrolyte[19]. No detailed study of this problem is available.

Applicability of conditions found for microscale voltammetry to macroscale electrolysis has limitations and significant differences prevail[20]. Electrolysis of several aromatic ethers in a very dry acetonitrile causes polymer deposition on the electrodes[21,22]. Our experiments were performed in acetonitrile with 0.03% (16.7 mmol l^{-1}) water content and in acetonitrile– water. In these solvents, polymer deposition is suppressed. At water concentra-



SCHEME 1

tions 0.017–0.2 mol l^{-1}, oxidation steps are well resolved in voltammetry and, in this respect, the results of electrolysis should reasonably reflect the observed voltammetry. Still, voltammetry does not reveal effects which are due to the larger scale and extended time required by electrolysis. These effects are specific in each case (Scheme 1).

As already mentioned, reactions of **1** become autocatalyzed in the presence of both water and ruthenium compounds as observed by voltammetry[8]. Electrolysis of **1** is very different from that of **2** or **3**.

Compound **3** shows the same trend as compound **2** – a faster reaction with water at the shifted potential in the presence of $RuCl_3 \cdot 3H_2O$ where *tert*-butyl-1,4-benzoquinone (**9**) and the hydroquinone (**10**) are produced. In the case of **3**, the situation is complicated in the presence of chloride due to interference of chlorination[11] (not observed with **1** and **2**), which is very fast already at 1.0 V, and obstructs detailed rate measurements. Chlorination is predominant in dry acetonitrile. At high water concentrations the quinone **9** and hydroquinone (**10**) are formed. Their formation is accelerated by $RuCl_3 \cdot 3H_2O$ at 1.75 V (Fig. 3).

CONCLUSIONS

Compounds **1**–**5** form in the first oxidation step a radical cation which is stable within the time scale of voltammetric measurements, even in the presence of water in concentrations exceeding 0.2 mol l^{-1}. A second step is an irreversible (reversible for **5**) oxidation of the radical cation at potentials by about 400 mV more positive. Its potential is shifted in the presence of $RuCl_3 \cdot 3H_2O$ negatively for **1**–**3**, positively for **4**. No shift was observed for compound **5**. $RuCl_3 \cdot 3H_2O$ has no effect on the first oxidation step. On the basis of the results, the second oxidation in the shifted position reflects the oxidation of a different species, not the radical cation itself but presumably either some transient complex with $RuCl_3 \cdot 3H_2O$ or a product of reaction between the radical cation and $RuCl_3 \cdot 3H_2O$. Interaction between the radical cation and $RuCl_3 \cdot 3H_2O$ was observed directly by SEESR and UV-VIS spectroscopy. Such reaction involves electron transfer between $[ArH]^{+\bullet}$ and $RuCl_3 \cdot 3H_2O$ causing its further oxidation or coupling with a high-spin position on $RuCl_3 \cdot 3H_2O$, as evident from the loss of ESR signal. The transfer is apparently from the radical cation to $RuCl_3 \cdot 3H_2O$. The other direction represented by recovery of ArH from $[ArH]^{+\bullet}$ would be indicated by a catalytic wave in the first oxidation step. Such situation has indeed been observed with **1** in the presence of $RuCl_3 \cdot 3H_2O$ or $Ru(acac)_3$ and water[8] but not with the other compounds.

$RuCl_3 \cdot 3H_2O$ provides faster reactions at lower potentials applied. This improves the cell performance and facilitates the use of undivided cells. It also enables more efficient separation of reactions that require different overpotentials (Scheme 1). The presence of $RuCl_3 \cdot 3H_2O$ may also reduce the concentration of radical cations at the electrode which would be otherwise available for side reactions such as coupling. This has been clarified particularly in the case of naphthalene and 2-methylnaphthalene, where catalysis distinctly improved conversion to quinone over dimerization[6].

The results show that $RuCl_3 \cdot 3H_2O$ affects several types of aromatic compounds but the activity of $RuCl_3 \cdot 3H_2O$ remains a very complex issue. In the "chemical" catalysis[23] like in recent reviews dealing mostly with reduction[24,25], the first step commonly involves ET of a catalytic pair in the context of indirect electrolysis. Here, $RuCl_3 \cdot 3H_2O$ appears to act as a "chemical" catalyst but in a different manner. The substrate ArH reacts directly to $[ArH]^{+\bullet}$ in a reversible step (reaction (*4*), irreversible with naphthalene). The additive, $RuCl_3 \cdot 3H_2O$, acts in the secondary oxidation (reaction (*5*)) followed by the reaction with water at a lower overpotential (Scheme 2).

Indirect electrolysis:

$$\text{Cat} - e \rightleftharpoons [\text{Cat}]^+ \qquad \text{E} \qquad (1)$$

$$[\text{Cat}]^+ + \text{ArH} \rightleftharpoons [\text{ArH-Cat}]^+ \qquad \text{C} \qquad (2)$$

$$[\text{ArH-Cat}]^+ - e + \text{Nu} \longrightarrow \text{Products} \qquad \text{E} \qquad (3)$$

This work:

$$\text{ArH} - e \rightleftharpoons [\text{ArH}]^{\bullet +} \qquad \text{E} \qquad (4)$$

$$[\text{ArH}]^{\bullet +} + \text{Cat} \longrightarrow [\text{ArH-Cat}]^+ \qquad \text{C} \qquad (5)$$

$$[\text{ArH-Cat}]^+ - e + \text{Nu} \longrightarrow \text{Products} \qquad \text{E} \qquad (6)$$

SCHEME 2

This work was supported by a research grant from the German–Israeli Fund (GIF). We thank Dr Y. Norbert for technical help. The authors also thank Dr D. A. Fiedler and Dr R. D. Webster for carrying out SEESR studies with the facilities of La Trobe University, Bundoora, Australia, and Prof. A. Bond for encouraging this cooperation.

REFERENCES

1. Eberson L.: *Electron Tranfer Reactions in Organic Chemistry*, p. 4. Springer, Berlin 1987.
2. Eberson L., Utley J. H. P., Hammerich O. in: *Organic Electrochemistry* (H. Lund and M. M. Baizer, Eds), p. 505. Dekker, New York 1991.
3. Anne A., Fraousa S., Grass V., Moiroux J., Saveant J. M.: *J. Am. Chem. Soc.* **1998**, *120*, 2951.
4. Parker V. D.: *J. Electroanal. Chem.* **1969**, *21*, App. 1.
5. Burke L. D., O'Meara T. O.: *J. Electroanal. Chem.* **1972**, *36*, App. 25.
6. Chocron S., Michman M.: *J. Mol. Catal.* **1991**, *66*, 85.
7. Michman M.: *J. Mol. Catal.* **1996**, *107*, 393.
8. Michman M., Oron M.: *Electrochim. Acta* **1994**, *39*, 2781.
9. Matsuura T., Ogura K.: *J. Am. Chem. Soc.* **1967**, *89*, 3846.
10. Oesper P. F., Smyth C. P., Kharasch M. S.: *J. Am. Chem. Soc.* **1942**, *64*, 937.
11. Appelbaum L., Lazanes G., Michman M., Oron M.: *195th ECS Meeting, Seattle 1999*. Book of Abstracts. The Electrochemical Soc. Inc., Pennington, New Jersey 1999.
12. Fiedler D. A., Koppenol M., Bond A. M.: *J. Electrochem. Soc.* **1995**, *142*, 862.
13. Bocarsly A. B., Walton E. G., Bradley M. G., Wrighton M. S.: *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *100*, 283.
14. a) Cauquis G., Fauvelot G., Roguardy J.: *Bull. Soc. Chim. Fr.* **1968**, 4928; b) Cauquis G.: *Bull. Soc. Chim. Fr.* **1968**, 1618.
15. Jiang X. K., Zhao C. X., Gong Y. F.: *J. Phys. Org. Chem.* **1991**, *4*, 1.
16. Greef R., Peat R., Peter L. M., Pletcher D., Robinson J.: *Instrumental Methods in Electrochemistry*. Southampton Electrochemistry Group, Ellis Horwood, Chichester 1985.
17. a) Appelbaum L., Heinrichs C., Demtschuk J., Michman M., Oron M., Schäfer H. J., Schumann H.: *J. Organomet. Chem.* **1999**, *592*, 240; b) Appelbaum L.: *MS Thesis*. Hebrew University of Jerusalem, Jerusalem 1998.
18. Shono T.: *Electroorganic Chemistry as a New Tool in Organic Synthesis*, p. 96. Springer, Berlin 1984.
19. Nyberg K.: *J. Chem. Soc., Chem. Commun.* **1969**, 774.
20. Amatore C. in: *Organic Electrochemistry* (H. Lund and M. M. Baizer, Eds), p. 207. Dekker, New York 1991.
21. Fabre B., Michelet K., Simonet N., Simonet J.: *J. Electroanal. Chem.* **1997**, *425*, 67.
22. Marquez O. P., Marquez J., Choy M., Ortiz R.: *Electrochim. Acta* **1994**, *39*, 1927.
23. a) Andrieux C. P., Dumas-Bouchiat J. M., Saveant J. M.: *J. Electroanal. Chem.* **1978**, *87*, 39; b) Andrieux C. P., Dumas-Bouchiat J. M., Saveant J. M.: *J. Electroanal. Chem.* **1978**, *87*, 55.
24. Simonet J. in: *Organic Electrochemistry* (H. Lund and M. M. Baizer, Eds), p. 1217. Dekker, New York 1991.
25. Efimov O. N., Strelets V. V.: *Coord. Chem. Rev.* **1990**, *99*, 15.