

Homogeneous vs. heterogeneous processes in electrocatalysis. Different types of catalysis in organic electrooxidation¹

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Abstract

Electrochemical reactions involve surface–solution interface that may display properties relevant to homogeneous and heterogeneous catalysis. Examples are taken from the catalysis by RuCl_3 and $\text{Ru}(\text{acac})_3$ of the accelerated electrooxidation of water when it is linked with oxidation of naphthalene, 2-methylnaphthalene and some aryl ethers. The influence of tetrabutylammonium dichromate and of diisobutylamine on the electrochemical reaction is discussed in terms of interface effects on the diffuse layer and selectivity to naphthoquinone, and 2-methylnaphthoquinone as products.

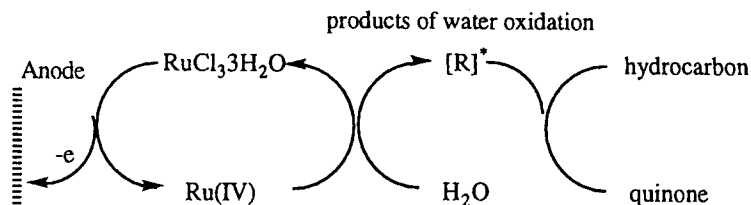
Keywords: Homogeneous catalysis; Heterogeneous catalysis; Electrooxidation; RuCl_3 ; $\text{Ru}(\text{acac})_3$; Oxidation; Tetrabutylammonium dichromate; 2-Methylnaphthalene; Diisobutylamine; Diffuse layer; Electrochemistry; 2-Methylnaphthoquinone

1. Introduction

The term electrocatalysis is meant to present the acceleration or the increasing of selectivity of electrochemically performed reactions [1]. As such it covers a wide range of phenomena originating in the large number of parameters controlling electrodic reactions. Basically, electron transfer and initial processes take place at the electrode surface and the primary reactions should therefore be considered heterogeneous. Inevitably, under the influence of the potential difference an interfacial boundary region is formed in the solution facing the electrode. This comprises of relatively organized domains within the solvent, differing from the bulk solu-

tion by high degrees of molecular orientation, concentration gradients, ion strength, dipole interactions and solvation conditions. Detailed models have been proposed [2] and criteria for inter-phase components were recently defined [2,3]. Formation of a double layer of charged ions next to the surface plays a dominant role in modifying the solid–liquid interface [4]. This may be a mono- or bimolecular layer, the Outer Helmholtz layer. Modified models account for self volume and solvation, the Gouy–Chapman and the Stern models [2]. Reaching further into the solution is the diffuse layer in gradual density. Specific arrays of organization are expected for charged ions, neutral molecules with varying degrees of solvation, dipoles and polarization [3,5]. Electrochemical reactions are therefore under the constraints of both heterogeneous conditions as surface reactions and homogeneous, solution reactions in the very special

¹ This work is dedicated to Prof. H. Schumann on his 60th birthday.



Scheme 1. The indirect electrocatalysis of hydrocarbon oxidation by RuCl₃. An intermediate step of water oxidation increases the rate of hydrocarbon oxygenation.

terms of the boundary domain. The expected effects of the double layer on electrode kinetics have indeed been modeled by Frumkin [6]. Then, since the primary electrode reactions produce highly reactive ion radicals, their subsequent reactions may occur either at the electrode surface or further into the solution domain in the diffuse layer, as homogeneous reactions. Catalysts can affect these at the surface, or activate a mediator catalytic cycle for secondary reactions. Modifications at the electrode surface are clearly heterogeneous, whereas a mediator's is often considered in terms of a homogeneous reaction (indirect electrolysis) [1](c). The electrode vicinity, where reactions take place, has characteristics of both and is in a way, unique. Our present task is to reason the implications of the boundary layer effects for catalysts in electroorganic reactions, as these are reflected in reaction rates and products. The examples are taken from our studies.

2. Experimental

Generally experimental conditions, cell, electrodes and apparatus and methods of analysis were maintained as reported in preceding publications cited here. Experiments with DIBA were carried out in CH₃CN/H₂O 6.5/3.5, Pt electrodes, Ag/AgCl or were specified Ag/AgbF₄ [7] reference, 0.1 M Bu₄NClO₄ electrolyte. 20°C UV-VIS spectra in CH₃CN–H₂O 3.5/6.5. RuCl₃ has λ_{max} at 400 and 585 nm. DIBA has no absorbency above 400 nm. Background absorbency is at 280 nm. In mixtures of DIBA–RuCl₃ 0.0025 M the Ru lines are slightly dimin-

ished, in DIBA 0.25 M–RuCl₃ 0.0025 M they are completely removed. Instrument: Kontron Uvicon 820.

3. Results and discussion

RuCl₃ induces the accelerated oxidation of water at a low anodic potential. The reaction is complicated and not fully understood but it can be used to induce the oxygenation of hydrocarbons [8,9]. The reaction of RuCl₃ with water in CH₃CN, may involve an active ruthenium oxide layer on the electrode surface though no permanent coating is formed [10]². It is certainly a surface reaction and can be followed by voltammetry. Increased water concentrations cause significant increases in current densities. This reaction can be linked to subsequent oxygenation of hydrocarbons. The link is possible by the ability of RuCl₃ to form complexes with aromatic cation-radicals. That step is evident in current/potential scans [8], so it takes place in the diffuse layer — a boundary between homogeneous and heterogeneous criteria. Scheme 1 presents the general chain of steps.

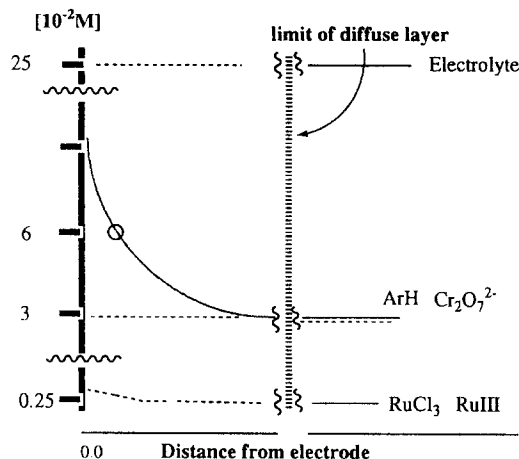
This reaction was run under various conditions two of which are discussed below in the present context.

² The possibility of Ru coating of Pt is realistic. The question of its possible effect on the present cases is a matter of separate studies. So far, no influence on the present results is apparent and the current densities involved here are 3 and 4 orders of magnitude higher than those involved in detection of coatings on Pt. The author appreciates a referee's comment on this.

3.1. The diffuse layer

An intriguing example deals with utilization of concentration excess Γ , in the diffuse layer. Concentration gradients in diffuse layers of specific ions may reach several orders of magnitude depending on selective adsorption, and applied potential. Thermodynamics have been studied in great detail [11] but only one previous specific application for a preparative reaction is known to us [12]. Oxidations with dichromate illustrate this to advantage [9]. Dichromate oxidations are catalyzed by RuCl_3 [7]. In solutions of $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ with electrolytes (0.25 M), a hydrocarbon such as 2-methylnaphthalene or naphthalene (10^{-2} M), RuCl_3 (2.5×10^{-3} M) and ammonium or tetrabutylammonium dichromate (3×10^{-2} M), oxidation of the hydrocarbon is slow ($0.23 \times 10^{-6} \text{ M s}^{-1}$). Under applied potential, hydrocarbon oxidation is ca. 10^2 faster: (4.5, 10, 25 in 10^{-6} M s^{-1} , at 1.6, 1.7 and 1.8 V, respectively). The results are explained by concentration excess of dichromate $\Gamma\text{Cr}_2\text{O}_7^{2-}$. In the charged cell, concentration gradients of individual constituents form independently, each with a different affiliation to the applied potential. The gradient for the hydrocarbon should be small whereas that of $[\text{Cr}_2\text{O}_7]^{2-}$ is expected to be large. That of the solvent should grow with potential as polarization increases, with differences between CH_3CN and H_2O . As a rule due to solvation, adsorption of ions is considered non-specific and related to their charge. The double anion $[\text{Cr}_2\text{O}_7]^{2-}$ should have a strong affinity for the anode and when concentrated, tends to form polyanions [13]. The neutral hydrocarbon is least affected by the low potential field and being unsolvated, can penetrate far into the inner Helmholtz plane. Consequently, the concentration pattern in the diffuse layer differs substantially from that in the bulk (Scheme 2).

A good indicator as to the nature of oxidation is the selectivity for quinone. Dichromate and anodic oxidations strongly differ in their product selectivity. Concentrated dichromate yields



Scheme 2. Schematic expectation of concentration excess $\Gamma\text{Cr}_2\text{O}_7^{2-}$ and diffuse layer boundary, induced by low positive potential. Ratio of concentrations of $[\text{Cr}_2\text{O}_7^{2-}]$ (full line) and $[\text{ArH}]$ (dotted line), is estimated analogous to a homogeneous reaction. Exact ratios depend on potential and $\Gamma\text{Cr}_2\text{O}_7^{2-}$ is expected to have a maximum value between 1.0 and 2.0 V.

the quinone with very high selectivity (> 90%). The direct anodic oxidation yields mostly other products. The effect is most evident at low potentials (1.4–1.6 V) at which anodic oxidation is negligible. At 1.6 V naphthalene oxidizes with 70% selectivity for quinone. The selectivity drops to 40% under 2.0 V, at which the anodic oxidation is dominant. The selectivity for quinone observed in non-electrodeic homogeneous oxidation under the same conditions, is 43, 71 and 90% when $[\text{Bu}_4\text{NCr}_2\text{O}_7]$ is 3, 6 and 12×10^{-2} M. Hence the selectivity observed at 1.6 V appears as if $[\text{Cr}_2\text{O}_7^{2-}]$ equals 6×10^{-2} M in the diffuse layer as a mid-point value. Scheme 2 is drawn in accordance with this estimate. The background anodic reaction at 1.6 V is negligible. At the high potential range selectivity decreases because the direct anodic oxidation becomes fast above 1.6 V and because $\Gamma\text{Cr}_2\text{O}_7^{2-}$ may be past its maximum value where competition from other adsorbents increases, especially polarized solvent molecules.

Important evidence for the proposed role of $\Gamma\text{Cr}_2\text{O}_7^{2-}$ in the diffuse layer is: firstly, there is a strong negative temperature effect on reaction

rates [9] whereas the homogeneous oxidation by dichromate is as expected, accelerated by heating. This is in accordance with the realization that elevated temperatures favour diffusion and will be destructive to the organization within the diffuse layer. Secondly, the observation that the effect is most conspicuous with low bulk concentrations of $[\text{Cr}_2\text{O}_7]^{2-}$. Above 0.03 M $[\text{Cr}_2\text{O}_7]^{2-}$, the rate becomes zero order in $[\text{Cr}_2\text{O}_7]^{2-}$ and the limit is also related to electrode size. Again by contrast, the homogeneous reaction is first order in $[\text{Cr}_2\text{O}_7]^{2-}$ up to a concentration of 0.12 M. Thirdly, competing ion strength (of Cl^- or electrolyte), slows down the reaction. In fact lowering the concentration of electrolyte below 0.05 M, increases the selectivity to quinone up to 90%, implying unhindered increase in $\Gamma\text{Cr}_2\text{O}_7^{2-}$. Actually in general practice, diffuse layer effects are suppressed by keeping electrolyte concentrations high.

In this case, the mere application of low potential creates a local concentration of an oxidation agent in solution. Oxidation is thus made possible under mild bulk conditions. In addition, since oxidation by dichromate is accelerated by RuCl_3 , the build-up of $\Gamma\text{Cr}_2\text{O}_7^{2-}$ in the diffuse layer improves the performance of the RuCl_3 catalyst.

3.2. Effects on surface linked with homogeneous catalysts

Diisobutylamine (DIBA), has been noted to improve the catalyst performance of RuCl_3 [8] (Scheme 1). Current–potential scans compare the oxidation of RuCl_3 , DIBA and both (Fig. 1). DIBA oxidizes at a lower potential than RuCl_3 and solutions containing both show a further significant cathodic shift. This indicates formation of a DIBA– RuCl_3 complex. Formation of a weak DIBA– RuCl_3 complex with $K \cong 10^{-2}$ is also observed by UV-VIS spectra where λ_{max} for RuCl_3 at 585 and 400 nm are suppressed by DIBA. Hence, such a complex when oxidized at low potential, may either cause the easier oxidation of DIBA, or also carry-on the extended

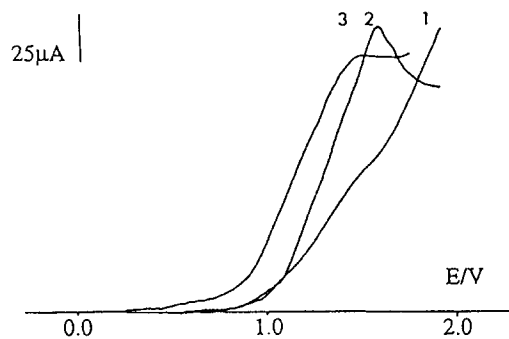


Fig. 1. Current–potential scan on Pt anode, TBAP in acetonitrile/water 35:65, 20°C. Ag/AgCl reference. Sweep rate 50 mV s^{-1} . Also in solution: (1) RuCl_3 $2.5 \times 10^{-3} \text{ M}$. (2) DIBA 0.1 M. (3) RuCl_3 $2.5 \times 10^{-3} \text{ M}$ + DIBA 0.1 M. Current of $25 \mu\text{A}$ stands for current density $10.5 \mu\text{A mm}^{-2}$.

reaction cycle of water and hydrocarbon oxidation. The second possibility is itself further evidence for the role of a DIBA– RuCl_3 complex.

Controlled potential electrolysis (CPE) identifies these shifts with accelerated electrooxidation of the 2-methylnaphthalene and naphthalene at low potentials, at which otherwise no uncatalyzed hydrocarbon oxidation is observed at all. RuCl_3 and DIBA each have some effect. The rates of hydrocarbon consumption are given under three potentials in non catalyzed runs, in presence of RuCl_3 , in presence of DIBA and in presence of both RuCl_3 and DIBA. The effect of both additives combined, is evident from the ratios 4/2 and 4/3 (Table 1). RuCl_3 and DIBA together, increase the rate over a much wider

Table 1
Rates of oxidation of 2-methylnaphthalene 10^{-4} M h^{-1} , in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 6.5/3.5, Pt electrodes, Ag/AgCl reference, 0.1 M Bu_4NClO_4 electrolyte. Concentration of RuCl_3 when present 0.0025 M, DIBA 0.25 M, 18°C

Additive	Potential, V		
	1.2	1.5	1.8
1. –	0	0	0.05
2. RuCl_3	0.05	0.3	0.46
3. DIBA	0.16	0.42	3.08
4. RuCl_3 + DIBA	1.12	3.3	3.85
ratio 3/2	3.2	1.4	6.7
ratio 4/3	7	7.9	1.25
ratio 4/2	22.4	11	8.36

potential range and the effect is synergistic. The ratio of 4/2 is particularly high at 1.2 V (CPE)

Here too, selectivity for 2-methylnaphthoquinone is the indication that the two additives strongly differ in their role. Whereas catalysis by RuCl_3 in presence of water increases the selectivity, DIBA accelerates the hydrocarbon oxidation but not the formation of quinone. In smaller concentrations of DIBA hydrocarbon (I) oxidation ($-dI/dt$) slows down and selectivity for quinone (II) increases (Fig. 2). This trend is clearest at 1.5 V. At 2.2 V, differentiation is practically lost and any specific influences of DIBA or the complex within the diffuse layer are probably screened by solvent's increased penetration of the diffuse layer and the direct electrooxidation which is fast at this potential. It should also be mentioned that quinone forms only in presence of both additives (Table 2).

Hence, DIBA which is itself oxidized, provides a completely different scenario than the dichromate case. It forms a highly dissociative

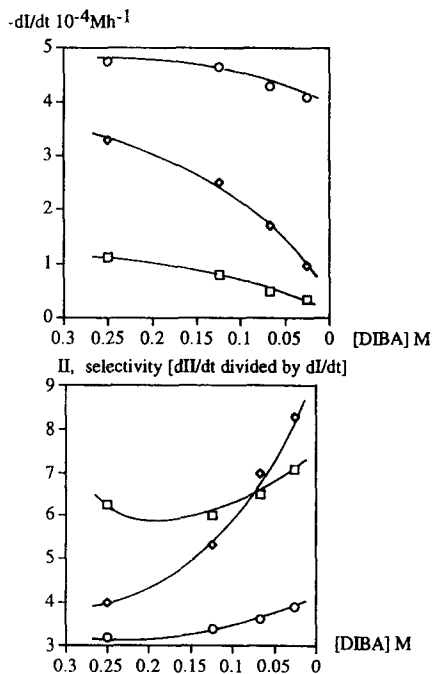


Fig. 2. Rates of oxidation of 2-methylnaphthalene ($-dI/dt$) 10^{-4} M h^{-1} , and selectivity for 2-methylnaphthoquinone (II) as function of [DIBA] obtained by CPE under three potentials. RuCl_3 0.0025 M is present in all tests. \square , 1.2 V; \diamond , 1.5 V; \circ , 2.2 V.

Table 2

Rates of formation of 2-methylnaphthoquinone 10^{-4} M h^{-1} , in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 6.5/3.5, Pt electrodes, Ag/AgCl reference, 0.1 M Bu_4NClO_4 electrolyte. Concentration of RuCl_3 when present 0.0025 M, DIBA 0.25 M

Additive	Potential, V		
	1.2	1.5	1.8
1. –	0	0	0.0
2. RuCl_3	0	0.01	0.08
3. DIBA	0	0.02	0.11
4. RuCl_3 + DIBA	0.07	0.13	0.14

complex with the ruthenium salt which is in any case hydrated (formally: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$). Being a weak ligand, it only partially competes with associations of water and hydrocarbon (radical-cation) to ruthenium which are essential for the subsequent oxidation chain. The balance is a lower oxidation potential for Ru(III) and improved catalyst performance at lower potentials. More stable ruthenium complexes which could be isolated such as L_2RuCl_2 ($\text{L} = \text{Ph}_3\text{P}, \text{CH}_3\text{CN}$), also show shifted redox potentials for the Ru(III) level but completely lack catalytic activity [14] possibly due to the blocked coordination sphere. That does not rule out catalysis of stable complexes in the role of reversible mediators.

3.3. Indirect electrolysis by mediators.

A distinction of the homogeneous and heterogeneous effects can be made when $\text{Ru}(\text{acac})_3$ is used as catalyst. $\text{Ru}(\text{acac})_3$ has a stable coordination sphere and is not influenced by weak donor ligands as the amines nor does it bind to the aromatic radical-cations. $\text{Ru}(\text{acac})_3$ has completely reversible redox characteristics as shown by CV and acts as a reversible mediator for the oxidation of water [15,16]. These processes can be followed by voltammetry and being reversible, are in complete accord with the notions of reversible homogeneous reactions. In the subsequent oxygenation and oxidation processes, aromatic ethers like dimethoxy benzene, and *tert*-butyldimethoxy benzene, di-*tert*-butyldimethoxy benzene are oxidized by

products of water oxidation. Voltammetry of these can be followed and their consumption in the homogeneous phase is reflected by the diminishing reverse current. These oxidations take place as if in homogeneous solution, no surface or diffuse layer effects are observed. It is not quite clear why particularly $\text{Ru}(\text{acac})_3$ should be a successful mediator. Other ruthenium *tris*-diketonates like $\text{Ru}[(\text{CH}_3)_3\text{COCH}_2\text{COC}(\text{CH}_3)_3]_3$ [17] are not active at all.

4. Conclusion

Electrochemical reactions take place between the solid electrode and solution phase. All processes in the first two cases take place in solutions, there is no apparent role played by the modification of the electrode [10]. Yet, the constraints of the boundary domain of the diffuse layer, the affiliated processes occurring on the liquid side, provides intriguing conditions for low potential electrolysis. It is our aim to consider known properties of diffuse layers and concentration excess and their possible influence on or as catalysts. This is done through examination of reaction rates and products. The direct measurement of specific effects in such complicated solutions and their relation to the outcome is yet incomplete, though the principles of electrodic processes are well known. Enforced potential, especially low potentials, is an additional parameter which will induce significant effects on reactivity and selectivity not available otherwise.

The boundary zone created by reduced overpotentials provides a complicated balance between parameters of heterogeneous and homogeneous control. It is noted that low overpoten-

tials rather than high values may have interesting practical value besides their being especially important for reactions in organic solvents, as they facilitate improved energy balance, selectivity, safety and reduced corrosion.

Acknowledgements

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