A MICROELECTRODE STUDY OF AROMATIC NUCLEOPHILIC SUBSTITUTION

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Summary: Results of an investigation of electrochemically catalysed nucleophilic substitution of 4-bromobenzophenone in the presence of phenoxide ions, as nucleophile, are reported. The data obtained are analysed by comparing the limiting currents of the reduction waves in the presence and in the absence of the nucleophile, and a value of 1.9 x 10^5 M^{-1} s^{-1} was obtained for the rate constant of the substitution reaction.

Nucleophilic aromatic substitutions catalysed by electron injection, i.e., reactions occuring by an $S_{RN}1$ mechanism (1), can be induced in various manners of injecting electrons: photochemically (2), electrochemically (3), by solvated electrons from alkali metals dissolved in liquid ammonia (2), or by other electron-transferring reagents (4).

Several examples of electrochemically induced aromatic nucleophilic substitution reactions in organic solvents have been reported (5) which confirms that a large variety of nucleophiles react with aromatic substrates in $S_{RN}1$ processes.

However, the reaction is indeed enough complex because some side reactions can occur which compete with the substitution process (3).

In this paper we present the results obtained in the study of the nucleophilic substitution of 4-bromobenzophenone by phenoxide ions as

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nucleophile, in N,N-dimethylformamide, at gold microdiscs of different radii.

The voltammograms of Br-$C_6H_4COC_6H_5$ in 0.1 M TBAB/DMF in the absence of $C_6H_5O^-N^+(CH_3)_4$, show two very close successive waves, as shown in figure 1.

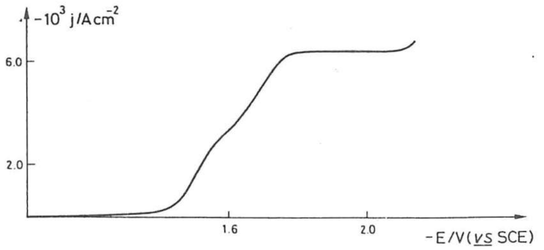

Figure 1 - I-E curve for a solution of 1.5 mmol dm^{-3} *p*-Br-$C_6H_5COC_6H_5$ in 0.1 mol dm^{-3} Bu_4NBF_4/DMF.

The first wave, probably, corresponds to the electron transfer to the substrate, ArX, featuring the reaction sequence:

$$ArX + e^- \rightleftharpoons ArX^{\cdot -}$$

$$ArX^{\cdot -} \xrightarrow{k_1} Ar^{\cdot} + X^-$$

$$Ar^{\cdot} + e^- \longrightarrow Ar^-$$

or:

$$Ar^{\cdot} + ArX^{\cdot -} \longrightarrow Ar^- + ArX$$

$$Ar^- + \text{proton source} \longrightarrow ArH$$

although the aryl radical, Ar·, is well known to be able to abstract an hydrogen atom from the solvent:

$$Ar^{\cdot} + SH \xrightarrow{k_3} ArH + S^{\cdot}$$

which may explain the experimental observation that the ArX reduction wave seems to involve the exchange of less than two electrons per molecule. This feature is still under investigation.

The second wave probably corresponds to the exchange of another electron per molecule. It features the reduction of benzophenone, ArH, formed at the first wave, into its anion radical:

$$ArH + e^- \rightleftharpoons ArH^{\cdot -}$$

Upon addition of phenoxide ions, we observed that the height of the two waves of bromobenzophenone decrease and a new wave appears at more negative potential which probably corresponds to the reduction of the substituted product (figure 2).

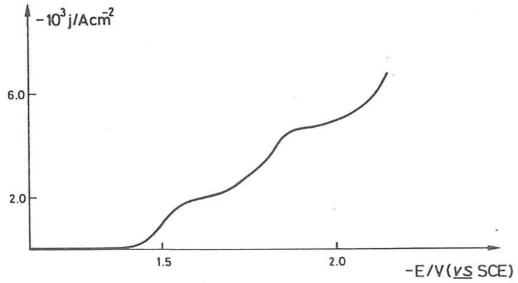

Figure 2 - I-E curve for a solution of 1.5 mmol dm^{-3} *p*-Br-$C_6H_5COC_6H_5$, 0.6 mmol dm^{-3} $C_6H_5O^-N^+(CH_3)_4$ in 0.1 mol dm^{-3} Bu_4NBF_4/DMF.

The extent of the substitution increases when raising the nucleophile concentration, for a given substrate concentration, as it is shown in the table 1.

TABLE 1

Data obtained in the aromatic nucleophilic substitution of bromobenzophenone.

10^4 d / cm (WE = Au)	1.5 mM $BrC_6H_5COC_6H_5$ 0.075 M $C_6H_5O^-N^+(CH_3)_4$ 0.1 M TBAB DMF			1.5 mM $BrC_6H_5COC_6H_5$ 0.15 M $C_6H_5O^-N^+(CH_3)_4$ 0.1 M TBAB DMF			1.5 mM $BrC_6H_5COC_6H_5$ 0.3 M $C_6H_5O^-N^+(CH_3)_4$ 0.1 M TBAB DMF		
	$10^9 i_d$ / A	$10^9 i_c$ / A	i_c / i_d	$10^9 i_d$ / A	$10^9 i_c$ / A	i_c / i_d	$10^9 i_d$ / A	$10^9 i_c$ / A	i_c / i_d
10	2.6	1.8	0.69	2.6	1.6	0.62	2.2	1.2	0.55
25	6.4	4.5	0.70	6.4	4.1	0.64	5.4	3.0	0.56
60	19	14	0.73	19	12	0.63	16	8.8	0.55

i_d - diffusion wave current of the substrate in the absence of nucleophile
i_c - diffusion wave current of the substrate in the presence of nucleophile
i_c / i_d - current function

From the data in table 1 we can also observe that the current function (i_c/i_d) is independent of the radius of the microelectrode. This fact, together with low efficiency of the substitution process (as one can see through the values of the current function which do not decrease down to zero) lead us to conclude that probably there is a competition between the nucleophilic attack and electron transfer from the electrode to the aryl radical, or H-atom transfer.

Thus, the mechanism that we assume is:

$$ArX + e^- \rightleftharpoons ArX^{\cdot -}$$

$$ArX^{\cdot -} \xrightarrow{k_1} Ar\cdot + X^-$$

$$Ar\cdot + Nu^- \xrightarrow{k_2} ArNu^{\cdot -}$$
$$ArNu^{\cdot -} - e^- \rightleftharpoons ArNu$$

and / or

$$ArNu^{\cdot -} + ArX \rightleftharpoons ArX^{\cdot -} + ArNu$$

although a competing reaction occurs which is the reduction of Ar· at the electrode:

$$Ar\cdot + e^- \longrightarrow Ar^-$$

Ar^- is then finally converted into ArH by proton abstration from the solvent in the absence of added water:

$$Ar^- + SH \longrightarrow ArH + S^-$$

Another competing reaction that may occur is the H-atom abstraction from the solvent by Ar·:

$$Ar\cdot + SH \xrightarrow{k_3} ArH + S\cdot$$

with further electron transfer to S· leading to S^-.

In the situation where there is ECE/$S_{RN}1$ competition, the height of the substrate wave must vary with the phenoxide concentration according to the following equation:

$$(i_d/i_c) - 1 = (k_2/k_1)^{1/2} ([Nu^-])^{1/2} \qquad (1)$$

where:

k_2 - second-order rate constant of the nucleophilic substitution
k_1 - rate constant for the cleavage of the initial anion radical, $ArX^{\cdot -}$

But if there is ECH/$S_{RN}1$ competition the height of the substrate wave must vary with [Nu^-], according to :

$$(i_d/i_c) - 1 = (k_2/k_3) ([Nu^-]) \qquad (2)$$

However, a poor agreement was obtained with the equation (2) since in the corresponding plot does not give a zero intercept. This fact leads to the discarding an ECH/$S_{RN}1$ competition.

On the other hand, the plot of the parameter, $(i_d/i_c) - 1$, against the square root of the nucleophile concentration gives a straight line which passes through the origin, as it is shown in the figure 3.

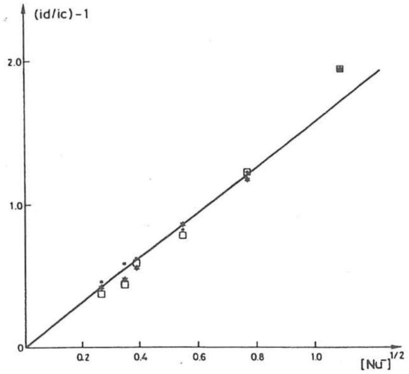

Figure 3 - A plot of the parameter $(i_d/i_c) - 1$ as a function of the square root of the nucleophile concentration.

The value of the rate constant of the substitution reaction, k_2, can be obtained from the slope of the straight line. Thus, using the value of k_1 found in the literature and equal to 8×10^4 s^{-1}, it is found that $k_2 = 1.9 \times 10^5$ M^{-1} s^{-1}.

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ELECTROCATALYTIC BEHAVIOUR OF DIFFERENT SUBSTRATES FOR THE ELECTROOXIDATION OF DMAB IN ELECTROLESS METAL DEPOSITION

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ABSTRACT - The electrooxidation of dimethylmineborane (DMAB) on specpure and electrolytic Ni and Co in succinate containing solutions of slightly acid pH has been studied by cyclic voltammetry and potential time measurements. The results have shown differences in electroactivity which can be related with surface morphologies. The study has been extended to electroless Ni-B and Co-B substrates and the electrocatalytic properties of the alloys compared to those of pure metals.

INTRODUCTION

It is usual practice to evaluate the conditions for electroless metal deposition (EMD) by the measurement of the potential evolution with time of a given substrate in the electroless solution [1]. Therefore, the substrate catalytic activity can be referred to its ability to reach the stable EMD potential. Being this critical potential closely related with the behaviour of the system substrate/reducing agent [2], the evaluation of the relative catalytic activity of different substrates can be carried out in metal ions free media.

Extensive investigation on suitable experimental conditions (presence of complexants, pH, temperature) for electroless Nickel and Cobalt deposition, using dimethylamineborane (DMAB) as reductant, was recently reported [3]. The aim of this work is to present the influence of substrate morphology on the first stages of the deposition. Considering that the process evolution is determined by the deposited first layers, the electrooxidation of DMAB on Ni-B and on Co-B is also investigated.

EXPERIMENTAL

Cyclic voltammetry and potential time measurements were carried out in adequate electrochemical cells with specpure and electrolytic metals, electroless Ni-B and Co-B working electrodes. The counter electrode was a platinum foil and electrode potentials were controlled with respect to a saturated calomel electrode by EG & G potentiostat/galvanostat model 273. Rotating electrode experiments were performed with a RDE EG & G model 616. The results were collected with a XY-t recorder.

The solutions were prepared with Analar grade reagents and de-ionised bidestilled water and specpure substrates were polished to a mirror finishing before each experiment. All measurements