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PREPARATIVE USE OF ELECTRODE CATALYZED SUBSTITUTION REACTIONS; SYNTHESIS OF $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)COCH_3$

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Summary

It is shown that electrode catalysis of substitution reactions can operate even for systems with rather slow chemical steps and, furthermore, for those which are electrochemically irreversible. A procedure is described for synthesis of $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)COCH_3$ from $Fe(CO)_2(\eta^5\text{-}C_5H_5)CH_3$ and triphenylphosphine. A simplified mechanism for the catalytic chain, is given and discussed in terms of the structure of the reacting species.

Introduction

Products of electrochemical (or chemical, in general) oxidation or reduction quite frequently undergo subsequent chemical reactions. The redox orbital concept [1] rationalizes this behaviour in terms of the tendency of the molecule to compensate for the change of electronic distribution caused by the redox process.

Generally, any process which causes the number of electrons in (M–L) π- or σ-antibonding orbital to increase or that in (M–L) π- or σ-bonding orbitals to decrease labilizes the coordination sphere. Induced electron shifts or strong intramolecular interactions could exert the same labilizing influence [2]. This redox labilization might be such that after the redox process the molecule becomes intrinsically unstable and decomposes spontaneously. In most cases, however, the labilized primary product is stable unless there is a specific substance (X) present in the solution capable of reacting with it. This general principle can be used to tailor the final product of the electrode, or redox, reaction by the appropriate choice of X [3].

Electrode Catalyzed Substitution Reactions (ECSR)

A special case arises when the substitution following the electrode reaction (A → B) results in the formation of a species (C) which is a stronger reducing (or

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oxidizing) agent than the primary product B. Species C thus formed has to react at the electrode or with the original depolarizer A to give the final product D which is in the same oxidation state as A. These processes are in principle substitution reactions catalyzed by the electrode reaction, and can be described by the following set of equations:

$$A \underset{n_1}{\overset{E_1^0}{\leftrightarrow}} B \qquad (1)$$

$$B + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \qquad (2)$$

$$D \underset{n_2}{\overset{E_2^0}{\leftrightarrow}} C \qquad (3)$$

$$A + C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D + B \qquad (4)$$

For this sequence of reactions to operate, the condition $E_1^0 > E_2^0$ must hold (when reaction $A \rightarrow B$ is a reduction).

Electrode reactions involving this mechanism have been described for several systems [4–15]. Nucleophilic substitution reactions of organic compounds have been reviewed by Saveant [10]. However, not in all cases was the full sequence of reactions 1 to 4 taken into account (reaction 4 tends often to be neglected) and systematic consideration of the influence of relative rates of reactions 2 and 4 is lacking. Feldberg [7] analyzed this mechanism for two extreme situations (reaction 4 very fast and non-operative, respectively) assuming both electrode reactions, 1 and 3 to be fast and reversible. This latter assumption was also made by most of the other authors.

A detailed analysis of the set of reactions 1–4 points to the conclusion that the rate of reaction 2 relative to the rate of diffusion and/or rate of changing the potential of the electrode is one of the most important factors governing the mechanism. For low values of k_1 (or $k_1 \rightarrow 0$) only process 1 is observed when cyclic voltammetry or dc polarography is used. On the other hand, for $k_1 \rightarrow \infty$ the behaviour observed mimics that of simple D/C redox couple, even if the mechanism of the reaction is rather complex.

Our analysis shows that the influence of k_1 becomes even more pronounced when coulometric conditions (i.e. electrolysis at constant potential) are used. Under these conditions the electrochemical catalysis of substitution reactions operates even for values of k_1 which make it impossible to observe the catalytic nature of the process in dc polarography or cyclic voltammetry. The range of applicability of ECSR is thus greatly increased, and ECSR can be used as a very convenient preparative method.

The use of coulometric conditions not only extends the range to systems with low values of k_1 but also to those with low values of k_2, or even to those in which the electrode reaction 3 is electrochemically irrreversible or non-operative.

For all possible combinations of rates of chemical or electrochemical reactions in the sequence 1–4 the overall charge exchanged at the electrode for the total electrolytic conversion of A into D (Faraday mol^{-1}, n_{app}) approaches zero (assuming $n_1 = n_2$) in ideal case, i.e. the electrode functions as a catalyst without any net exchange of overall charge. In most cases an electrolytic pulse generating a kinetically significant concentration of B (or C) is sufficient to trigger the sequence of reactions leading from A to D. However, for $k_2 \rightarrow 0$ the electrode has to be kept under potential $E_a < E_1^0$ to ensure the conversion of C into D via electrode reaction 3.

The electrolytic generating pulse triggers the catalyzed reaction also for systems for which reaction 1 requires high overvoltage (i.e. ${}_1E_{1/2} < {}_2E_{1/2}$, assuming of course $E_1^0 > E_2^0$) if reaction 4 is fast enough to maintain the propagation of the catalytic chain). In the rare case with $k_2 \rightarrow 0$ and highly irreversible oxidation of C into D at the electrode, a more sophisticated mode of polarization of electrode, pulsing between potentials $E_a < E_1^0$ and $E_b > {}_2E_{1/2}$ (due to irreversibility, ${}_2E_{1/2} > E_2^0$) is necessary. However, even in this special case n_{app} measured coulometrically should approach zero for total conversion of A into D.

In the present paper we report the preparative use of ECSR for a system in which the electrode reaction 3 is fully irreversible, i.e. C cannot be oxidized at the electrode at all, and, the propagation of the catalytic chain of reactions is maintained by reaction 4 only.

Experimental

The general experimental procedure and equipment for polarographic, cyclic voltammetric and coulometric measurements as well as the methods for identification of products was described previously [16].

Chemicals. $Fe(CO)_2(\eta^5\text{-}C_5H_5)CH_3$ was prepared according to ref. 17. $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)COCH_3$ was prepared using the procedure described in ref. 18. Bu_4NPF_6 was a Fluka product dried over P_2O_5 in vacuo at 80°C. PPh_3 was a Merck product, used directly.

Electrolytic procedure. 25 ml of THF solution 0.1 *M* in Bu_4NPF_6, 0.01 *M* in $Fe(CO)_2(\eta^5\text{-}C_5H_5)CH_3$ and 0.03 *M* in PPh_3 was electrolyzed (for the cell arrangement see [16]) in an argon atmosphere using a potentiostatically controlled potential − 1.80 V (SCE) and coulometric measurement of the charge passed through the cell. After about 60 min the conversion was complete. The solution was reduced by vacuum distillation to about one half the original volume and diluted with benzene (1/3). After standing for about 1 h the precipitated base electrolyte was filtered off and the solution evaporated the dryness in vacuo. The solid material was extracted with dichloromethane and the resulting solution treated as described in ref. 18. The product was shown by analysis and spectroscopy to be identical with $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)COCH_3$ obtained as described in ref. 18. The yield of the solid material was averaged 85%.

Results and discussion

As we have shown in a detailed study of the electrochemical behaviour of compounds of the type $Fe(CO)_2(\eta^5\text{-}C_5H_5)X$ [16,19], the mechanism of the electrode processes of these compounds is rather complicated and involves several intermediates. A similar situation is now found in the case of $Fe(CO)_2(\eta^5\text{-}C_5H_5)CH_3$.

In the course of the investigation of the fate of the anion-radical formed by a one-electron reduction of the latter methyl compound, we have established that the coordination sphere of the complex becomes highly labilized in the one-electron reduction product [20]. This led to the idea of inducing a tailored substitution by trapping the primary product of the one-electron reduction with a suitable reagent. Phosphine was selected as the most appropriate. It is known that introduction of a phosphine ligand into the coordination sphere instead of CO results in the shift of the reduction potential towards more negative potentials [2], so that the mechanism depicted by eq. 1 to 4 could be expected, i.e. an electrolytically catalyzed substitution reaction should operate.

$Fe(CO)_2(\eta^5\text{-}C_5H_5)CH_3$ in THF at DME gives two reduction steps with ${}_1E_{1/2}$ -1.90 V and ${}_2E_{1/2}$ -2.31 V (SCE). The first wave is partly obscured by a maximum. The overall current corresponds to a two electron, diffusion controlled process. Both reduction steps are electrochemically as well as chemically irreversible. If triphenyl phosphine is added to the solution there is no observable change in the dc-polarographic or cyclic voltammetric picture nor any time change in the polarographic picture, indicating that under these conditions no reaction takes place at the electrode or in the bulk of the solution.

The large scale electrolysis, on the other hand, reveals substantial changes in the nature of the products when the potential is kept more positive (at -1.8 V) than ${}_1E_{1/2}$. The infrared spectra of the electrolyzed solution and isolation of the product of electrolysis have shown that under these conditions the final product is solely $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)COCH_3$. In the solution the electrochemical conversion of the methyl compound into the latter product is complete, without any detectable side products, provided the electrode is kept at the given potential without interruption throughout the whole procedure. The coulometric measurements show that for the total conversion only 0.15–0.2 Faraday mol^{-1} are needed. The process described thus fulfils the conditions for ECSR as analyzed above. The fact that the ECSR is observed only under coulometric conditions points to the conclusion that both reaction 2 and 4 are rather slow. No attempt has been made to measure the rate constants of these processes.

The system investigated has, however, some other features which distinguish it from those in which the ECSR mechanism has been established previously:

(i) $Fe(CO)_2(\eta^5\text{-}C_5H_5)CH_3$ (corresponding to A in eq. 1) is reduced irreversibly, the corresponding product (i.e. B) being not oxidizable at potentials near to ${}_1E_{1/2}$ [20]. It is, noteworthy, however, that this reaction shows partial chemical reversibility, i.e. the intermediate of one-electron reduction of $Fe(CO)_2(\eta^5\text{-}C_5H_5)CH_3$ in absence of phosphine can be converted into the original compound by chemical oxidation, e.g. with oxygen.

(ii) $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)COCH_3$ (i.e. D in eq. 3) is reduced in a double wave similar to that of the methyl derivative with reduction potentials only slightly shifted towards more negative potentials, ${}_1E_{1/2}$ -1.95, ${}_2E_{1/2}$ -2.39 V (SCE).

(iii) The one-electron reduction product of $Fe(CO)(PPh_3)_3(\eta^5\text{-}C_5H_5)COCH_3$ is not oxidizable electrochemically, as was shown by cyclic voltammetry or Kalousek commutator.

From these facts it follows firstly that the preparative electrolysis has to be triggered by setting the potential of the electrode at a value at which the reduction of the final product (D) is negligible (-1.8 V was chosen) and, secondly, that the catalytic sequence is carried by reaction 4 only. This means a short electrolytic pulse should be sufficient to carry the reaction to completion. A typical run is shown in

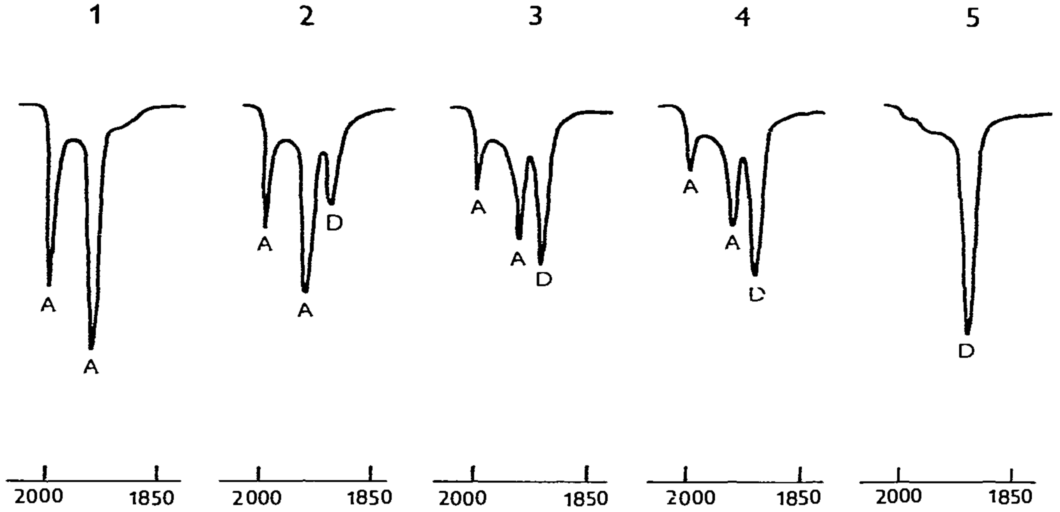
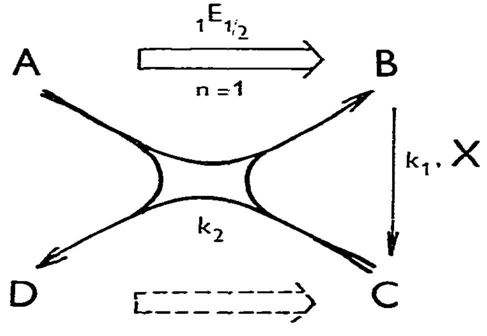


Fig. 1. Progress of electrode catalyzed formation of Fe(CO)(PPh$_3$)(η^5-C$_5$H$_5$)COCH$_3$ as monitored by IR spectra: (1) 0.01 *M* Fe(CO)$_2$(η^5-C$_5$H$_5$)CH$_3$, 0.03 *M* PPh$_3$, 0.1 *M* Bu$_4$NPF$_6$ in THF; (2) After partial reduction (n_{app} 0.05 F mol^{-1}); (3) Solution (2) 5 min after interruption of electrolysis; (4) Solution (2) 25 min after interruption of electrolysis; (5) Complete conversion (n_{app} 0.15 F mol^{-1}); A-CO-bands of Fe(CO)$_2$(η^5-C$_5$H$_5$)CH$_3$; D-CO band of Fe(CO)(PPh$_3$)(η^5-C$_5$H$_5$)COCH$_3$.

Fig. 1, and it will be seen that a small fraction of charge causes a considerable conversion and the reaction continues after interruption of the polarization of the electrode. However, after few minutes the reaction stops and can be triggered again



A : Fe(CO)$_2$(η^5-C$_5$H$_5$)CH$_3$
B : Fe(CO)$_2$(η^5-C$_5$H$_5$)CH$_3^{\cdot-}$
C : Fe(CO)PPh$_3$(η^5-C$_5$H$_5$)COCH$_3^{\cdot-}$
D : Fe(CO)PPh$_3$(η^5-C$_5$H$_5$)COCH$_3$
X : PPh$_3$

Fig. 2. Scheme for electrode catalyzed conversion of Fe(CO)$_2$(η^5-C$_5$H$_5$)CH$_3$ into Fe(CO)(PPh$_3$)(η^5-C$_5$H$_5$)COCH$_3$.

only by a repeated electrolytic pulse. Detailed investigation of this phenomenon has shown that it is connected with the presence of impurities, traces of oxygen, proton-donors, etc., which consume in side reactions or chemical back reaction of B into A, see above, the intermediates (i.e. B and C) and stop thus the catalytic chain. The overall charge consumed is thus not used to carry on the catalytic cycle but to protect it by removing traces of impurities or products of chemical back or side reactions.

From the results described and known mechanism of reduction of $Fe(CO)_2(\eta^5\text{-}C_5H_5)CH_3$ [20] it can be concluded that the observed process follows the mechanism in which the main steps are described in Fig. 2.

Reaction B → C in Fig. 2 is obviously a complex process which can be rationalized in a simplified way as described below.

As was shown for compounds of the type $Fe(CO)_2(\eta^5\text{-}C_5H_5)X$ [16,19,21] the reduction proceeds in such a way that the first electron is accepted into a *d*-orbital which is involved in the σ-system, i.e. reduction results in an increase of electron density in σ-antibonding orbitals. This process results in the labilization of the coordination sphere and eventually in a subsequent fragmentation of the compounds. The mechanism of this process, which tends to compensate for the unfavourable change in electronic density, depends strongly on the possible mechanism of stabilization of the fragments. For $X = CH_3$, when no electrophiles are present which could trap the methyl group, an intramolecular process takes place within the one-electron reduction product. As a result a $COCH_3$-group is formed, and one coordination site would become vacant. This site is occupied by phosphine, the ligation of which stabilizes the coordination sphere.

$Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)(COCH_3)$ has been previously prepared by thermal reaction [18,22] and was shown also to be formed in a photochemical reaction (see [23] and references therein). The thermal reaction is complicated by a subsequent decarbonylation at elevated temperatures. The photochemical reaction is not a simple process, and there has been some dispute about it. Our preliminary photochemical experiments, carried out in tetrahydrofuran, have revealed the formation of the acetyl compound, but with several other by-products in substantial amounts. For the synthesis of $Fe(CO)(PPh_3)(\eta^5\text{-}C_5H_5)(COCH_3)$ the electrocatalyzed substitution seems to be the most satisfactory procedure, giving high yields without any by-products.

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