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Cobalt(salen)-Electrocatalyzed Conversion of Benzotrichloride Into Tolane. A Triply Catalytic and Overall Quintuple Electrochemical Transformation

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Abstract: Electrochemical reduction of a mixture of cobalt(II)(salen) and benzotrichloride (**4**) results in transformation of **4** successively into 1,1,2,2-tetrachloro-1,2-diphenylethane, 1,2-dichlorostilbene, diphenylacetylene, stilbene, and bibenzyl. The first three reactions are electrocatalyzed by the cobalt complex; the last two are direct reductions.

We reported earlier that reduction of cobalt(II)(salen)[1] in the presence of benzal chloride (**1**) results in electrocatalytic conversion of **1** into a mixture of *cis*- and *trans*-stilbenes.[2-4] The initial electrochemical event is reduction of the cobalt complex to a highly reactive Co(I) species, which then undergoes rapid oxidative insertion into a carbon-chloride bond of **1**. The product of this reaction, an alkylcobalt(III) species, is reducible at the potential at which it is formed. This initiates a complex reaction cascade resulting in formation of 1,2-dichloro-1,2-diphenylethane (**2**) followed by a second oxidative insertion by Co(I) and, ultimately, stilbenes (**3**).[2-4] The novel feature of the transformation of **1** into **3** is the fact that in the course of this reaction sequence Co(salen) catalyzes two distinct processes, conversion of **1** into **2** and **2** into **3**. For this reason we called the overall process a "doubly catalytic" electrode process. We later observed other doubly catalytic processes in a study of the nickel(salen)-electrocatalyzed reduction of **1**.[5] We were intrigued by the general concept of multiply electrocatalytic processes, since they have the potential for effecting deep-seated transformations of organic substrates. We wish to report an example of a triply electrocatalytic chemical transformation, which has the further feature that the product undergoes two successive further (uncatalyzed) electrochemical reductions, resulting in an overall quintuple electrochemical transformation.

Co(II)(salen) exhibits a reversible wave at –1.72 V (*vs.* Ag/0.1 M $AgNO_3$) in acetonitrile (AN)/0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP). Benzotrichloride (**4**) is not reduced before –2.2 V, hence it is possible to reduce the metal complex selectively in the presence of **4**. Addition of a small amount (35 mol %) of **4** to a solution of Co(II)(salen) results in formation of two voltammetric prewaves at –1.5 and –1.6V. Appearance of the voltammetric prewave at –1.5 V is diagnostic behavior for rapid reaction between Co(I)(salen) and **4**,[3] and in fact Rusling has shown[6] that the rate of reaction between Co(I)(salen) and benzyl bromide is *ca.* 3×10^7 M^{-1} s^{-1} in DMF; that of **4** is unlikely to be much less than 10^5 M^{-1} s^{-1}, even after factoring in the presumably lower reactivity of **4** toward nucleophilic attack by agents such as Co(I)(salen). The prewave at –1.6 V is presumably associated with electrocatalytic reduction of the initial product of the electrocatalytic process (*vide infra*). Controlled-potential electrolysis of a solution of **4** in AN/0.1 M TBAHFP containing 50 mol % of Co(II)(salen) was carried out at – 1.8 V and the solution composition was sampled and analyzed by gas chromatography periodically throughout the electrolysis. The results of these analyses are shown in Figure 1. As **4** disappeared, a new substance, identified as 1,1,2,2-tetrachloro-1,2-diphenylethane (**5**) by comparison with an authentic sample, appeared in the solution. However, **5** never accumulated in substantial amounts. Shortly after it began to be formed, two new components (in a ratio of ca 3:1) appeared. These were identified as E- and Z-1,2-dichlorostilbenes (**6**), again by comparison with authentic samples prepared as described below. The relative proportion of **6** in the medium reached a maximum of about 77% after about 2400 coulombs (about two equivalents) of current had passed. After this point, **6** gradually disappeared and diphenylacetylene (**7**) was produced. From these data one may conclude that the relative order of reactivity of the three halides toward Co(I)(salen) is **5** > **4** > **6**.

Tetrachloride **5** could be prepared by exhaustive chlorination of **7** in chloroform at 0° C.[7] In our hands, this afforded **5** in higher yield than did the radical-catalyzed coupling of **1**.[8,9] **5** exhibits a very broad voltammetric wave centered at –1.6 V but beginning as early as –1.3 V (suggesting a low heterogeneous electron transfer rate constant), as well as a second wave at –2.13 V. Addition of small amounts (less than equivalent) of **5** to a 2 mM solution of Co(salen) resulted in appearance of a new voltammetric prewave at –1.62 V; as above, this is evidence for a rapid reaction between Co(I)(salen) and **5**. Indeed, electrolysis of a mixture of **5** and Co(salen) (15 mol %) at –1.8 V resulted in conversion to **7** in high yield after passage of the calculated amount of current; slow conversion of **7** to **3** and **8** then began. Electrolysis of **5** at –1.6 V, either with or without added catalyst, afforded **6** in quantitative yield.

Although the dichlorides **6** could be prepared independently by incomplete chlorination of **7** or the action of zinc on **5**,[8] we found that the best way to prepare them is by electrolytic reduction of **5** at –1.6 V as mentioned above. We were unable to separate the stereoisomers of **6** by flash chromatography, so all subsequent experiments were carried out on a mixture of the two. **6** exhibits a well-formed voltammetric wave with $E_p = -2.1$ V. Addition of small amounts (again, less than equivalent) of **6** to a solution of Co(salen) did ***not*** produce a voltammetric prewave, but the voltammogram of equimolar solution of the two did exhibit a substantial increase in the height of the Co(II)(salen) wave and a much smaller wave for **6** at –2.1 V. This demonstrates that Co(salen) does electrocatalyze the reduction of **6**, although the rate of reaction of Co(I)(salen) with **6** is not as high as that of **4** or **5**. This is consistent with the results of the preparative electrolysis and is understandable; benzylic halides tend to react facilely with Co(I) reagents by an S_N2 path[10,11] which should be slow with **6**; presumably it reacts by an alternate path involving electron transfer.[10,11]

Scheme I

First catalytic cycle:

$$\underset{\mathbf{4}}{C_6H_5CCl_3} + e^- \xrightarrow{\text{Co(salen)}} 0.5\ \underset{\mathbf{5}}{C_6H_5CCl_2CCl_2C_6H_5} + Cl^-$$

Second catalytic cycle:

$$0.5\ \mathbf{5} + e^- \xrightarrow{\text{Co(salen)}} 0.5\ \underset{\mathbf{6}}{C_6H_5CCl{=}CClC_6H_5} + Cl^-$$

Third catalytic cycle:

$$0.5\ \mathbf{6} + e^- \xrightarrow{\text{Co(salen)}} 0.5\ \underset{\mathbf{7}}{C_6H_5C{\equiv}CC_6H_5} + Cl^-$$

Scheme I, which is based on our previously established mechanism for the conversion of **1** to **3**,[2-4] summarizes the main reaction sequence. [Because of space considerations we do not show the individual steps in each catalytic cycle, but we have done so at length elsewhere for benzal chloride (**1**).[3,4]] In addition to substances **4** through **7**, the sampling process identified benzal chloride (**1**) as a component of the solution during electrolysis. This substance appeared early in the electrolysis, reached a maximum of 9% at about 1500-1800 coulombs and slowly disappeared thereafter. It is apparently formed by hydrogen atom or proton abstraction from the solvent by the α-chlorobenzyl radical or its carbanion counterpart.[4] We have shown previously that **1** undergoes catalytic conversion into **3**, and indeed **3** can be seen to appear at low levels in the solution *before* the formation of **7**, the other precursor of **3**.

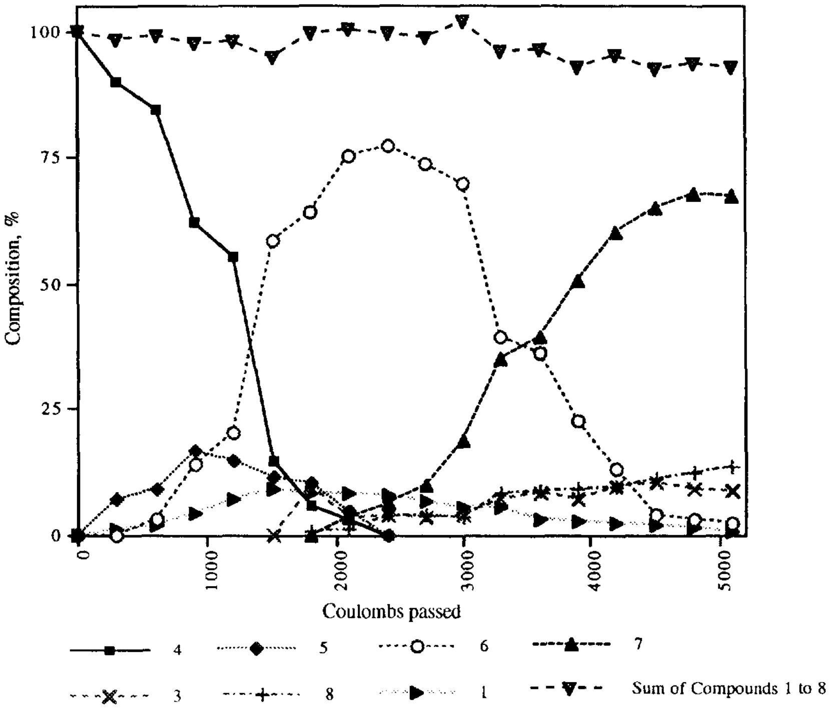

Figure 1. Electrolysis Composition as a Function of Time

The yield of **7** reaches a maximum of about 67 % after about 4800 coulombs, after which it begins to drop and stilbenes (**3**) are formed. These are then transformed into bibenzyl (**8**). The initial stages of the conversion of **7** into **3** and then **3** into **8**, a known process,[12,13] are shown in Fig. 1. We found by independent experiments that this conversion occurs at the same rate in the absence or presence of Co(salen). The overall conversion of **4** into **8** (Eqs. 1 and 2) may therefore be recognized as involving five distinct electrode reactions (**4** → **5** → **6** → **7** → **3** → **8**), each of which consumes 1 e$^-$ per molecule of **4** .

$$3\,e^- + \underset{\mathbf{4}}{C_6H_5CCl_3} \longrightarrow 0.5\ \underset{\mathbf{7}}{C_6H_5C{\equiv}CC_6H_5} + 3\,Cl^- \qquad (1)$$

$$2\,e^- + 0.5\ \mathbf{7} + 2\,H^+ \longrightarrow 0.5\ \underset{\mathbf{8}}{C_6H_5CH_2CH_2C_6H_5} \qquad (2)$$

Reduction of **7** to **8** consumes four protons per molecule of **7**. These are apparently supplied by Hoffmann elimination by an anionic intermediate on the supporting electrolyte, a tetrabutylammonium salt. Tributylamine can be detected in the solution in the latter stages of electrolysis in quantities consistent with this conjecture. More to the point, the electrical resistance of the solution increases late in the electrolysis because of this destruction of the supporting electrolyte. For this reason, electrolyses were generally not carried out to complete formation of **8**. The experiment carried out to the greatest degree of completion consisted of a roughly 50:50 mixture of **3** and **8**.

The conversion of **4** into **7** occurs with good, but less than 100 % current efficiency. For example, to completely destroy **4**, **5**, and **6**, the electrolysis run represented by Fig. 1 should have consumed 3,648 coulombs for the 5.4 mmol of Co(salen) and 10.8 mmol of **4** employed, but it can be seen that after this amount of current had passed, some **6** still remained (although some of the current required for conversion of **6** into **7** had actually already been consumed for the reduction of **7** to **3** and **8**). Likewise, at the point at which the most extensive electrolysis experiment (see preceding paragraph) was stopped, 5,676 coulombs had passed; 5,211 coulombs would theoretically have been required to produce the observed 50:50 mixture of **3** and **8**.

Finally, the top line in Fig. 1 shows the total amounts of components **4**, **5**, **6**, **7**, **3**, **8**, and **1** throughout the electrolysis. This total remains between 93 and 99 % throughout the experiment, demonstrating that Scheme I and Equations (1) and (2) account for the major reaction pathways in this system.

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