Electroprotic reactions

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Abstract. Reactions involving the coupled transfer of electrons and protons are called electroprotic reactions. In this article we briefly describe some of our experiences with electroprotic reaction as a tool for executing interesting chemical transformations.

Keywords. Electroprotic reactions; two-electron transfer; isomerisation; proton switch; organic refunctionalisation.

1. Introduction

The reaction below represents a general electroprotic transformation (Ghosh and Chakravorty 1984; Chakravorty 1985)

$$A + ne + mH^+ \rightleftharpoons H_m A^{(m-n)+}. \tag{1}$$

Here n electrons and m protons are transferred to molecule A in a "concerted" or "coupled" manner. In this article we present a few instances where electroprotic reactions lead to interesting chemistry.

2. One-step 2e transfer

The $m = 0$ case of (1) corresponds to pure electron transfer which usually occurs in discrete one-electron steps. In the presence of proton transfer, say $m = n = 2$, the process of (1) could proceed as a single step particularly under low pH conditions (figure 1). The physical basis for this is the proton-affinity order $A^{2-} > A^- > A$.

A good example of this situation is shown in figure 2 (Goswami *et al* 1982). Here the two-electron step is realised in the pH-range 1–4 (py = pyridine). The formal potential of the two-electron couple (figure 2) is 1·20 V vs s.c.e. and the cyclic voltammetric peak-to-peak separation is 30 mV as expected for two-electron transfer. The two-electron oxidation process can be chemically brought about by Ce(IV). The $Ru^{IV}O$ complex is a rare species that is able to oxidise water to oxygen.

3. A proton switch

In some cases a sluggish proton can control the flow of electrons in one direction. A case is provided by the strongly antiferromagnetic ($S = 1/2$) trinuclear copper(II)
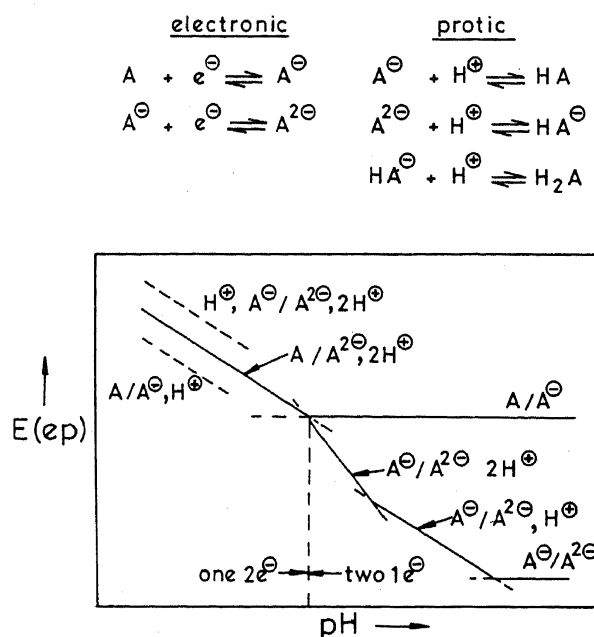
electronic   protic

$A + e^{\ominus} \rightleftharpoons A^{\ominus}$ $A^{\ominus} + H^{\oplus} \rightleftharpoons HA$

$A^{\ominus} + e^{\ominus} \rightleftharpoons A^{2\ominus}$ $A^{2\ominus} + H^{\oplus} \rightleftharpoons HA^{\ominus}$

$HA^{\ominus} + H^{\oplus} \rightleftharpoons H_2A$

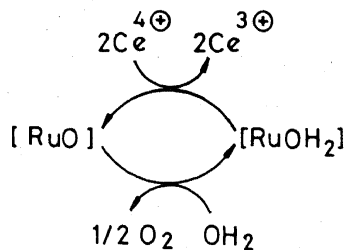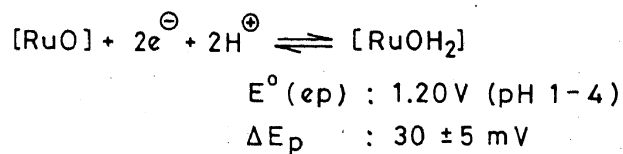**Figure 1.** Plot of observed potential vs pH for the electroprotic reaction having $m = n = 2$; the single-step two-electron process starts at the top of the vertical dotted line.
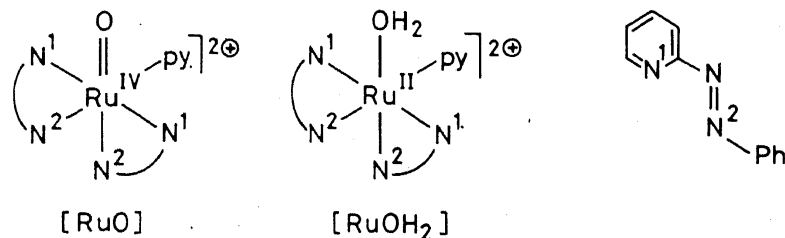
[RuO]   [RuOH$_2$]

$[RuO] + 2e^{\ominus} + 2H^{\oplus} \rightleftharpoons [RuOH_2]$

$$E^{0}(ep) : 1.20\,V \ (pH \ 1-4)$$
$$\Delta E_p \quad : 30 \pm 5\,mV$$

Figure 2. A single-step two-electron electroprotic reaction of a ruthenium complex and water oxidation by the oxidised complex.

*iso*nitrosoketonates (Beckett and Hoskins 1972; Baral and Chakravorty 1980; Butcher *et al* 1981; Gross *et al* 1991).

The results are depicted in figure 3. The X=O species display a reversible $Cu^{III}Cu_2^{II}/$ Cu_3^{II} couple in MeCN and MeOH ($E^0 \sim 0.3$ V). On the other hand, the Cu_3OH complexes do not show any oxidative response upto 1.0 V but these are reversibly
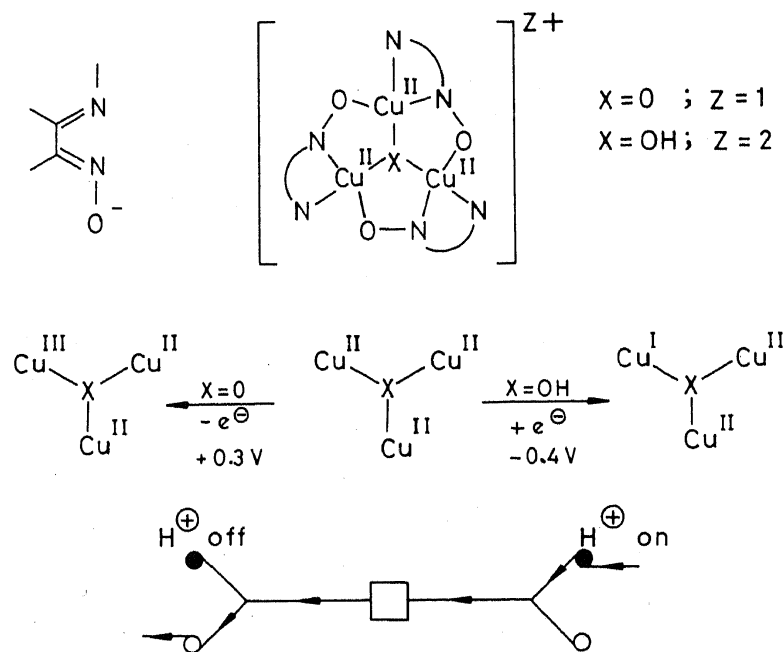

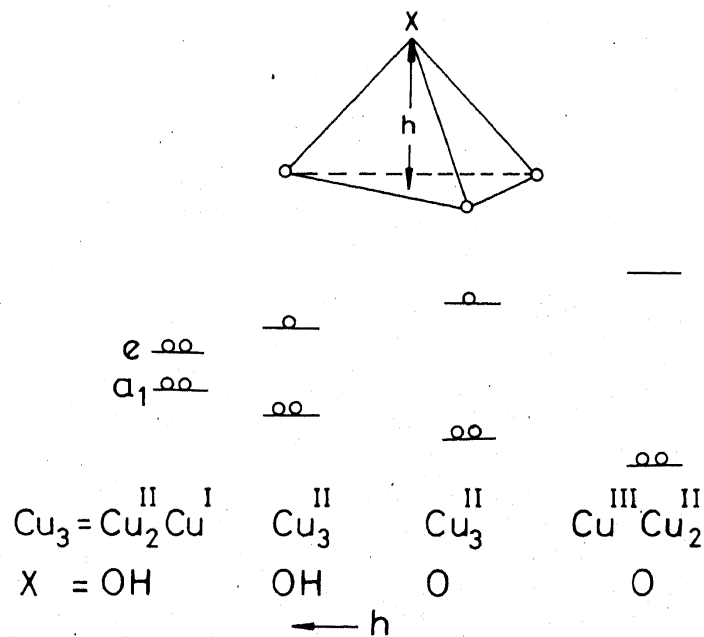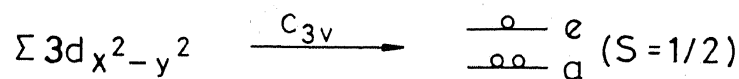**Figure 3.** Trinuclear copper species with proton switch action.

$$\Sigma \, 3d_{x^2-y^2} \xrightarrow{\;C_{3v}\;} \quad (S = 1/2)$$

Figure 4. Interaction within the Cu_3X group in trinuclear copper species.

reducible: $Cu_3^{II}/Cu_2^{II}Cu^I$ ($E^0 \sim 0\cdot4$ V). In effect, the proton in Cu_3OH acts as a switch allowing an extra electron to come in but blocking the removal of any of the original electrons (Datta *et al* 1981; Datta and Chakravorty 1982, 1983).

While the weak acidity of the Cu_3OH moiety is a factor, the electronic interactions within the Cu_3X fragment are believed to play an important role. The oxygen-mediated intermetal interaction increases as the pyramid height h decreases (figure 4). In C_{3v} symmetry the $d_{x^2-y^2}$ orbitals of the Cu_3 unit furnish molecular orbitals of e and a_1 symmetry. The relative energies of the e level of Cu_3OH and Cu_3O suggest that the oxidation of the former should occur at a higher potential than that of the latter. This shift will be further augmented by the charge of the proton. In practice, no oxidation is observed for Cu_3OH. By the same logic, reduction of Cu_3OH should be easy and that of Cu_3O difficult. We thus have a molecular basis for the proton switch action.

4. Geometrical isomerisation

We cite here an example of spontaneous isomerisation associated with an electro-protic reaction (figure 5). The *trans* planar arylazooximate of bivalent platinum adds
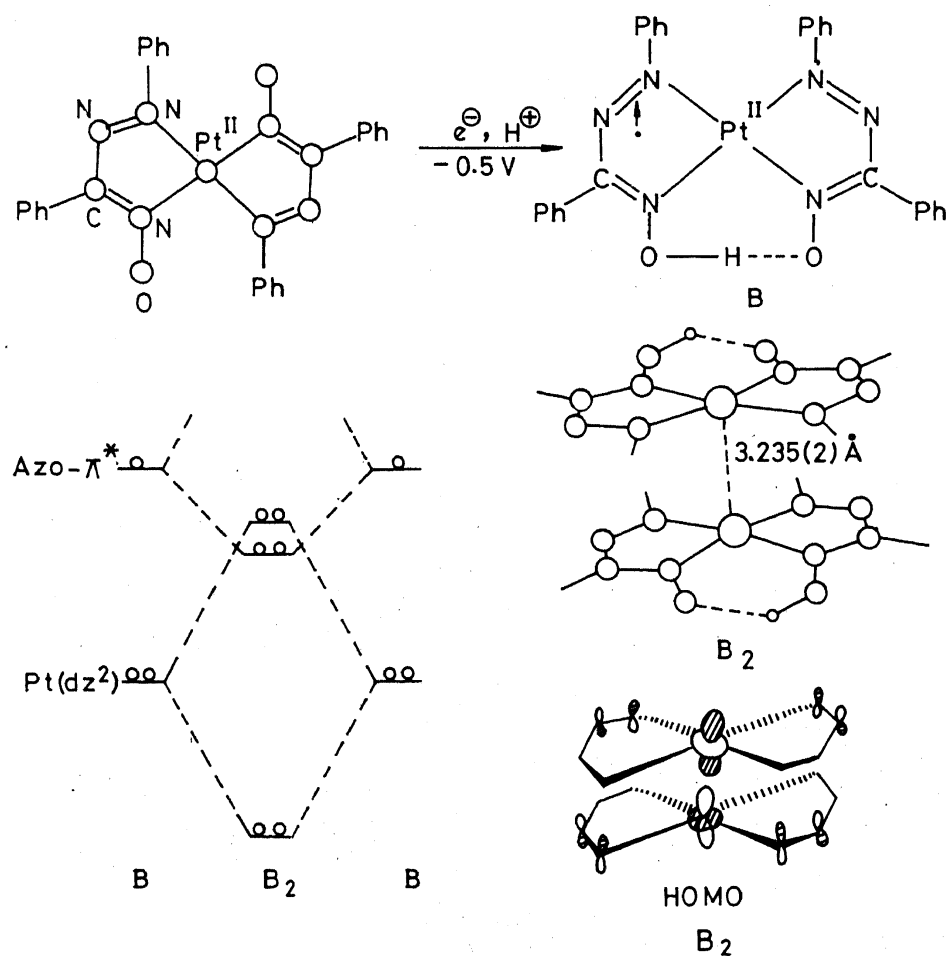

Figure 5. Isomeric transformation of platinum arylazooximates; structure and bonding in the *cis* dimer.

an electron to an azo group and a proton to an oximato oxygen. There is concomitant isomerisation to the paramagnetic *cis* complex B. It reversibly dimerises in solution affording diamagnetic B_2 which alone is present in the crystalline *cis* complex. The Pt...Pt distance is 3·235(2) Å and extended Hückel treatment of B_2 reveals that the HOMO is primarily metal d_{z^2} in character (Chattopadhyay *et al* 1993).

5. Organic refunctionalisation

Two examples will be considered here where metal bound organic functions are transformed via electroprotic pathways.

Addition of water to a Schiff base function normally leads to hydrolysis affording an aldehyde and an amine. An electroprotic transformation to the amide function can be conceived (figure 6) but it is difficult to achieve in practice (Chum and Helene 1980). We have employed metal binding as a tool for achieving this end. Through selection of the donor D and the charge z^+ on the metal, C–N cleavage which is. crucial for hydrolysis could be bypassed making amide formation facile. A particular reaction is shown in figure 7. Here [Re^{IV}] represents the Re^{IV} analogue of the Re^{III} precursor. The reactant and the product have been structurally characterized and the reaction rate is found to be first order with respect to the water concentration (Menon *et al* 1994).

A fascinating case of thioether activation by cobalt is depicted in figure 8. Oxidation of the metal from the bivalent to the trivalent state is attended with the deprotonation of an α-methylene group. When the SS chelate ring is six-membered, the carbanionic
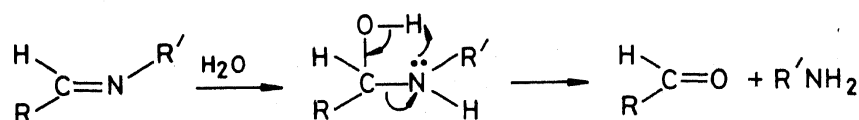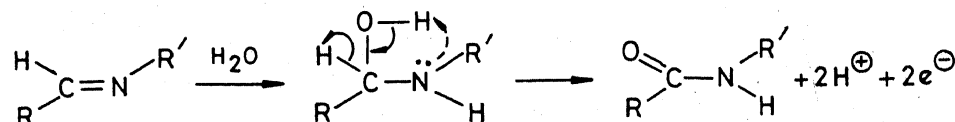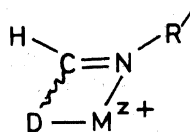

Figure 6. Two possible modes of transformation of the Schiff base function and strategy for achieving the electroprotic pathway.
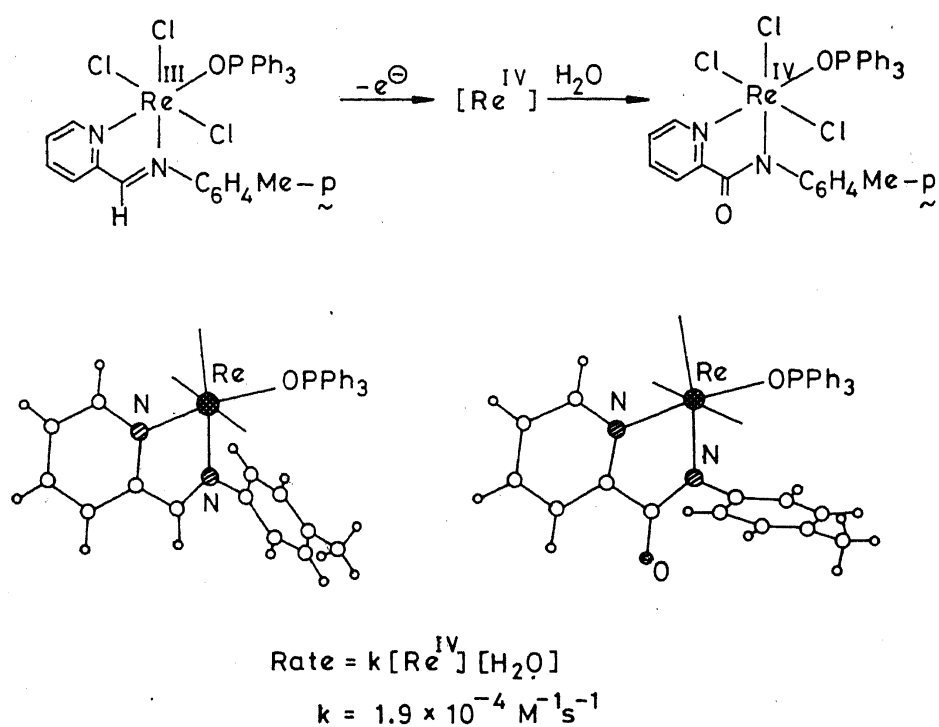
$$Rate = k[Re^{IV}] [H_2O]$$

$$k = 1.9 \times 10^{-4} \ M^{-1}s^{-1}$$

Figure 7. Oxidation of Schiff base to amide in a rhenium complex; structure and rate.

$$Co^{II} \ z=0$$
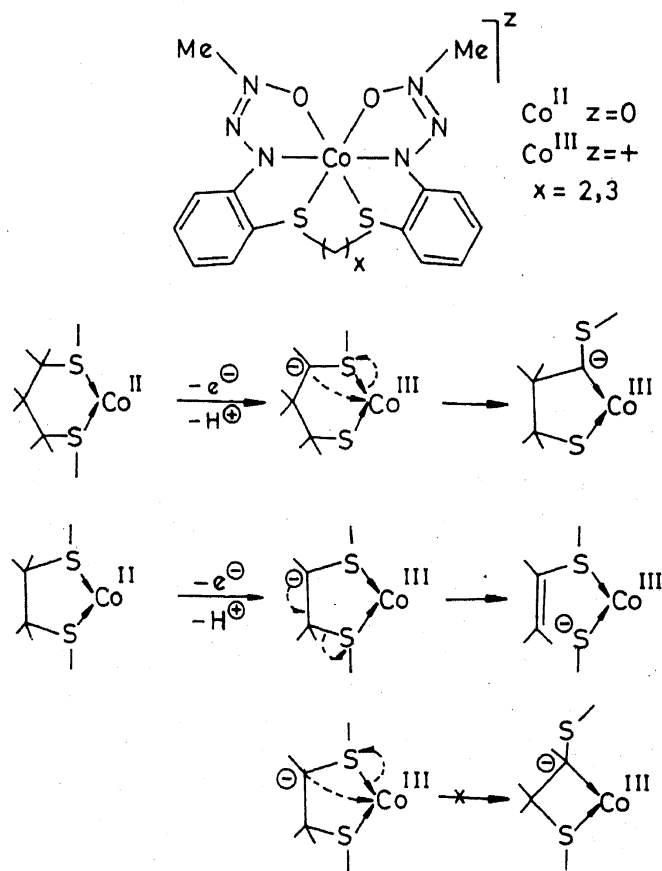$$Co^{III} \ z=+$$
$$x = 2,3$$

Figure 8. Thioether activation via electroprotic change in cobalt complexes.
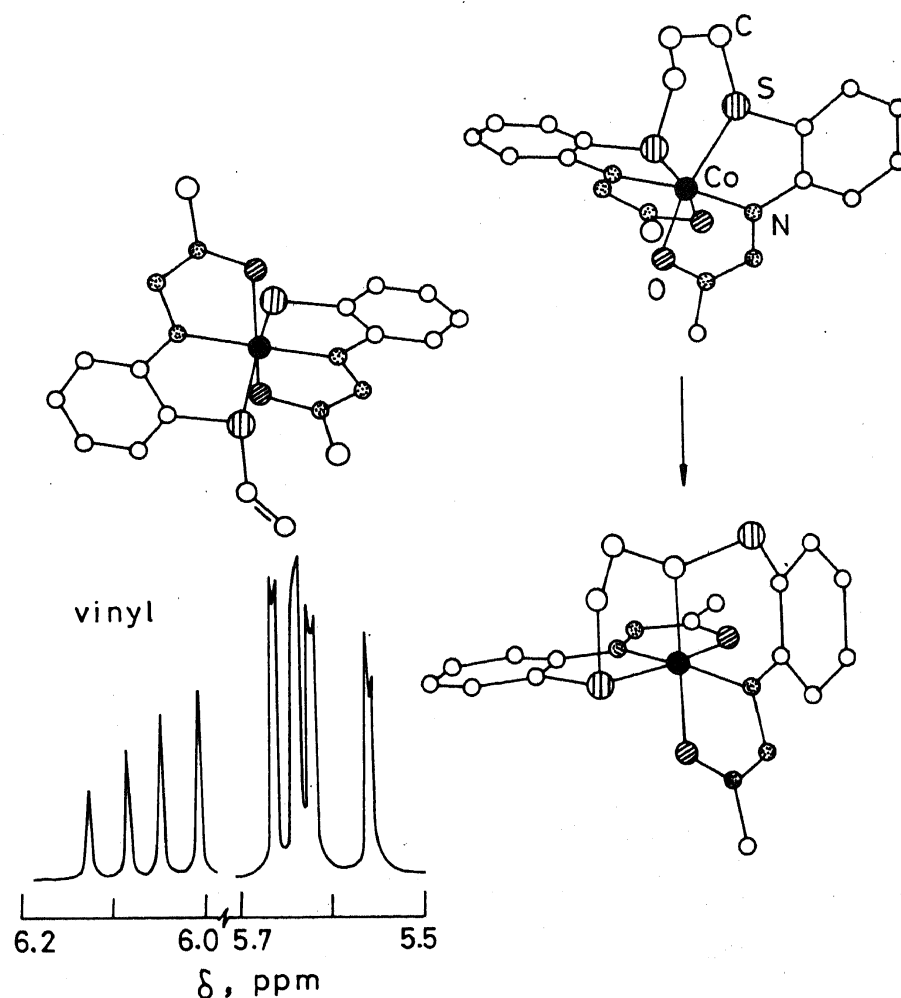
Figure 9. Structures of parent and transformed cobalt species and proton nmr of the vinyl group in the cleaved complex in CDCl₃.

site displaces a thioether function affording cobalt(III) organometallics. When the SS ring is five-membered this does not happen since the organometallic ring would be four-membered. Instead a C–S bond is cleaved leading to coordinated thiolate. The transformation is thus ring-size specific (Chakraborty *et al* 1993, 1994). The products from both types of reactions have been fully characterized (figure 9). The reaction scheme of figure 8 has helped rationalisation of apparently disparate literature results (Blake *et al* 1989; Bennet *et al* 1992; Kofod *et al* 1992).

6. Conclusions

We have demonstrated that electroprotic reactions can be a source of fascinating chemistry. It can effect geometrical isomerisation, single-step multielectron transfer and organic refunctionalisation. In one case, the proton is shown to act as a switch that can control the direction of electron flow.

Acknowledgements

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