Hydroxide-promoted Reduction of the Corrole Complexes of Cobalt(III) and Iron(III) in the Presence of Olefin

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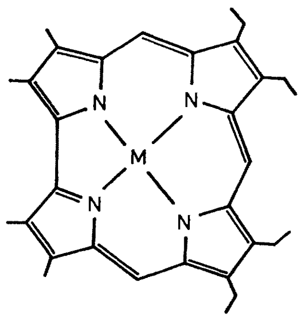
Summary An oxygenation system effective for electron-rich olefins which involves the hydroxide ion, provides electrons required for reduction of the corrole complexes of cobalt(III) and iron(III).

Much recent interest has been shown in the development of metal complex systems as redox catalysts.[1] We report here that electrons required for reduction of the corrole complexes of cobalt(III) (**1a**) and iron(III) (**1b**)[2] can be derived from an oxygenation system effective for olefins in which the hydroxide ion is involved.†

In the presence of ethyl vinyl ether in an aprotic solvent (dichloromethane, benzene, or *NN*-dimethylformamide), pyridine(2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)cobalt(III)[2] and the corresponding iron(III) complex‡



(1) a ; M = Co^{III}/Co^{II}
b ; M = Fe^{III}/Fe^{II}

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† The cobalt complexes of corrole (ref. 3) and tetradehydrocorrin (ref. 4) can be reduced with hydroxide ion in the absence of any additive.

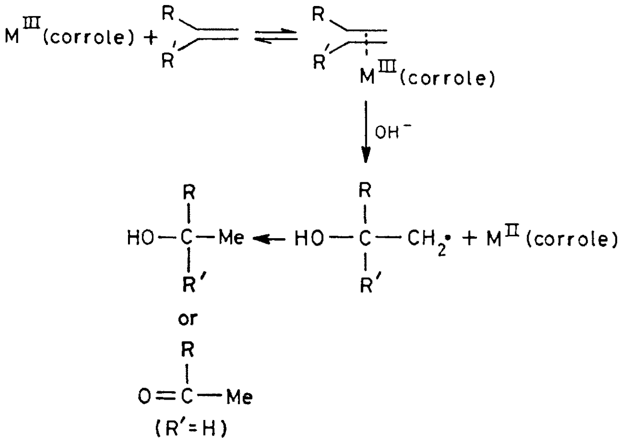
‡ A sample of analytically pure quality was prepared by cyclization of the corresponding biladiene-ac dihydrobromide in the presence of $FeCl_3$ and sodium acetate in pyridine–methanol (1 : 1 v/v) (ref. 5). For an alternative procedure, see ref. 6.

were quite readily reduced with $\mathrm{Bu^n{}_4NOH}$ to the corresponding metal(II) complexes which were identified by comparison (u.v.-visible spectroscopy) with authentic samples obtained by $\mathrm{NaBH_4}$ and electrochemical[5] (for the cobalt complex) reduction. The reaction went nearly to completion under anaerobic conditions, but afforded an equilibrium mixture of the tervalent and bivalent complexes under aerobic conditions owing to re-oxidation of the bivalent complex with oxygen (at normal atmospheric pressure) as shown by equation (1).

$$\mathrm{M^{III}(corrole)} \underset{\mathrm{O_2}\ (k_{-1})}{\overset{\mathrm{OH^-,\ olefin}\ (k_1)}{\rightleftharpoons}} \mathrm{M^{II}(corrole)} \tag{1}$$

The first-order pre-equilibrium process was investigated in $\mathrm{CH_2Cl_2}$–MeOH (100:3 v/v) at 20·0 °C in the presence of ethyl vinyl ether (0·0278 mol $\mathrm{l^{-1}}$) and hydroxide ion (3·0 mmol $\mathrm{l^{-1}}$): (**1a**) $k_1 + k_{-1} = 0{\cdot}0367\ \mathrm{s^{-1}}$, $k_1 = 0{\cdot}033\ \mathrm{s^{-1}}$, $K = k_1/k_{-1} = 8{\cdot}4$; (**1b**) $k_1 + k_{-1} = 0{\cdot}026\ \mathrm{s^{-1}}$, $k_1 = 0{\cdot}026\ \mathrm{s^{-1}}$, $K > 100$. Kinetic measurements for solutions containing varying amounts of the olefin at constant hydroxide-ion concentration (3·0 mmol $\mathrm{l^{-1}}$) showed that k_1 is proportional to the olefin concentration.

Styrene was found to be far less effective (by a factor of 500) than vinyl ether in promoting hydroxide-mediated reduction of the cobalt complex, and dec-1-ene showed almost no effect. For runs at constant concentration of ethyl vinyl ether, k_1 was found to be linearly proportional to the hydroxide-ion concentration. The introduction of an oxygen-containing group into the olefins was confirmed by analysis of the products obtained from the reactions of hydroxide ion (0·31 mmol), $\mathrm{Co^{III}}$(corrole) (0·017 or 0·033 mmol), and olefin (in an excess) in dichloromethane (or benzene) at room temperature for 17—18 h; 1,1-diphenylethanol was obtained from 1,1-diphenylethylene and acetophenone from styrene. Control experiments indicated that both the cobalt complex and hydroxide were necessary for the formation of these products.



SCHEME

Kinetic results and product analyses suggest that the reduction of the metal site and the incorporation of hydroxide into an olefin are concerted processes. The most plausible mechanism is shown in the Scheme and involves initial π-complex formation, attack of hydroxide ion on the π-complex, and one-electron transfer from the olefin–$\mathrm{OH^-}$ complex to the metal site affording the bivalent corrole complex and the β-hydroxyalkyl radical which may either abstract hydrogen from an n-butyl group of the counter cation of hydroxide ion or lose hydrogen. The final product from the olefin is either a hydrated compound or a ketone. Spectroscopic evidence rules out the existence of any stable intermediate having a carbon–cobalt or –iron bond, in contrast with reactions with cobalt corrinoid complexes.[7] The following experimental observations are consistent with this mechanism: ethyl vinyl ether has the greatest reactivity among olefins used in this work because it can form the most stable π-complex with the tervalent corrole complex, and the hydroxide ion attacks only at the phenyl-bearing carbon if the olefin contains such a group.

The most important point in the present findings is that the oxygenation of olefins with hydroxide ion provides electrons required for reduction of the metal complexes; the resulting complexes, $\mathrm{Co^{II}}$(corrole)[6] and, more favourably, $\mathrm{Fe^{II}}$(corrole),§ may be utilized as reductants for separate reduction processes. Thus, the present system may open a way to couple the oxygenation of olefins, which in itself is an important industrial process (Hoeckst–Wacker), with fuel-making reduction processes (*e.g.*, reduction of $\mathrm{H^+}$ to $\mathrm{H_2}$).

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§ The redox potential for the $\mathrm{Fe^{III}/Fe^{II}}$ couple in *NN*-dimethylformamide containing pyridine (2·5 mol $\mathrm{l^{-1}}$) is −0·92 V *vs.* standard calomel electrode.

[1] *E.g.* in the oxidation of water, C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. USA*, 1975, **72**, 2858; also see *Chem. Eng. News*, 1979, July 23, 24.
[2] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1965, 1620.
[3] N. S. Hush and I. S. Woolsey, *J. Chem. Soc., Dalton Trans.*, 1974, 24.
[4] Y. Murakami and Y. Aoyama, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 683.
[5] Y. Murakami, Y. Matsuda, and S. Yamada, unpublished results.
[6] M. Conlon, A. W. Johnson, W. R. Overend, D. Rajapaksa, and C. M. Elson, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2281.
[7] R. B. Silverman and D. Dolphin, *J. Am. Chem. Soc.*, 1976, **98**, 4626.