Nucleophilic Attack on Cyanoformate Induced by Co-ordination to Ruthenium Ammines

By STEVEN E. DIAMOND and HENRY TAUBE*

(*Department of Chemistry, Stanford University, Stanford, California* 94305)

Summary The nitrile and ester hydrolysis of ethyl cyanoformate using the Ru(II)–Ru(III) couple are examined.

EXAMPLES of metal-catalysed hydrolysis of nitriles to amides which have been reported either involve hydroxide ion as a reactant,[1] or require refluxing conditions.[2] The ruthenium ammines offer some special opportunities for studying metal-assisted nucleophilic attack on ligands. These arise from the ready substitution on Ru^{II}, the stabilization of the Ru^{II}–ligand interactions by back-bonding, and the ready oxidation of Ru^{II} to Ru^{III}; all of these factors are brought into play in the work which is to be described.

A solution of $(NH_3)_5RuCl_3$ (*ca.* 5×10^{-2} M) was reduced to $[(NH_3)_5RuH_2O]^{2+}$ with zinc amalgam.[3] A ten-fold excess of ethyl cyanoformate was added and after 1 h the Ru^{II} nitrile was precipitated, as orange needles, with NH_4PF_6. Microanalytical data are in agreement with the formula $[(NH_3)_5Ru(NCCO_2Et)][PF_6]_2$.

The solution containing the Ru^{II} nitrile described above was oxidized using silver oxide followed by NH_4PF_6 addition. Yellow-green crystals formed which were found to have the composition $[(NH_3)_5Ru(NHCOCO_2Et)][PF_6]_2$. It is to be noted that under these conditions the ester group remains intact.

The i.r. spectra of the Ru^{II} nitrile and the Ru^{III} amide

salts show the expected behaviour.[3] The nitrile has a strong absorption in both the C≡N (2144 cm^{-1}) and C=O (1709 cm^{-1}) regions. The amide spectrum shows only the ester carbonyl (1724 cm^{-1}), the amide carbonyl being masked by the ammonia absorptions.

Cyclic voltammetry of the nitrile complex shows an irreversible peak at 0·742 V *vs.* NHE. From data presented herein it seems reasonable to postulate that the oxidized nitrile complex is undergoing hydrolysis to the amide complex on the time scale of the cyclic voltammetry experiment. Cyclic voltammetry of the amide complex shows different behaviour. The amide couple is reversible, but in the Ru^{II} state the amide ligand is labile as shown by a build-up in aquopenta-ammineruthenium(II) concentration with multiple cycles. The formal potential for the amide couple is consistent with those for other known complexes.[4]

As confirmation of the conclusion that amide is readily released in the Ru^{II} state, the amide complex was reduced in the presence of an excess of isonicotinamide. The visible spectrum of the penta-ammineisonicotinamide-ruthenium(II) complex appeared at the rate expected for the reaction of isonicotinamide with aquopenta-ammine-ruthenium(II)[5]

The amide complex undergoes further reaction in mildly alkaline media (pH *ca.* 9, 30 min) to produce an oxamic acid derivative of ruthenium. Spectral data and analysis of the solid PF_6^- salt lead to the formulation $[(NH_3)_5RuNHCOCO_2H]^{2+}$.

There is no evidence that ammonia molecules *cis* to the ligand are implicated in the foregoing experiments. When *cis*-$[(NH_3)_4Ru(H_2O)_2]^{2+}$ is used, as before, ethyl cyanoformate adds intact, but now, on oxidation, not only does hydrolysis of the nitrile ensue, but also ester hydrolysis. N.m.r. experiments demonstrated that the ester hydrolysis occurs subsequent to oxidation even in acidic solution. It should be noted that, in the Ru^{II} state, owing to the linearity of the ruthenium nitrile bond, nucleophilic attack at the ester function by co-ordinated water is impossible. On oxidation, followed by hydrolysis of the nitrile, the ligand can now adopt a chelating configuration.

Financial support for this research from the National Institutes of Health is gratefully acknowledged.

(*Received*, 17*th May* 1974; *Com.* 571.)

[1] R. Breslow, R. Fairweather, and J. Keana, *J. Amer. Chem. Soc.*, 1967, **89**, 2135; D. Pinnell, G. B. Wright, and R. B. Jordan, *ibid.* 1972, **94**, 6104; D. A. Buckingham, A. M. Sargeson, and A. Zannella, *ibid.*, p. 8246; D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *ibid.*, 1973, **95**, 5649.

[2] K. Sakai, I. Ito, and K. Watanabe, *Bull. Chem. Soc., Japan*, 1967, **40**, 1660; S. Komiya, S. Suzuki, and K. Watanabe, *ibid.*, 1971, **44**, 1440; P. F. D. Barnard, *J. Chem. Soc.* (*A*), 1969, 2140.

[3] R. E. Clarke and P. C. Ford, *Inorg. Chem.*, 1970, **9**, 495; R. E. Clarke and P. C. Ford, *ibid.*, 1970, **9**, 227.

[4] H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 1972, **11**, 1460.

[5] R. E. Shepherd and H. Taube, *Inorg. Chem.*, 1973, **12**, 1392.