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Evidence for the Heterolytic Fission of H_2 by Cobalt Cyanide Complexes

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Summary The relative intensities of the Co–H/D stretching vibrations in the precipitated products show that the reaction of H_2 with $[Co^{II}L_5]^{3-}$ ($L = CN^-$) in D_2O produces equal amounts of $[Co^{III}L_5H]^{3-}$ and $[Co^{III}L_5D]^{3-}$ which, taken together with kinetic and electrochemical data, indicates that H_2 reacts with a binuclear $[Co_2L_{10}]^{6-}$ ion by heterolytic fission.

THE fastest known reaction of H_2 with a metal complex in homogeneous solution at room temperature is that with aqueous solutions of cobalt(II) cyanide complexes,[1] in which the main complex is $[Co^{II}L_5]^{3-}$ (**1**) where $L = CN^-$, possibly with a very labile H_2O as the sixth ligand.[2,3] The rate increases with ionic strength and cobalt concentration and $t_{1/2}$ can be less than 1 min.[4] We report here the first test for homolytic *versus* heterolytic fission for this reaction, which provides evidence that this very efficient 'activation' of H_2 involves heterolytic fission by a binuclear complex.

The main product of hydrogenation is $[Co^{III}L_5H]^{3-}$ (**2**)[5] and the reaction, which reaches equilibrium with *ca.* 10% of unchanged (**1**) under an atmosphere of H_2, can be written as in equilibrium (1), even though the equilibrium is only completely reversible after the first hydrogenation.[6] The rate of H_2 uptake in 0·1M KCl shows a second-order dependence on the concentration of (**1**), a first-order dependence on $P(H_2)$ and independence of cyanide and hydroxide concentrations;[7] *cf.* also references 8—10. We have found that in 3M KCl the initial rate of the reverse dehydrogenation (which is easier to study than the faster H_2 uptake) also shows a second-order dependence on the concentration of (**2**), but is independent of cyanide and hydroxide concentrations.† The kinetic evidence therefore indicates that H_2 reacts with an intermediate of composition $[Co_2L_{10}]^{6-}$ (**3**). A mechanism involving the rapid, reversible reaction of H_2 with (**1**) to give $[CoL_5H_2]^{3-}$, followed by a slower reaction with a second molecule of (**1**), cannot be excluded on kinetic grounds alone, but would involve structures and mechanisms without any known analogues. There is no experimental evidence to indicate whether H_2 undergoes homolytic fission (as is generally assumed[7-11]) or heterolytic fission. To test for homolytic *versus* heterolytic fission, solutions of (**1**) in D_2O (2 ml samples of 0·1M $CoCl_2$, 0·55M NaCN, 2M NaCl, pH 11·4) were treated with a brisk stream of H_2 for varying periods of time (5—90 min). The product was precipitated by the addition of 0·7 g of CsCl as the mixed Cs_2Na salt of (**2**)[5] and, after filtration and drying under N_2, the relative intensities of the Co–H and Co–D stretching vibrations, at 1840 and 1340 cm^{-1} respectively, were measured. Under these conditions $t_{1/2}$ is *ca.* 5 min, *i.e.* the reaction mixtures were sampled from the position of *ca.* 50% reaction to the steady-state condition under H_2. Neglecting any isotope effect on the evolution of gas, the relative steady-state concentrations of the Co–H and Co–D complexes should reflect the relative rates of formation of Co–H (from H_2) and of Co–D (from heterolytic fission of H_2 and/or independent Co–H/D_2O exchange). Complications due to further reactions with HD or D_2 are prevented because these products are swept away in the stream of H_2. However, reactions such as the evolution

$$2[Co^{II}L_5]^{3-} + H_2 \rightleftharpoons 2[Co^{III}L_5H]^{3-} \qquad (1)$$

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† Studied spectrophotometrically using a cell[2] in which a brisk stream of H_2 or N_2 could be passed through the solution. Full details and results, including the effects of mass transfer and of various 'inert' electrolytes, will be published elsewhere.

of NH_3 and/or $MeNH_2$ connected with the 'ageing' of the solutions proceed even during the steady-state under H_2[5] and may therefore cause gradual changes both in the species present and in the available mechanistic pathways. If there is no pathway for Co–H/D_2O exchange independent of the pathway for reversible hydrogenation, then we expect homolysis to produce exclusively Co–H, and heterolysis to give equal amounts of Co–H and Co–D, and we expect‡ the ratios of the integrated intensities of the Co–D to Co–H stretches to be 0:1 and 0·53:1 for homolytic and heterolytic fission respectively; both values would, of course, be increased by the existence of a separate pathway for Co–H/D_2O exchange.

All samples gave single bands in the Co–H and Co–D stretching regions though the latter band at 1340 cm^{-1} overlaps with the H_2O bands at *ca.* 1450 cm^{-1}, which increases the error in determining the integrated intensities. The following values were obtained for the ratios of the integrated intensities of the Co–D to Co–H stretching vibrations: 5 min, 0·26; 10 min, 0·58; 15 min, 0·36; 20 min, 0·68, 0·43, and 0·44; 30 min, 0·71; 50 min, 0·75; and 90 min, 1·04. In spite of the relatively large error and possible slight increase with time (perhaps connected with 'ageing'), the experimental results (average 0·58) clearly distinguish between the values expected for heterolytic (0·53) and simple homolytic (0·0) fission, although they could also be explained by a mechanism involving homolytic fission and a separate pathway for exchange together with a quite fortuitously correct ratio of rates. However, since the ion $[Co_2(CN)_{10}H]^{7-}$ (**4**), which would be the immediate product of heterolysis, has already been identified as the immediate product of the polarographic reduction of various pentacyanocobalt(III) complexes,[13] the balance of probability strongly favours heterolytic fission of H_2. We therefore propose the sequence of reactions§ shown in the Scheme, where ion-pairs have been omitted and formal oxidation states written for (**3**), (**4**), and (**5**), even though there would probably be extensive delocalisation in such structures. In fact, the marked reactivity towards H_2 can probably be ascribed to the ease with which such a delocalised system can be polarised under the influence of the attacking H_2.

$$\begin{array}{c}
2[Co^{II}L_5]^{3-} + H_2 \\
2\ (\mathbf{1}) \\
\rightleftharpoons \\
[L_5Co^{III}{\cdot}NC{\cdot}Co^{I}L_4]^{6-} + H_2 \\
(\mathbf{3}) \\
\rightleftharpoons \\
[L_5Co^{I}{\cdot}NC{\cdot}Co^{III}L_4H]^{7-} + H^+ \\
(\mathbf{4}) \\
\rightleftharpoons \\
[(HL)L_4Co^{I}{\cdot}NC{\cdot}Co^{III}L_4H]^{6-} \\
(\mathbf{5}) \\
\rightleftharpoons \\
[Co^{I}L_4(HL)]^{3-} + [Co^{III}L_5H]^{3-} \\
(\mathbf{6}) \qquad\qquad (\mathbf{2}) \\
\rightleftharpoons \\
2[Co^{III}L_5H]^{3-} \\
2\ (\mathbf{2})
\end{array}$$

SCHEME. $L = CN^-$.

The reaction of H_2 with (**3**) appears to be the first example of heterolysis by a transition-metal complex containing more than one metal atom. It is interesting to note that the hydrogenases, which possess Fe–S clusters, also activate H_2 by heterolytic fission.[15] Similar mechanisms are apparently exploited both by enzymes and by the most active known protein-free metal complex.

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‡ The summation $\Sigma(I_i/\omega_i^2)$, where I is the intensity and ω the frequency, over all vibrations within a given symmetry species, is invariant to isotopic substitution.[12] If, because of the small mass of H/D compared to Co, we ignore the possibility of coupling between the Co–H/D and CN (2110 cm^{-1}) stretching vibrations, then $I_{Co\text{-}D}/I_{Co\text{-}H} = (1340/1840)^2 = 0{\cdot}53$.

§ The inability[14] to account for the reaction of (**1**) with benzoquinone *via* the loss of H^+ to give $[Co^{I}L_5]^{4-}$ provides independent evidence for the existence of a second pathway [such as (**2**) → (**6**)] for the 'labilisation' of (**2**).

[1] M. Iguchi, *J. Chem. Soc. Jpn.*, 1942, **63**, 634.
[2] J. M. Pratt and R. J. P. Williams, *J. Chem. Soc. A*, 1967, 1291.
[3] A. G. Sharpe, 'The Chemistry of Cyano Complexes of the Transition Metals,' Academic Press, London, 1976.
[4] G. A. Mills, S. Weller, and A. Wheeler, *J. Phys. Chem.*, 1959, **63**, 403.
[5] R. G. S. Banks and J. M. Pratt, *J. Chem. Soc. A*, 1968, 854.
[6] R. G. Banks, P. K. Das, H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Discuss. Faraday Soc.*, 1968, **46**, 80.
[7] J. Halpern and M. Pribanić, *Inorg. Chem.*, 1970, **9**, 2616.
[8] B. De Vries, *J. Catal.*, 1962, **1**, 489.
[9] L. Simándi and F. Nagy, *Acta Chim. Acad. Sci. Hung.*, 1965, **46**, 101.
[10] M. G. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc. A*, 1967, 800.
[11] G. G. Strathdee and M. J. Quinn, *Can. J. Chem.*, 1972, **50**, 3144.
[12] B. Crawford, *J. Chem. Phys.*, 1952, **20**, 977.
[13] N. Maki, *Inorg. Chem.*, 1974, **13**, 2180.
[14] G. D. Venerable and J. Halpern, *J. Am. Chem. Soc.*, 1971, **93**, 2176.
[15] P. H. Gitlitz and A. I. Krasna, *Biochemistry*, 1975, **14**, 2561.