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Mechanism of the Splitting of Dihydrogen by Pentacyanocobaltate(II). A Reappraisal

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Mooiman and Pratt [1] have concluded that the reaction of H_2 with $[Co(CN)_5]^{3-}$ in aqueous solution [eqn. (1)] proceeds through heterolytic splitting according to eqn. (2). This conclusion is at variance with the widely held view of homolytic splitting based on prior evidence [2–5] and is based on premises that are seriously flawed. Since the system in question has attracted widespread attention and since the mechanistic distinction at issue is of some importance, it seems appropriate to reassess the evidence.

Mooiman and Pratt [1] attempted to distinguish between the alternative homolytic and heterolytic modes of splitting of H_2 [reactions (1) and (2), respectively] by examining the isotopic composition of the $[Co(CN)_5H]^{3-}/[Co(CN)_5D]^{3-}$ mixture resulting from the reaction of H_2 with $[Co(CN)_5]^{3-}$ in D_2O.

$$H_2 + 2[Co(CN)_5]^{3-} \longrightarrow 2[Co(CN)_5H]^{3-} \qquad (1)$$

$$H_2 + 2[Co(CN)_5]^{3-} \longrightarrow [Co_2(CN)_{10}H]^{7-} + H^+ \longrightarrow 2[Co(CN)_5H]^{3-} \qquad (2a)$$

or, in D_2O

$$H_2 + 2[Co(CN)_5]^{3-} \xrightarrow[-HDO]{D_2O} [Co_2(CN)_{10}H]^{7-} + D^+ \rightarrow [Co(CN)_5H]^{3-} + [Co(CN)_5D]^{3-} \qquad (2b)$$

The two alternative schemes lead to different predictions concerning the Co–D/Co–H ratio, as follows:

(1) According to the *homolytic* splitting scheme of reaction (1) the Co–D/Co–H ratio should be zero initially, but could increase with time due to exchange between $[Co(CN)_5H]^{3-}$ and D_2O.

(2) According to the *heterolytic* splitting scheme of reaction (2b) the *initial* Co–D/Co–H ratio should be 1.0, corresponding to a calculated value of 0.53 for the Co–D/Co–H infrared stretching intensity ratio ($I_{Co-D}/I_{Co-H} = I_{1340}/I_{1840}$) cm^{-1} that was used to monitor the isotopic composition.

The values of I_{Co-D}/I_{Co-H} reported by Mooiman and Pratt [1] for different reaction times are as follows: 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. Citing agreement between the experimental results (*average* 0.58) and the value expected for heterolytic (0.53) rather than homolytic (0.0) splitting, they concluded that their results provide support for the former, *i.e.*, for alternative (2).

Clearly, the 'average' value of 0.58 for I_{Co-D}/I_{Co-H} yielded by the above treatment is meaningful and the interpretation of Mooiman and Pratt is valid only if the fluctuations in I_{Co-D}/I_{Co-H} are random and do not reflect a systematic time-dependence. The data of Mooiman and Pratt are plotted in Fig. 1. Notwithstanding the significant scatter, the data clearly show a time-dependent trend such that the value of I_{Co-D}/I_{Co-H} at zero time is small and the formation of most of the $[Co(CN)_5D]^{3-}$ is attributable to the *previously demonstrated* [3, 4, 6, 7] secondary exchange of $[Co(CN)_5H]^{3-}$ with D_2O. Contrary to the assertion of Mooiman and Pratt, this strongly favors alternative (1) over (2).

One *demonstrated* [7] mechanism of exchange $[Co(CN)_5H]^{3-}$ with D_2 is through the reaction of $[Co(CN)_5H]^{3-} + OH^-(OD^-) \rightleftharpoons [Co(CN)_5]^{4-} + H_2O(HDO)$, for which a rate constant of 0.36 M^{-1} sec^{-1} (extrapolated to an ionic strength of *ca.* 3.0 at which these experiments were performed) has previously been reported [5]. At the pH of 11.4 used in

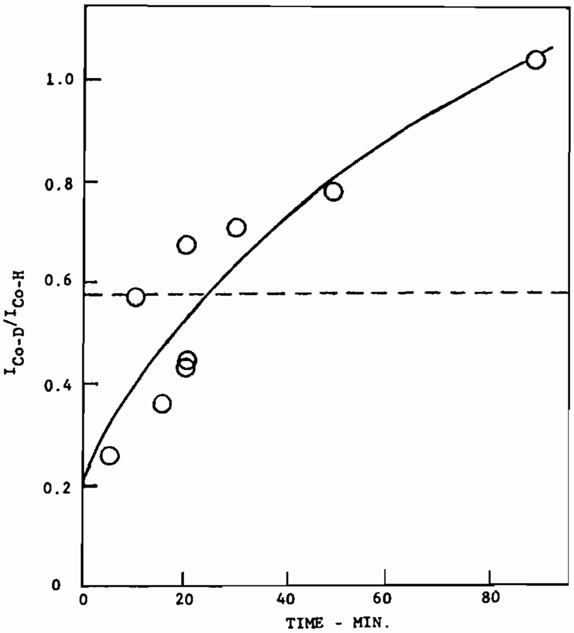

Fig. 1. Plot of the data of Mooiman and Pratt [1]. The solid curve represents the least squares fit to the experimental data (open circles) of a four term power series. The dashed line corresponds to Mooiman and Pratt's fitting of the data to an average I_{Co-D}/I_{Co-H} value of 0.58.

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these studies, the half-life of exchange of $[Co(CN)_5H]^{3-}$ with D_2O by this route alone would be only *ca.* 13 min, *i.e.*, considerably shorter than the time scale of these experiments and more than adequate to account for *all* the $[Co(CN)_5D]^{3-}$.

Thus, we conclude that all the evidence to date, including that advanced by Mooiman and Pratt [1], is consistent with and supports the widely accepted homolytic splitting mechanism for the reaction of H_2 with $[Co(CN)_5]^{3-}$.

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References

1 M. B. Mooiman and J. M. Pratt, *J. Chem. Soc., Chem. Comm.*, 33 (1981).
2 B. De Vries, *J. Catalysis, 1*, 489 (1962).
3 U. Schindewold, *Ber. Bunsengesellschaft, 67*, 220 (1963).
4 M. G. Burnett, P. J. Connolly and C. Kemball, *J. Chem. Soc. (A)*, 800 (1967).
5 J. Halpern and M. Pribanic, *Inorg. Chem., 9*, 2616 (1970).
6 J. Halpern and M. Pribanic, *Inorg. Chem., 11*, 658 (1972).
7 G. G. Strathdee and M. J. Quinn, *Canad. J. Chem., 50*, 3144 (1972).
8 M. B. Mooiman, J. M. Pratt and E. H. R. von Barsewisch, *S. Afr. J. Chem., 35*, 175 (1982).

Note added in proof

In a subsequent report which came to our attention following preparation of this manuscript, Mooiman, Pratt and von Barsewich [8] have confirmed that the Co–D/Co–H ratio of the product of reaction of H_2 with $[Co(CN)_5]^{3-}$ in D_2O indeed is pH (pD) dependent and have modified the earlier conclusion of Mooiman and Pratt [1] accordingly. However, neither the significance of the *time-dependence* of the Co–D/Co–H ratio which is addressed in this communication, nor the origin of the pD dependence of the Co–D/Co–H ratio and the connection of this dependence with the earlier studies cited in Refs. [6] and [7] of this communication, appear to have been appreciated or addressed. As pointed out in the present communication, the latter studies do serve to demonstrate direct H/D exchange between $[Co(CN)_5H]^{3-}$ and D_2O, induced by OD^-.