Donor and Ligand Effects on Acetylene Reduction with Cobalt(II)–Thiol Complex Catalysts

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Summary Donor and ligand effects on acetylene reduction with thiol–Co^{II} complex catalysts have been investigated and compared with results for the corresponding Mo catalysts, which show a different product distribution; sulphydryl- and imidazole-containing peptide ligands show high catalytic activity.

SEVERAL molybdenum–complex catalysts mimic nitrogenase in the reduction of acetylene to ethylene.[1] In addition, donor and ligand effects on product distribution (ethylene, ethane, butadiene, *etc.*) have been systematically investigated.[2,3] We recently initiated a study of Co complexes containing cysteine and cysteamine related ligands which show promise as potential catalysts, and obtained results which are somewhat different from published results.[4] The discrepancy is presumably due to the difference in pH of the reaction and the reducing agents used.

A typical catalytic system consisted of a 20 ml glass container fitted with a rubber serum cap containing borate buffer (pH 9·2; 3·5 ml), $CoCl_2$ (0·5 ml; 0·1 mM aqueous solution), and the ligand (0·5 ml of 0·2 mM solution; borate buffer). The solution was flushed with water-washed acetylene (1 atm) and the reaction was initiated by injection of 0·5 ml of $NaBH_4$ (0·5 ml of 2 mM solution; borate buffer). Reaction mixtures were then shaken at 20 °C and the gas phase analysed by g.l.c. Two-component systems consisting of solutions of the cobalt salt and $NaBH_4$ alone exhibited no significant catalytic activity.

Table 1 shows the yield and rate of the reduction of acetylene with the Co^{II}–cysteine and –cysteamine related ligand systems in the presence of sodium borohydride. The formation of buta-1,3-diene and higher hydrocarbons was negligibly small. The cysteine–Co and –Mo systems consume C_2H_2 at comparable rates but the product distributions are very different. The major product from reduction of C_2H_2 with the Mo–cysteine catalyst in borate buffer is C_4H_6, not C_2H_4 [C_2H_4(52·5 μmol), C_2H_6(0·6), and C_4H_6(142)].[3] Selenocysteine– and selenocysteamine–Co^{II} complex systems show a higher ethylene–ethane ratio than cysteine– and cysteamine–Co^{II} complex systems, though the total yield is lower. In the Mo catalyst systems, the C_2H_4 : C_2H_6 ratios with cysteamine and selenocysteamine are 16·5 : 1 and 1·9 : 1, respectively.[2] The effect of co-ordination donor atoms on the catalytic activity clearly increases in the order S>Se≫O. This order is consistent with that of the corresponding Mo ligand systems.[2] The maximal activity of the cysteine– and cysteamine–Co^{II} complexes occurred in the pH region 8·5—10·0. The optimum pH region for the formation of these Co^{II} complexes was *ca.* 8·0—10·5.

TABLE 1. Yield and rate of ethylene and ethane production from acetylene with Co^{II} complexes of cysteine, cysteamine, and related ligands.[a]

Ligand	C_2H_4/μmol	C_2H_6/μmol	Total yield/μmol	Relative yield (%)	C_2H_4 : C_2H_6	Rate /μmol min^{-1}	Relative rate (%)
Serine	4	0	4	0·8	—	0	0
Cysteine	428	92	519	100	4·7 : 1	47	100
Selenocysteine ..	220	14	234	45	15·6 : 1	25	52
Ethanolamine ..	3	0	3	0·6	—	0	0
Cysteamine	406	40	446	100	10·2 : 1	64	100
Selenocysteamine ..	154	5	159	36	30·8 : 1	38	60

[a] Yields of the products were determined after a reaction time of 30 min; rates refer to (C_2H_4 + C_2H_6)/min for the initial 5 min.

TABLE 2. Effect of amino-acid residues on acetylene reduction with 2:1 sulphydryl-containing peptide–Co^{II} complex catalysts.

	R^1	R^2	Yield[b]/μmol C_2H_4	Yield[b]/μmol C_2H_6	Rate[c] /μmol min^{-1}
(A)[a]	Ph	H	154	60	19·7
	Me	H	141	35	13·7
	Pr^i	H	59	5	9·0
	Me	Ph	159	21	23·0
	H	Imidazol-4-ylmethyl	256	49	27·5
	H	Indol-3-ylmethyl	62	7	2·5
	Me	CH_2SH	83	8	6·4
	Pr^i	CH_2SH	70	8	8·3
(B)[a]	H	H	63	4	9·4
	H	Imidazol-4-ylmethyl	84	4	13·0
(C)[a]	H	H	180	29	16·2
	H	Imidazol-4-ylmethyl	291	81	47·0

[a] Ligands: (A), $R^1CH(SH)CONHCH(CO_2H)R^2$; (B), $R^1CH(SH)CH_2CONHCH(CO_2H)R_2$; (C), $4\text{-}R^1CH(SH)CONHCHR^2CONHCH(CO_2H)CH_2$-imidazole. [b] Yield after 30 min reaction. [c] Rates refer to $(C_2H_4 + C_2H_6)$/min for the initial 5 min.

These results suggest that complex formation plays a specific role in the reduction of acetylene with these Co^{II} complex catalysts.

Table 2 summarizes the effect of amino-acid residues on the reduction of acetylene with various sulphydryl-containing peptide–Co^{II} complex catalysts. The effect of amino-acid residues increases in the order histidine>glycine>cysteine>tryptophan. The high catalytic activity of the sulphydryl- and imidazole-containing peptides, *N*-mercaptoacetyl-L-histidine[5] and *N*-mercaptoacetyl-DL-histidyl-DL-histidine, is of special interest. The results suggest participation of the histidine imidazole group in the active site of nitrogenase. Co-ordination of the cysteine sulphydryl group at the Mo site has been indicated by *X*-ray absorption-edge spectra.[6]

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[1] G. D. Schrauzer, *Angew. Chem.*, 1975, **87**, 579.
[2] Y. Sugiura, T. Kikuchi, and H. Tanaka, *J.C.S. Chem. Comm.*, 1976, 519.
[3] J. L. Cordin, N. Pariyadath, and E. I. Stiefel, *J. Amer. Chem. Soc.*, 1976, **98**, 7862.
[4] G. N. Schrauzer and G. Schlesinger, *J. Amer. Chem. Soc.*, 1970, **92**, 1808; G. N. Schrauzer and P. A. Doemeny, *ibid.*, 1971, **93**, 1608.
[5] Y. Sugiura and Y. Hirayama, *J. Amer. Chem. Soc.*, 1977, **99**, 1581.
[6] S. P. Cramer, T. K. Eccles, F. W. Kutzler, K. O. Hodgson, and L. E. Moetenson, *J. Amer. Chem. Soc.*, 1976, **98**, 1287.

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