

Donor Effect and Selectivity of Ethylene-Ethane Production in the Reduction of Acetylene with the Molybdenum-Cysteamine-related Ligands Catalyst System

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Summary The catalytic effect of co-ordination donor atoms on the reduction of acetylene with the Mo-cysteamine-related ligands system increases in the order $S > Se \gg O$; the selectivity of ethylene-ethane production in acetylene reduction by cysteamine-Mo and *NN*-dimethylcysteamine-Mo catalysts is of interest, the $C_2H_4:C_2H_6$ ratios being 16.5:1 and 0.14:1, respectively.

Mo-cysteamine (2-mercaptoethylamine)-related ligands system in the presence of sodium borohydride. The effect of co-ordination donor atoms on the catalytic activity clearly increases in the order $S > Se \gg O$. Of special interest is a large variation in the selectivity of ethylene-ethane production in these catalyst systems. The catalytic reduction of acetylene by the cysteamine-Mo system gave ethylene as the main product, the $C_2H_4:C_2H_6$ ratio being 16.5:1, which is higher than with the cysteine-Mo and 2-mercaptoethanol-Mo catalysts. In contrast, the *NN*-dimethylcysteamine-Mo system, in which the co-ordination of the amino-group is blocked by dimethyl groups, produced ethane as the main product, the $C_2H_4:C_2H_6$ ratio being 0.14:1.

PHYSICO-CHEMICAL studies suggest that Mo co-ordinated by one or more sulphur atoms may be an important feature in the action of molybdoenzymes.¹ A cysteine-Mo complex is known to play a specific role as a chemical model in the reduction of nitrogenase substrates, acetylene, azide, and

TABLE. Yields of ethylene and ethane produced from acetylene with Mo-cysteamine-related ligands catalyst systems^a

| Ligand | $C_2H_4/\mu\text{mol}$ | $C_2H_6/\mu\text{mol}$ | $C_2H_4:C_2H_6$ |
|-------------------------------|------------------------|------------------------|-----------------|
| Cysteamine | 329.2 | 20.0 | 16.5:1 |
| Selenocysteamine .. | 92.4 | 47.7 | 1.94:1 |
| <i>NN</i> -Dimethylcysteamine | 51.6 | 365.1 | 0.14:1 |
| Ethanolamine | Traces | Traces | — |
| 2-Mercaptoethanol .. | 490.3 | 74.1 | 6.6:1 |
| Cysteine | 349.0 | 48.0 | 7.3:1 |

^a Reaction conditions: solutions containing 0.029 mol of Na_2MoO_4 , 0.029 mol of ligand, and 0.15 mol of $NaBH_4$ in 3.5 ml of borate buffer (pH 9.5) were placed in glass vials and sealed with rubber serum caps. The air inside the vials was then replaced by water-washed acetylene under 1 atm pressure. The yields reported are for 60 min reaction periods at 20 °C.

dinitrogen.² We now describe the donor effect of Mo ligands and the selectivity of ethylene-ethane production in the reduction of acetylene. The Table shows the yield and ethylene-ethane ratio in the reduction of acetylene with the

The formation of ethylene and ethane from acetylene requires transfer of two and four electrons, respectively, from the catalyst to the substrate, *i.e.*, $Mo^{III} \xrightarrow{2e} Mo^V$, and $(Mo^{III}-Mo^{III}) \xrightarrow{4e} (Mo^V-Mo^V)$. The *NN*-dimethylcysteamine-Mo system presumably involves a binuclear catalytically active species. A dioxo-bridged cysteine-Mo^V complex has been fully characterized by X-ray crystallography³ and e.s.r. spectroscopy.⁴ The Mo^{III} complex of 2-mercaptoethanol was also isolated recently.⁵ The present communication concerning the ethylene-ethane selectivity in the acetylene reduction will perhaps lead to a better understanding of correlation between reactivity and structure in Mo complexes of sulphur-donor ligands, and of the mechanism of the action of nitrogenase.

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