# Cobalt-catalysed Reaction of Carbon Monoxide–Hydrogen Mixtures in Alkoxy-terminated Polyglycol Solvents

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*Summary* Under pressures of *ca.* 200 bar (3000 lb in$^{-2}$) in $CO$–$H_2$ at *ca.* 200—250 °C in methoxy-terminated polyglycol (glyme) solvents, [$Me(OCH_2CH_2)_nOMe$], cobalt carbonyls catalyse the formation of a number of oxygenated products in which ethanol predominates (up to 70% selectivity); experiments with $^{13}C$ labelled CO and unlabelled diglyme suggest that > 90% of the ethanol was derived from the solvent and only *ca.* 5% from pure syn gas chemistry.

With the current interest in coal-derived fuels (syn-fuels) and chemicals, coupled with the initial publication of the Union Carbide work on the rhodium-catalysed conversion of syn gas into glycols,[1] industrial and academic research laboratories have given increasing importance to catalysed syn gas (mixtures of CO and $H_2$) conversion reactions. Prompted by several recent publications[2a–c] involving cobalt carbonyl-catalysed reactions, we report an observation similar to that found by others,[2c] and a partial explanation of the chemistry involved *via* the use of $^{13}C$ labelled carbon monoxide.

Table. Selectivity and solvent effects in the cobalt carbonyl-catalysed reactions of syn gas.[a]

| Solvent (mmol) | Selectivity, mol % $CO_2$ | $CH_4$ | $C_2H_6$ | MeOH | EtOH | Pr$^n$OH | MeCHO | mmol of products (total)[c] |
|---|---|---|---|---|---|---|---|---|
| $(MeOCH_2CH_2)_2O$ (280) | 1·2 | 21·0 | — | 2·6 | 67·8 | 5·2 | 2·2 | 40 |
| $(EtOCH_2CH_2O)_2O$ (224) | 2·1 | 30·0 | — | — | 28·0 | 39·9 | — | 16 |
| $OCH_2CH_2CH_2CH_2$ (494) | 9·3 | 68·0 | 22·7 | — | — | — | — | 10 |
| $OCH_2CH_2OCH_2CH_2$ (494) | 27·3 | 72·7 | — | — | — | — | — | 4 |
| $SO_2CH_2CH_2CH_2CH_2$ (419) | Trace conversion | | | | | | | |
| $MeOCH_2CH_2OH$ (504) | 4·1[b] | 26·0[b] | — | 5·8 | 52·6 | — | 11·4 | 20 |
| $MeOCH_2CH_2OMe$ (386) | 35·7 | 54·5 | 9·8 | — | — | — | — | — |

[a] Conditions: 300 cm$^3$ autoclave; 220 °C; 4 h; 1 : 1 $H_2$–CO, 200 bar pressure; 40 cm$^3$ solvent, 1 mmol of $Co_4(CO)_{12}$. [b] $HOCH_2CH_2OH$ also detected. [c] Excluding $CO_2$.

The Table shows that relatively high selectivities for the formation of ethanol are achieved when using diglyme (or tetraglyme, not shown in Table) solvents. Assuming the ethanol to be syn gas-derived, we examined the chemistry more thoroughly. The remaining data in the Table, however, raised suspicions regarding the source of the ethanol. Under the relatively short reaction times we employed, we detected *no* ethanol in reactions which used tetrahydrofuran, dioxan, or sulpholan as solvent; the selectivity for n-propanol formation dramatically increased when the solvent 2-ethoxyethyl ether, $(EtOCH_2CH_2)_2O$, was used.

We were tentatively led to the hypothesis that the terminal methoxy moieties were incorporated as the methyl group of the ethanol product. [Similarly, the EtO group of $(EtOCH_2CH_2)_2O$ would supply the connected Me and $CH_2$ groups of the propanol product.] Supporting this hypothesis was the observation that in reactions which utilized 2-methoxyethanol, $MeOCH_2CH_2OH$, as solvent ethylene glycol was detected. However, in these same experiments the total amount of possible carbonylation products, *i.e.* methane, methanol, ethanol, and acetaldehyde, was greater than the amount of ethylene glycol. Further complicating the chemistry was the inability to account accurately for the contribution of ethylene glycol (and other solvent fragments) which might result from any thermal decomposition of the solvent, and the result that in 1,2-dimethoxyethane, $MeOCH_2CH_2OMe$, no oxygenated hydrocarbons of any sort were obtained in two experiments.

Thus we investigated the use of $^{13}C$ labelled syn gas (from Alfa-Ventron) and unlabelled diglyme solvent. If ethanol were derived purely from the syn gas, the $^{13}C:^{12}C$ ratios in the methyl methylene groups should be equal,† but if solvent participation predominated, these ratios would not be equal. The experiment was carried out under the same conditions as previously employed except that 10% $^{13}C$ enriched cobalt carbonyl and syn gas were used. The resultant ethanol was isolated *via* distillation and analysed by $^{1}H$ n.m.r. spectroscopy. The $^{13}CH_3$ and $^{13}CH_2$ satellites were distinguished from other resonances due to minor components by their multiplicities and $^{13}C$–H coupling constants. The latter are equal within experimental error to those found in the proton-coupled $^{13}C$ n.m.r. spectrum of ethanol[3] [$J(^{13}CH_3)$ 125·3 Hz; $J(^{13}CH_2)$ 141·0 Hz]. Calculation reveals that *ca.* 1·5% of the methyl groups and 9·7% of the methylene groups are $^{13}C$ labelled. Allowance for the natural abundance of 1·1% $^{13}C$ in diglyme led to the conclusion that only about 5% of the ethanol was derived from pure syn gas chemistry.

Solvent cleavage could occur *via* the mechanism proposed by Wilkinson *et al.*[2c] or we suggest, alternatively, by a simple acid-catalysed scission employing the relatively strong acid $HCo(CO)_4$, which is known to be formed from cobalt carbonyls and $CO–H_2$ mixtures.[4] Protonation of the methoxy oxygen atoms of the methyl-capped glyme solvent would lead to scission of the glyme solvent forming an $HOCH_2CH_2O$ moiety and a methyl cobalt species which could then rearrange to form an acyl cobalt complex. This material subsequently could react with hydrogen ultimately to yield the ethanol and regenerate a cobalt hydride species.

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† Since the literature (W. H. Tamblyn, E. A. Vogler, and J. K. Kochi, *J. Org. Chem.*, 1980, **45**, 3912; J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962, pp. 71—72), suggests that $^{13}C$ isotope effects are relatively small, we feel we can ignore the perturbation caused by this effect.

[1] *E.g.* see J. L. Vidal, W. E. Walker, R. L. Pruett, R. C. Schoening, and R. A. Fiato, in 'Fundamental Research in Homogeneous Catalysis, 3,' ed. M. Tsutsui, Plenum Press, New York, 1979, pp. 499—518, and references therein.
[2] (a) D. R. Fahey, 'Synthesis Gas Conversion to Ethanol and Other Alcohols Catalyzed by Cobalt Carbonyl,' Symposium on Alternative Feedstocks for Petrochemicals, Division Petroleum Chemistry, Am. Chem. Soc., Las Vegas, Aug. 24—28, 1980; (b) H. M. Feder and J. W. Rathke, *Ann. N.Y. Acad. Sci.*, 1980, **333**, 45; (c) R. S. Daroda, J. R. Blackborow, and G. Wilkinson, *J. Chem. Soc., Chem.Commun.*, 1980, 1098.
[3] C. A. Reilly, unpublished work.
[4] A. M. Lennertz, J. Laege, and M. J. Mirbach, *J. Organomet. Chem.*, 1979, **171**, **203**; R. B. King, A. D. King, Jr., M. Z. Iqbal, C. C. Frazier, K. Tanaka, and D. B. Yang, 'Transition Metal Chemistry under Carbon Monoxide Pressure. An Infrared Spectroscopic Study of Catalysis in the Fischer-Tropsch Reaction,' U.S. Department of Energy Report, 1979.