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NOTE

Pentachlorobenzenethiol: A New Promotor for the Rh(I)-Complex-Catalyzed Methanol Carbonylation

An industrial process for the production of acetic acid from methanol and CO was reported by Roth *et al.* (*1*); a 315 million lb/yr plant was brought on stream in 1970 (*1, 2*), and a 600 million lb/yr plant is under construction (*3*). The economic advantage of the new process is a consequence of the high activity and selectivity of the catalyst system, a solution of a Rh(I)-complex promoted by HI or CH_3I, which converts about 99% of the methanol and 90% of the CO into acetic acid at 175°C and 15 atm CO partial pressure (*2*).

A mechanism of this carbonylation reaction was suggested by Roth *et al.* (*1*) and clarified by Forster (*4*). An equilibrium is set up

$$HI + CH_3OH \rightleftharpoons CH_3I + H_2O,$$

and the rate-determining step is the oxidative addition of CH_3I to $[Rh(CO)_2I_2]^-$, which can be formed from any of a number of Rh-complexes initially added to the reactant mixture (*1, 4*). The following steps are insertion of CO between Rh and CH_3, reductive elimination, and exchange between acetyl iodide and methanol to give acetic acid and regenerate the promotor.

Details of the commercial process are not published, but it is known that the reactant solutions of Rh-complexes and HI are highly corrosive, and it is probable that the reactors, separators, and recycle loops must be constructed of expensive corrosion-resistant materials. The recovery of the catalyst and promotor from the reaction products requires several separators because of the relatively high volatility of the iodide compounds (*5*). The process could be improved if a promotor could be found having an activity analogous to that of HI while being less corrosive and having a relatively high boiling point.

The goal of this research was to find improved promotors. The patent literature provided guidance, referring to numerous promotors for Rh-complex-catalyzed alcohol carbonylation (*1, 5–7*) and olefin carboxylation (*8*).

The batch reactor used to determine kinetics of the methanol carbonylation reaction was a 300-cm³ autoclave supplied by Autoclave Engineers. It was equipped with a thermostat, a magnetically driven impeller, gas feed and exit lines, a thermocouple well, a heating jacket, a pressure gauge, and a liquid sample line. A typical run was carried out as follows. The liquid reactants, catalyst, promotor, and solvent were weighed into the glass liner of the autoclave; 3×10^{-4} mole of catalyst, 0.03 mole of promotor, 0.3 mole of methanol, and 1 mole of benzene solvent were used. The liner was placed in the autoclave and the reactor was leak-tested, heated to the desired reaction temperature, and pressurized with CO. Samples were drawn periodically and analyzed with a Hewlett–Packard 5750 gas chromatograph interfaced to a Hewlett–Packard 5930A mass spectrometer.

In the first experiments, methyl tosylate,

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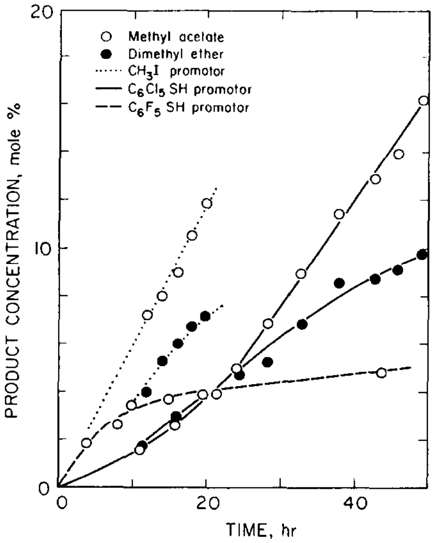

Fig. 1. Comparison of promotors of the methanol carbonylation reaction: CH_3I (5.0 g) with $RhCl_3 \cdot 3H_2O$ (0.017 g) in CH_3OH (12.2 g) and benzene (90.1 g) at 95°C and 41.1 atm; C_6Cl_5SH (8.14 g) with $Rh(PPh_3)_3Cl$ (0.25 g) in CH_3OH (13.0 g) and benzene (84.0 g) at 189°C and 41.8 atm; C_6F_5SH (5.0 g) with $Rh(PPh_3)_3Cl$ (0.071 g) in CH_3OH (11.5 g) and benzene (90.0 g) at 227°C and 41.8 atm.

p-$CH_3C_6H_4SO_3CH_3$, was tested as a promotor for the methanol carbonylation reaction. Methyl tosylate was chosen because it has been mentioned in a patent (*8*) as a substitute for iodide promotors and because it has been reported that iodide and tosylate ions have similar leaving group character (*9*). This choice is based on the supposition of a mechanism involving rate-determining S_N2 attack by Rh on the methyl carbon:

$$Rh^{I} + CH_3X \rightleftharpoons [Rh^{III}\text{-}CH_3]^{+} + X^{-}.$$
$$X = I, \quad p\text{-}CH_3C_6H_4SO_3.$$

When such a mechanism is operative (cf. *10–12*), the effectiveness of a promotor CH_3X depends on the leaving group ability of X.

The results showed that methyl tosylate was ineffective as a promotor for methanol carbonylation. This ineffectiveness might be related to the hardness of the tosylate anion compared to iodide. Therefore, a softer promotor species was sought, and sulfur compounds seemed to be appropriate. Pentafluoro- and pentachlorobenzenethiol were chosen because they have been found to be promotors for the Rh(I)-catalyzed conversion of olefins, CO, and water into carboxylic acids (*8*). The electron withdrawing property of F and Cl makes the methyl derivatives, $C_6X_5SCH_3$, better alkylating agents than unsubstituted $C_6H_5SCH_3$, since $C_6X_5S^-$ has greater stability and, consequently, increased leaving group ability compared to $C_6H_5S^-$.

Pentafluoro- and pentachlorobenzenethiol are indeed effective promotors, as shown by the results of Fig. 1; the reaction conditions reported in the figure caption were chosen to give approximately equal rates of carbonylation reaction with CH_3I promotor, on the one hand, and with pentachlorobenzenethiol, on the other. It is clear that the two promotors behave similarly, although the latter is less effective. With each promotor, methyl acetate was the main product, and dimethyl ether was a side product. (The ether can be recycled and converted through methanol into the carbonylation product.) No detectable

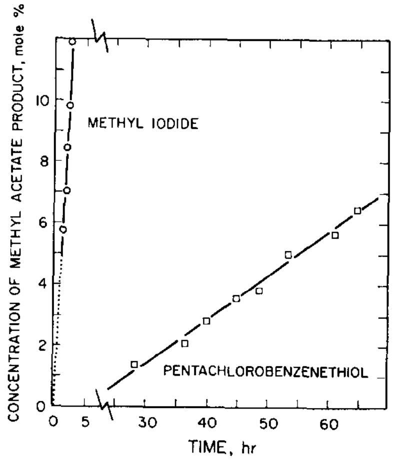

Fig. 2. Comparison of methyl iodide and pentachlorobenzenethiol promotors for Rh-complex-catalyzed methanol carbonylation at 156°C and 41.8 atm. CH_3I promotor (4.25 g) with $RhCl(PPh_3)_3$ (0.25 g) in CH_3OH (11.7 g) and benzene (88.0 g); C_6Cl_5SH promotor (8.48 g) with $RhCl(PPh_3)_3$ (0.25 g) in CH_3OH (12.0 g) and benzene (86.4 g).

quantities of other possible by-products, such as methane, CO_2, higher alcohols, and higher esters, were observed (*5*). Consequently, the results show that the selectivity with the new promotor is high and comparable to that with iodide promotors.

The effectiveness of the new promotors is less than that of methyl iodide. The data of Fig. 2 show that the rate of methanol carbonylation with pentachlorobenzenethiol at 156°C (after an induction period in which the actual promotor, $C_6Cl_5SCH_3$, and the active form of the catalyst are presumably formed) is about 4% of the rate with methyl iodide at that temperature.[1] To compensate for the lower activity, higher concentrations of pentachlorobenzenethiol and higher temperatures could be applied. The conditions would still be mild compared to those of older methanol carbonylation processes (*2*). The new promotor is expected to be relatively noncorrosive, since Cl^- ions are reportedly not formed from it (*8*). Since the boiling point of pentachlorobenzenethiol ($\cong$280°C) is much higher than that of any product of the carbonylation reaction, the promotor, along with the rhodium catalyst, could be easily separated from the products by distillation.

Analysis of the reactant solutions by gas chromatography/mass spectrometry showed that pentachlorobenzenethiol reacts with methanol to form methylthiopentachlorobenzene.

Pentafluorobenzenethiol was not as effective a promotor as pentachlorobenzenethiol (Fig. 1). The decrease in effectiveness of the former as the experiment progressed is attributed to the occurrence of a side reaction consuming the promotor:

$$CH_3OH + C_6F_5SCH_3 \rightarrow CH_3SH + C_6F_5OCH_3,$$

$$CH_3SH + CH_3OH \rightleftharpoons CH_3SCH_3 + H_2O.$$

Dimethyl sulfide was detected in the reactant solution, which provides confirmation of the above suggestion. Such a nucleophilic substitution on the aromatic ring is expected to be slower with $C_6Cl_5SCH_3$ than with $C_6F_5SCH_3$, corresponding to the smaller inductive effect of Cl compared to F. The analytical data confirm that such a side reaction did not occur appreciably with pentachlorobenzenethiol.

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[1] The nearly constant rates (after the induction periods) are consistent with the literature (*1, 6*), which indicates that the reaction is zero order in the reactants.