

**Preliminary communication**

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**Formate reduction of aldehydes using a photogenerated chromium carbonyl catalyst \***

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**Abstract**

The aldehydes RCHO (R = *p*-tolyl, *p*-anisyl, n-hexyl) are reduced to the corresponding alcohols RCH<sub>2</sub>OH by sodium formate in 95% aqueous methanol in the presence of a catalyst photogenerated from Cr(CO)<sub>6</sub>.

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The standard methods for reduction of aldehydes to the corresponding alcohols use complex metal hydrides such as LiAlH<sub>4</sub> or NaBH<sub>4</sub> [1]. However, recent developments in chromium carbonyl chemistry based on a mechanistic understanding of the water gas shift [2] and formate decomposition [3] reactions provide alternatives for aldehyde reduction including the stoichiometric use of HM(CO)<sub>5</sub><sup>-</sup> (M = Cr, W) [4] or H<sub>2</sub> in the presence of group 6 metal carbonyl derivatives [5,6]. This communication describes an operationally more convenient variation of this approach for aldehyde reduction where inexpensive formate is used as the stoichiometric reducing agent in the presence of a chromium carbonyl catalyst photogenerated from the commercially available Cr(CO)<sub>6</sub>. This method thus avoids the inconvenience of gaseous H<sub>2</sub> or stoichiometric metal carbonyl reagents.

In a typical experiment a Pyrex glass reaction vessel was charged successively with 1.7 g (25 mmol) of sodium formate, 0.03 g (0.136 mmol) of Cr(CO)<sub>6</sub>, and 50 ml of a 95% aqueous methanol solution containing 1.0 g (8.33 mmol) of *p*-tolualdehyde. After purging with argon, the mixture was irradiated at 60 ± 0.5 °C for 6 h with a Westinghouse 100 W Model H44-GS-100 mercury vapor flood lamp approximately 22 cm from the center of the reaction vessel. The reaction mixture was then treated with 50 ml of water and the product was extracted with three 20 ml portions of diethyl ether. The combined ether extracts were washed successively with 5% aqueous sodium bisulfite, saturated aqueous sodium chloride, and water

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\* Dedicated to Prof. Dr. E.O. Fischer in recognition of his seminal contributions to transition metal organometallic chemistry.

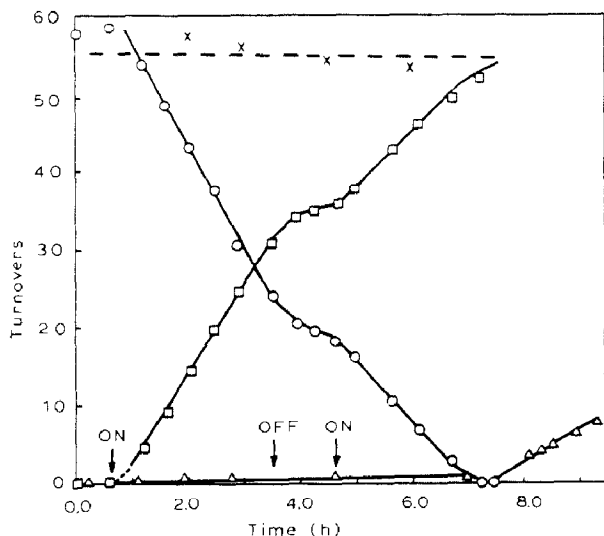


Fig. 1. Plot of *p*-tolualdehyde (expressed as turnovers, ○) consumed or *p*-methylbenzyl alcohol (expressed as turnovers, □) and hydrogen (expressed as turnovers, Δ) produced as a function of time; plot of the sum of the quantities of *p*-tolualdehyde and *p*-methylbenzyl alcohol (expressed as turnovers, ×) as a function of time. Catalyst solution:  $\text{Cr}(\text{CO})_6$  (0.148 mmol),  $\text{NaHCO}_2$  (13 mmol), *p*-tolualdehyde (8.6 mmol), 40 ml of 95% aqueous methanol under 1 atm. argon; temperature  $60 \pm 0.5^\circ\text{C}$ . The arrow indicates the time at which the solution was illuminated with a Westinghouse 100 W mercury spotlight.

and then dried over anhydrous magnesium sulfate. Removal of solvent from the dried ether extracts followed by sublimation at  $50^\circ\text{C}/0.1$  mmHg gave 0.61 g (60% yield) of *p*-methylbenzyl alcohol, identified by gas chromatography, NMR, and mass spectrometry.

Kinetic studies of these aldehyde reductions were carried out using an air-tight Pyrex glass reaction vessel having an internal volume of 83 ml. The progress of these reductions was monitored by gas chromatography using methods described in previous papers [2,3] for the gas phase analyses and a Varian 920 gas chromatograph with a 6 ft 80/100 mesh 10% OV-101 Chromosorb W-HP column for the liquid phase analyses. Examples of data obtained from the liquid phase analyses of the formate reductions of *p*-tolualdehyde and 1-heptanal are shown in Figs. 1 and 2, respectively, where turnovers are defined as moles product formed or substrate consumed per mole  $\text{Cr}(\text{CO})_6$ . These data indicate that these reactions are catalytic in both the amount of the  $\text{Cr}(\text{CO})_6$  catalyst precursor and the amount of light entering the system. In addition, such analyses indicate that the initial rates of alcohol formation by formate reduction of the diverse aldehydes  $\text{RCHO}$  ( $\text{R} = p$ -tolyl, *p*-anisyl, and *n*-hexyl) at  $60^\circ\text{C}$  using identical formate concentrations are the same within the experimental error (e.g.,  $256 \pm 18$  turnovers/day). This suggests that the rates of these reductions are coupled to the rate of formation of a common reducing species formed photolytically from  $\text{Cr}(\text{CO})_6$ , most likely  $\text{HCr}(\text{CO})_5^-$ , which is an intermediate in the water gas shift reaction cycle [2,3] and which has been shown [4] to be a stoichiometric reducing agent for the conversion of aldehydes to alcohols albeit under somewhat different conditions.

A number of interesting aspects of these aldehyde reductions are apparent from the data depicted in Figs. 1 and 2. The aromatic aldehyde, *p*-tolualdehyde, inter-

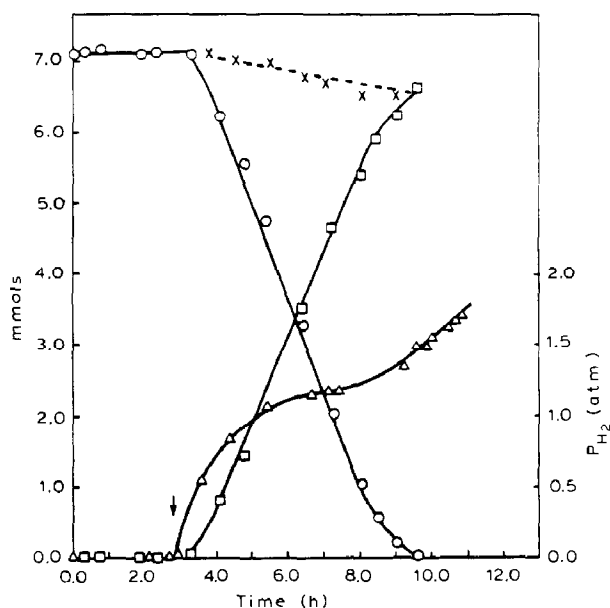


Fig. 2. Plot of 1-heptanal (expressed as mmol, ○) consumed or 1-heptanol (expressed as mmol, □) and hydrogen (expressed as atm, △) produced as a function of time; plot of the sum of the quantities of 1-heptanal and 1-heptanol (expressed as mmol, ×) as a function of time. Catalyst solution:  $\text{Cr}(\text{CO})_6$  (0.12 mmol),  $\text{NaHCO}_2$  (13 mmol), 1-heptanal (7.2 mmol), 40 ml of 95% aqueous methanol under 1 atm argon; temperature  $60 \pm 0.5^\circ \text{C}$ . The arrow indicates the time at which the solution was illuminated with a Westinghouse 100 W mercury spotlight. Data for hydrogen production, expressed in terms of partial pressure, are calculated from gas chromatographic measurements assuming ideal gas behavior using a void volume of 43 ml over the liquid phase within the reaction vessel.

cepts  $\text{HCr}(\text{CO})_5^-$  efficiently so that no  $\text{H}_2$  is produced from the water gas shift reaction cycle [2,3] as long as aldehyde reduction takes place (Fig. 1). Furthermore, the constancy of the sum of aldehyde and alcohol concentrations as indicated by the approximate horizontal line denoted by the symbols (×) in Fig. 1 indicates the absence of side reactions during the reduction of *p*-tolualdehyde. Figure 1 also shows that the reduction of *p*-tolualdehyde continues after termination of illumination at a progressively slower rate indicating the reversion of the photogenerated catalyst to its precursor. With the aliphatic aldehyde, 1-heptanal (Fig. 2), a small amount of hydrogen is seen to be produced in the early stages of the reduction suggesting that the aliphatic aldehyde, 1-heptanal, is less efficient than the aromatic aldehyde, *p*-tolualdehyde, in intercepting  $\text{HCr}(\text{CO})_5^-$ , the reducing species postulated above. In the case of 1-heptanal, a decrease in the sum of the aldehyde and alcohol concentrations occurs suggesting that side reactions, most probably aldol condensations, occur to a small extent as the reduction proceeds. In Fig. 1 it is seen that when the *p*-tolualdehyde is completely consumed (e.g., after 7.2 h)  $\text{H}_2$  production begins and continues for a least eight turnovers. This indicates that upon the exhaustion of *p*-tolualdehyde, the catalyst system responsible for *p*-tolualdehyde reduction smoothly switches modes to catalyze the decomposition of formate to produce  $\text{H}_2$  [2,3]. As might be expected, the rate of  $\text{H}_2$  production following the depletion of 1-heptanal in Fig. 2 is the same within experimental error as that found following the complete reduction of *p*-tolualdehyde ( $60 \pm 2$  turnovers/day).

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