Aldehydes *via* Palladium Catalysed Reductive Carbonylation of Esters

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Aldehydes are obtained in high selectivity *via* the low pressure, palladium catalysed reaction of esters and synthesis gas (CO–H_2).

The production of acetaldehyde from methanol and synthesis gas (CO–H_2) has been studied extensively in recent years.[1–6] The typical reaction, carried out at pressures exceeding 3500 p.s.i. and temperatures of 170—210 °C, employs an iodide promoter, a cobalt catalyst, and an optional cocatalyst, usually a group 8 metal. Acetaldehyde selectivities in excess of 85% can be obtained with by-products being ethanol, dimethyl ether, 1,1-dimethoxyethane, and methyl acetate. However, these high pressure, iodide promoted processes are highly corrosive, requiring equipment built from expensive materials. This detracts from the economic attractiveness for a route to acetaldehyde *via* current technology for reductive carbonylation of methanol. Either a high pressure, non-iodide promoted process or a low pressure ($\leq$1000 p.s.i.), iodide promoted process having high selectivity to acetaldehyde is desirable.

We report an alternative route which meets the above goal, *i.e.* a low pressure process for converting methanol into acetaldehyde *via* synthesis gas. It is based upon the reaction of methyl acetate and synthesis gas which ideally yields equimolar amounts of acetaldehyde and acetic acid, reaction (1).

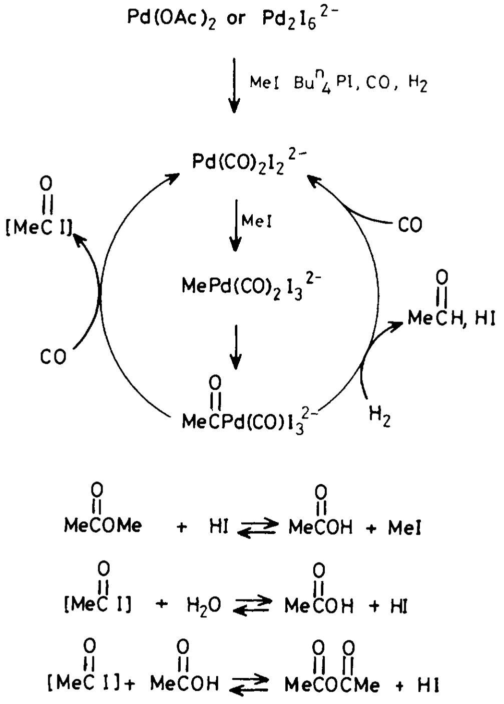
$$\mathrm{MeCO_2Me + CO + H_2 \longrightarrow MeCO_2H + MeCHO} \quad (1)$$

$$\mathrm{MeCO_2H + MeOH \longrightarrow MeCO_2Me + H_2O} \quad (2)$$

$$\mathrm{MeOH + CO + H_2 \longrightarrow MeCHO + H_2O} \quad (3)$$

The resulting acetic acid can be esterified with methanol and recycled as methyl acetate, reaction (2). The net reaction is the conversion of methanol into acetaldehyde *via* synthesis gas, reaction (3). Our low pressure methyl acetate–syngas reaction employs a catalyst based upon $Pd(OAc)_2$, MeI, and a cation such as R_4P^+, R_4N^+, or an alkali metal cation. High acetaldehyde selectivities are consistently obtained at 20% methyl acetate conversion. Prior reports show that cobalt–iodide[7] and palladium–iodide[8] catalyse the methyl acetate–syngas reaction. The cobalt–iodide catalyst gives high acetaldehyde selectivities but suffers from low reaction rates (8 mol MeCHO/mol Co/h), and high reaction pressures (5000 p.s.i.). Previous reports of the palladium–iodide catalyst indicate that acetaldehyde yields vary considerably depending upon reaction parameters, such as whether the reaction was run continuously or in the batch mode. Our palladium catalyst consistently gives acetaldehyde selectivities of 70—80% at 20% methyl acetate conversion. In contrast to the previous studies butyraldehyde is also obtained at higher methyl acetate conversions. In addition, we have extended this chemistry to ethyl acetate producing C_3 and C_6 aldehydes.

Using a catalyst prepared from $Pd(OAc)_2$ (15 mmol), MeI (60 mmol), and Bu_4PI (0.12 mol), 2.2 moles of methyl acetate were treated with CO–H_2 (1 : 1) in acetophenone, typically at 160 °C and 500—1000 p.s.i. Assuming that the acetic acid produced according to the stoicheiometry of reaction (1) is recycled, then acetaldehyde selectivities of nearly 80% are



Scheme 1. Proposed mechanism for the reductive carbonylation of methyl acetate.

Table 1. Representative data for the palladium catalysed reductive carbonylation of methyl acetate to yield acetaldehyde.[a]

I : Pd[b]	CO–H_2 pressure/ p.s.i.	*t*/h	% MeOAc[c] converted	% Product selectivities[d] AcH	C_3CHO	HOAc	Acetone	ETDA
30	565	1.5	24.4	58.4	0	21.8	6.6	13.2
30	1000	1.0	18.0	71.0	0	15.0	4.5	9.5
12	1000	1.0	16.0	79.4	0	18.2	0.4	2.0
12	1000	3.0	38.0	65.9	13.7	13.3	0.4	6.7

[a] Catalyst precursor $Pd(OAc)_2$ (15 mmol); promoters $Bu^n{}_4PI$, MeI; molar ratio cation: Pd = 8. Reaction carried out using 2.2 mol methyl acetate in acetophenone, 160 °C, 1 : 1 CO–H_2. [b] Mole ratios. [c] Methyl acetate conversion is expressed in mol%. [d] Product selectivities are expressed in mol%. AcH = acetaldehyde; C_3CHO = butyraldehyde, HOAc = acetic acid, ETDA = ethylidene diacetate.

obtained at 20% methyl acetate conversion. Observed by-products are ethylidene diacetate, acetone, and some acetic acid produced in excess of the stoicheiometry. At 40% methyl acetate conversion butyraldehyde is obtained, presumably *via* an *in situ* condensation of acetaldehyde. At this conversion level the total aldehyde selectivity still remains at nearly 80%. Typical turnover rates are 40 mol MeCHO/mol Pd/h. Representative data are shown in Table 1.

Both methyl iodide and a cation source, *e.g.* tetra-alkylphosphonium, tetra-alkylammonium, or an alkali metal cation, are necessary for the reaction to occur. The reaction is thought to involve Pd^0 and Pd^{II} carbonyl iodide anions as shown in Scheme 1. Methyl iodide can oxidatively add to a Pd^0 carbonyl iodide anion, yielding a Pd^{II} methyl carbonyl iodide complex. Carbon monoxide insertion into the Pd–Me bond yields a Pd acyl complex which reacts with H_2 forming acetaldehyde and HI, and regenerating the Pd^0 complex. The HI can react with methyl acetate generating acetic acid and methyl iodide which again reacts with the Pd^0 complex. The proposed reaction scheme is further supported by the fact that $Pd(OAc)_2$, MeI, and $Bu^n{}_4PI$ react at room temperature to give $[Pd_2I_6][Bu^n{}_4P]_2$. This palladium iodide dimer catalyses the reductive carbonylation of methyl acetate, giving results similar to $Pd(OAc)_2$. This palladium iodide dimer also reacts readily with CO (1 atm) at 27 °C yielding $[PdI_3(CO)][Bu^n{}_4P]$,[9] reaction (4). The reaction is readily reversed by N_2, indicative of a labile CO ligand.

$$[Pd_2I_6][Bu^n{}_4P]_2 \underset{N_2}{\overset{CO}{\rightleftharpoons}} 2[PdI_3(CO)][Bu^n{}_4P] \qquad (4)$$

The reaction of synthesis gas with methyl acetate can be extended to ethyl acetate, this reaction under similar conditions yielding propionaldehyde, 2-methylpentanal, propionic acid, ethyl propionate, and the stoicheiometric amount of acetic acid. Assuming that the acetic acid is recycled, then at 18% ethyl acetate conversion the product selectivities are 52% propionaldehyde, 10% 2-methylpentanal, 31% propionic acid, and 7% ethyl propionate. A total aldehyde selectivity of 62% has been obtained with ethyl acetate.

Thus, the low pressure palladium–iodide catalysed reaction of synthesis gas with methyl acetate and ethyl acetate offers a process for preparing C_2/C_4 aldehydes and C_3/C_6 aldehydes, respectively, in high selectivity. Since the acetate esters can themselves be produced from synthesis gas based chemicals, this chemistry offers a total synthesis gas route to C_2, C_3, C_4, and C_6 aldehydes.

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