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DIRECT SYNTHESIS OF ETHYLIDENE DIACETATE FROM METHYL ACETATE AND SYNTHESIS GAS BY MIXED RHODIUM-PALLADIUM CATALYST

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The direct hydrocarbonylation of methyl acetate to ethylidene diacetate by use of rhodium-palladium mixed catalysts with iodide and basic promoters in acetic acid solution was investigated at 160 °C under 200 kg/cm^2 of synthesis gas(H_2/CO=1/1). Conversion of methyl acetate up to 93% and yield to ethylidene diacetate as high as 68% were obtained.

Extensive studies on the synthesis of acetic anhydride($\underline{3}$) by carbonylation of methyl acetate($\underline{1}$) or dimethyl ether in the presence of transition metals have been carried out.$^{1)}$ In the prior art, ethylidene diacetate($\underline{2}$) was synthesized from acetic acid or by reacting acetaldehyde with $\underline{3}$.$^{2)}$ Much less is known about the direct hydrocarbonylation of $\underline{1}$ into $\underline{2}$ with synthesis gas although it is recently claimed that $\underline{1}$ or dimethyl ether gives $\underline{2}$ when treated with a rhodium or palladium compounds$^{3)}$ and rhodium-manganese,$^{4)}$ nickel-palladium,$^{5)}$ and nickel-cobalt mixed catalyst$^{6)}$ in the presence of iodide and organic bases. In these syntheses, however, the yields and selectivities of $\underline{2}$ were remain low. We found that $RhCl_3 \cdot 3H_2O$-$Pd(AcO)_2$ mixed catalyst system is greatly effective for the direct hydrocarbonylation of $\underline{1}$ to afford $\underline{2}$ (Eq.1) in the presence of organic bases and iodide promoters. Now we would like to report on some of the interesting findings that have been obtained.

$$\underset{\underline{1}}{2CH_3COOCH_3} \quad + \quad 2CO \quad + \quad H_2 \longrightarrow \underset{\underline{2}}{CH_3CH(OOCCH_3)_2} \qquad (1)$$

A typical reaction (run 15 in Table 1) was carried out as follow. A mixture of $Pd(AcO)_2$(6.54×10^{-2}mmol), $RhCl_3 \cdot 3H_2O$(5.81×10^{-2}mmol), MeI(4.81 mmol), n-Bu_3P(1.62 mmol), $\underline{1}$(24.62 mmol), and acetic acid(3 ml) as solvent were charged in a glass-tube placed in stainless steel autoclave(ca. 25 ml). After flushed with CO, H_2(100 kg/cm^2) and CO(100 kg/cm^2) were pressurized at room temperature. The temperature was raised to 160 °C within 25 min. After 4 h, the autoclave was cooled quickly with cold water to room temperature. The liquid products were analyzed by gas chromatography. In this system $\underline{2}$, $\underline{3}$ and acetic acid were the main products, and only minor amounts of acetaldehyde, methanol and propionic acid were formed.

In order to evaluate the relative catalytic activities of mixed catalysts, the hydrocarbonylation of 1 were carried out with various catalyst systems in the presence of methyl iodide(MeI) and tri-n-buthylphosphine(n-Bu_3P) in acetic acid solution, and the results were summarized in Table 1. Under the present conditions it is clear that the Rh-$Pd(AcO)_2$ system (runs 9-16) is a far superior precursor than the individual $RhCl_3\cdot3H_2O$ or $Pd(AcO)_2$ (runs 1,2), and that 2 and 3 can not be practically obtained in the absence of rhodium (run 2). In the Rh-Pd system, the rhodium analogues such as $Rh(CO)_2(acac)$, $RhCl(PPh_3)_3$, Rh_2O_3 and $Rh_6(CO)_{16}$(runs 9-12) are almost of the same activity with that of $RhCl_3\cdot3H_2O$ (run 15). On the other hand, when $PdCl_2$ or Pd-black was used as the souce of palladium cocatalyst (runs 7,8), their activities were much lower than that of $Pd(AcO)_2$ (run 16). A maximum yield of 2 was obtained at the $Pd(AcO)_2/RhCl_3\cdot3H_2O$ ratio of ca. 1, and the yield was decreased at either lower or higher ratio (runs 13-16). This reaction was

Table 1. Hydrocarbonylation of Methyl Acetate by Mixed Transition Metal Compounds a)

Run	Catalyst system	M/Rh	Conversion b)	Yield c)/mol%	
	Rh - M	mol/mol	of 1 / mol%	2	3
1	$RhCl_3\cdot3H_2O$		89.4	40.8	47.2
2	$Pd(AcO)_2$		32.9	4.6	0.7
3	$RhCl_3\cdot3H_2O$-$Co(AcO)_2\cdot4H_2O$	2.04	76.5	21.6	47.8
4	" -$Ni(AcO)_2\cdot4H_2O$	1.98	75.3	30.7	40.5
5d)	" -$RuCl_3\cdot3H_2O$	0.20	97.2	36.8	30.3
6	" -$H_2PtCl_6\cdot6H_2O$	2.40	73.6	24.8	55.1
7	" -$PdCl_2$	2.34	99.2	18.4	0.9
8	" -Pd black	2.22	98.7	3.0	2.0
9	Rh_2O_3 - $Pd(AcO)_2$	1.13	91.8	62.3	10.3
10	$Rh(CO)_2(acac)$-$Pd(AcO)_2$	1.24	92.6	68.1	5.3
11	$RhCl(PPh_3)_3$-$Pd(AcO)_2$	1.18	92.8	62.3	2.0
12	$Rh_6(CO)_{16}$ - $Pd(AcO)_2$	1.14	83.6	62.5	4.2
13	$RhCl_3\cdot3H_2O$ - $Pd(AcO)_2$	0.21	87.3	48.8	35.8
14	" - "	0.57	91.5	57.8	21.6
15	" - "	1.13	91.2	63.2	9.6
16	" - "	2.27	85.0	52.4	1.6
17e)	" - "	1.15	98.7	45.5	5.2
18f)	" - "	1.17	17.3	0	0.7

a) Rh=5.5-5.8×10^{-2} mmol, AcOMe=24.62 mmol, MeI=4.81 mmol, n-Bu_3P=1.62 mmol, AcOH= 3 ml, H_2/CO=100/100 kg/cm^2 at room temp, 160 °C, 4 h. b) (AcOMe consurmed/AcOMe charged)x100. c) Basedd on the theoretical amount of charged AcOMe. d) $RhCl_3\cdot3H_2O$=19.7×10^{-2} mmol, H_2/CO=100/160 kg/cm^2. e) I_2=2.38 mmol. f) KI=4.79 mmol.

strongly influenced by the experimental conditions, particularly by the nature and concentration of the iodide promoter which is essential to this reaction. MeI was found to be the most effective among the iodides examined. Moreover, the reaction was significantly affected by the ratio of MeI/n-Bu$_3$P and levelled off at excess amounts of MeI. Iodine was also effective (run 17), but potassium iodide was uneffective for the reaction, where MeI was not detected in the product solution.

The catalytic activity of RhCl$_3$·3H$_2$O-Pd(AcO)$_2$-MeI system for the reaction was largely improved by the addition of organic bases, such as n-Bu$_3$P and cyclic-tertiary amine. The results were summarized in Table 2. Among these basic promoters, n-Bu$_3$P gave the best yield of 2 when the molar ratio of n-Bu$_3$P/MeI was ca. 0.3 (run 10), and the further addition of n-Bu$_3$P decreased the yield of 2 (run 9) gradually. While, Ph$_3$P, Ph$_2$PCH$_2$CH$_2$PPh$_2$ and n-Bu$_3$N gave undesirable results (runs 6-8). This reaction was also controlled by the reaction temperature (runs 10-12) and the CO and H$_2$ partial pressure (runs 10,13,14). The selectivity of 2 increased with the increase in H$_2$ partial pressure reaching a maximum at a CO/H$_2$ ratio of ca. 1, despite CO/H$_2$ ratio of 2 in the stoichiometry of the synthesis. However the conversion and selectivity of 2 were less affected by the total

Table 2. Dependence of Products Distribution on the Type of the Base[a)]

Run	Base	H$_2$/CO[b)] kg/cm^2	Reaction temp/ °C	Conversion of 1/mol%	Yield/mol% 2	3
1	none	100/100	160	68.7	21.2	19.8
2	N-methyl-2·pyrrolidone	"	"	71.2	40.0	19.5
3	N-methylmorpholine	"	"	80.3	51.3	2.4
4	α-picoline	"	"	86.4	55.5	3.4
5	2,6-lutidine	"	"	77.1	57.8	10.5
6	n-Bu$_3$N	"	"	51.8	28.6	22.0
7	Ph$_3$P	"	"	75.9	37.6	32.0
8	Ph$_2$PCH$_2$CH$_2$PPh$_2$	"	"	32.2	2.1	21.5
9[c)]	n-Bu$_3$P	"	"	63.5	30.8	16.0
10	"	"	"	91.2	63.2	9.6
11	"	"	140	60.5	24.4	20.4
12	"	"	120	33.2	2.7	13.9
13	"	140/60	160	93.6	41.9	0.3
14	"	50/140	"	74.2	39.6	31.1
15	"	40/40	"	89.1	61.4	9.8

a) RhCl$_3$·3H$_2$O=5.5-5.8x10^{-2} mmol, Pd(AcO)$_2$=6.4-6.8x10^{-2} mmol, MeI=4.81 mmol, Base=1.62-1.68 mmol, See footnotes of Table 1. b) Initial pressure at room temp. c) n-Bu$_3$P/MeI=1.01 (mol/mol) pressure (runs 10,15).

In the reaction course, the major product at the early stage is 3 which gradually decreases accompanying an appearance of 2 and a small amount of acetaldehyde (≃5%). Therfore, this reaction presumably involves the following steps:

$$\underset{\underline{1}}{CH_3COOCH_3} + CO \longrightarrow \underset{\underline{3}}{(CH_3CO)_2O} \qquad (2)$$

$$\underline{3} + H_2 \longrightarrow CH_3CHO + CH_3COOH \qquad (3)$$

$$CH_3CHO + \underline{3} \longrightarrow \underset{\underline{2}}{CH_3CH(OOCCH_3)_2} \qquad (4)$$

Increase in the ratio of 2 to 3 as a function of $Pd(AcO)_2$ concentration suggests that the hydrogenolysis of 3 (Eq. 3) seems to be catalyzed mainly by the palladium cocatalyst.$^{7)}$ It has been reported that the catalytic hydrogenolysis of 3 to acetic acid and acetaldehyde takes place with synthesis gas in the presence of $Pd(AcO)_2$ as catalyst.$^{8)}$ Since, during the formation of 2, acetaldehyde was observed in only a small amount, it is likely to react rapidly with 3 to give 2 (Eq. 4).$^{9)}$ Therefore, the hydrogenolysis step (Eq. 3) is presumed to be the rate-determining. Work is now in progress to elucidate the detailed reaction mechanism.

References

1) M.Schrod and G.Luft, Ind. Eng. Chem. Prod. Res. Dev., 1981, 20, 649; G. Luft and M. Schrod, J. Mol. Cat., 20 (1983) 175; 22 (1983) 169.

2) T. Isshiki and T. Kondo, Japan Kokai (Mitsubishi Gas) 56-65844 (1981); 56-68643 (1981). C. G. Wan, Japan Kokai (Halcon) 54-98713 (1979).

3) N. Rizkalla and C. N. Winnick, German Patent (Halcon) 2610035 (1976).

4) H. K. Kubbeler, H. Erpebch, and K. Gehrman, Japan Kokai (Hoechst) 56-61324 (1981).

5) T. Isshiki, Y. Kijima, and T. Kondo, Japan Kokai (Mitsubishi Gas) 57-64644 (1982).

6) T. Isshiki, Y. Kijima, and T. Yasunaga, Japan Kokai (Mitsubishi Gas) 56-43241(1981).

7) 2 was obtained over 60% from 3 by using the $Pd(AcO)_2$-MeI-n-Bu_3P catalytic system at the present condition (3 h).

8) R. V. Porcell, German Patent (Halcon) 2952517 (1980).

9) J. W. Brocking and C. M. Bartish, ACS Div. Petrol. Chem. Preprint., 26 (3) 750 (1981).

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