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On the rhodium catalyzed formation of acetic acid from methyl formate – comparison with the rhodium catalyzed formation of acetic acid by direct carbonylation of methanol ¹

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Abstract

In presence of the homogenous Rh/Cr/I catalyst system methyl formate can be isomerized to acetic acid under CO-pressure with high conversion rates and excellent selectivity. This catalyst system has never been applied before for this reaction.

Keywords: Acetic acid; Carbonylation; Methanol; Methyl formate; Rhodium

1. Introduction

Experiments with carbon-14 labeled methyl iodide, formic acid, and carbon monoxide described in literature [2] have been the base for the assumption that the Rh/I catalyzed formation of acetic acid from methyl formate under CO pressure proceeds via decarbonylation of ester to methanol and subsequent carbonylation of methanol to acetic acid ([3], Monsanto process). It is shown that the results of these experiments are not conclusive and need some reinterpretation.

The basic differences between the Rh catalyzed routes of acetic acid by direct carbonylation of methanol and by isomerisation of methyl formate are discussed.

The experimental results presented here for the Rh/Cr/I catalyst system together with the findings for the Rh/Li/I catalyst system already known in the literature [1] suggest that the formation of acetic acid from methyl formate under CO pressure basically proceeds via the carbonylation of the ester to the mixed anhydride of formic and acetic acid (rds) with subsequent decomposition to acetic acid and CO. The formation of acetic acid from methyl formate via decomposition of methyl formate to methanol and CO with subsequent carbonylation of the methanol under CO pressure seems to be negligible with the Rh catalyst system.

2. Experimental

The experiments have been carried out in a 100 ml Hastelloy C autoclave with electrical heating, a magnetically coupled hoisting agitator, a ther-

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¹ Dedicated to Prof. Dr. M. Baerns on the occasion of his 60th birthday.

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Table 1
Conversion of methyl formate to acetic acid [4] and unpublished results

Example	Rh/Cr/I/P, g-at ratio ^a	mg-at Rh/mol m.f.	T, °C	P, bar	Activity g AcOH/g Rh·h	Conversion mol-%	Selectivity, mol-% AcOH/AcOMe
1	1/4.8/46.4/-	1.1	180	50	261 ^b	99.8	99.8
2	1/1/46.4/-	1.1	180	50	258	99.5	98/2
3	1/9.6/273/-	0.19	200	50	1520 (max.)	99.5 (max.)	99/1 (max.)
4	1/9.6/46.4/-	1.1 50% AcOH	180	12 (5 r.t.)	256	>99	97.5/2.5
5	1/4.8/23.2/-	1.1	180	50 (35 r.t.)	254	97.8	98.5/1.5
6	1/4.8/23.2/-	1.1	180	35 (20 r.t.)	221	88	92/8
7	1/4.8/11.6/-	1.1	180	50	14	8	37/62
8	1/4.8/11.6/-	1.1	200	50	262	99.9	99.9
9	1/4.8/23.2/-	1.1	180	50	317 (1 h)	63	92/8
Comparison examples:							
1	1/-/46.4/2	1.1	180	50	173	68.5	93.1/6.7
2	1/-/46.4/-	1.1	180	50	49	27.0	58.1/21.1
3	1/4.8/20.2/-	1.1	180	50	13	15.5	8/47

^a Rh = RhCl₃·3H₂O; Cr = Cr(CO)₆; I = CH₃I (comparison example 3: 57% HI solution in water); P = PPh₃.

^b Apparent activity due to excess reaction time; real activity approximately 380 g AcOH/g Rh·h.

mowell, a pressure gauge, and a connection for pressurizing the reactor with CO and depressurizing. Standard procedure was as follows (Table 1, example 1):

After carefully flushing the autoclave with nitrogen and filling in methyl formate (41 g, 683 mmol), rhodium trichloride trihydrate (0.2 g, 0.76 mmol), hexacarbonyl chromium (0.8 g, 3.6 mmol), and methyl iodide (5 g, 35.2 mmol) the autoclave was closed in a pressure-tight manner, flushed and pressurized with carbon monoxide (35 bar), then heated up to reaction temperature (180°C) within 0.75 h. The reaction pressure was adjusted to 50 bar by a slight addition of carbon monoxide and the reaction performed under vigorous agitation for two hours. After finishing heating and quenching the system to room temperature within 15 min by blowing compressed air into the heating jacket the autoclave was depressurized by a gas scrubber.

After addition of a defined amount of 1.4 dioxane as an internal standard the liquid reaction discharge and the scrubber content were analyzed by gas chromatography.

3. Results

When testing different metals as additional promoters for the Rh/I catalyzed system chro-

mium compounds proved to increase conversion rate and selectivity [4] of the conversion of methyl formate to acetic acid more efficiently than a P promotor, such as triphenyl phosphine (Table 1, example 1, comparison examples 1 and 2) which is preferred normally.

The use of some ionic Cr compounds (CrCl₃·6H₂O, Cr(III) acetylacetonate, Cr(III) acetate) instead of the hexacarbonyl gave similar results. Experiments with reaction times of 1 and 1.5 h showed a slightly higher activity for the chloride and the acetate and a lower one for the acetylacetonate compared to the carbonyl. A slight decrease in activity resulted when lowering the Cr/Rh ratio to 1 (Table 1, example 2).

Under otherwise identical conditions of example 1 Mo(CO)₆ proved to be less active (selectivity 90%, conversion 50%) whereas other metal carbonyls (W(CO)₆, Fe(CO)₅, Co₂(CO)₈) acted as inhibitors compared even to the system without a second promotor (Table 1, comparison example 2).

A similar action of chromium compounds is well known from the carbonylation of methyl acetate to acetic anhydride in presence of a Rh/I catalyst system [5]. The role of chromium is not quite clear. A general assumption is that chromium reduces the induction period and facilitates

the generation of the active catalyst [6]. More specific conceivable actions of chromium are

- (i) formation of chromium iodide, CrI_2 , and subsequently of chromium formate, $(\text{HCOO})_2\text{Cr}$, or acetate, $(\text{H}_3\text{CCOO})_2\text{Cr}$, which together with acetyl iodide, CH_3COI , easily form the respective anhydrides finally yielding acetic acid similarly to the Rh/Li/I catalyst system [1]
- (ii) enhancement of the rhodium catalyst's nucleophilicity by coordination of an anionic ligand such as $[\text{CrX}_3]^-$, X being iodide, acetate, and formate, respectively.

If Ru or Pd are substituted for Rh (e.g., $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$) low yields during methyl formate conversion have been achieved. $\text{Os}_3(\text{CO})_{12}$ was inactive. Only $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ behaved similarly as Rh (86% conversion, 83% selectivity for acetic acid, 10% for methyl acetate and formic acid) but showed a tendency of decomposing the formate to methane (5%).

A high activity of the catalyst system Rh/Cr was achieved at 200°C (Table 1, example 3), but at low Rh concentrations as applied here, wall effects in the autoclave began to influence the reaction. Under standard conditions as described above the conversion still was almost complete at 170°C. This seems to be the minimum temperature required as at 160°C conversion dropped drastically to 10%. Contrasting this finding, the active catalyst for methanol carbonylation forms from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and acts already at 100°C and 6 bar CO [8].

Although not consumed in the reaction, CO is required for the formation and stabilization of the active catalyst. With neat methyl formate 10 bar CO at r.t. are sufficient for a smooth conversion whereas at 5 bar almost no reaction takes place and a black deposit forms. Addition of acetic acid to the initial mixture has a stabilizing effect thus enabling 5 bar initial CO pressure (Table 1, example 4). $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ shows good activity in the presence of acetic acid even at 1.5 bar CO (r.t.). With the common assumption that a Rh(I) species plays a role in the catalytic cycle this behaviour points to an important role of CO in the transfor-

mation of Rh(III) into Rh(I). Further, at lower concentrations of the iodine promotor CO shows some influence on activity (Table 1, examples 5, 6). The existence of an optimum of Rh/I ratio is shown in Table 1, examples 1, 5, 7, and 8.

$\text{LiI} \cdot 2\text{H}_2\text{O}$ and, more markedly, NaI and $\text{NaI} \cdot 2\text{H}_2\text{O}$, are less active halogen promotors. Part of the salt is converted into methyl iodide during the reaction. Substituting molecular iodine in example 1 for methyl iodide does not influence the result. I_2 was completely converted into CH_3I .

Surprisingly, using aqueous HI as promotor, which is the most favourable form for methanol carbonylation in the Monsanto process, resulted in low yields (Table 1, comparison example 3). The reaction mixture contained formic acid formed by hydrolysis in addition to the amount expected to be coupled with transesterification, as well as methanol only some of which had been carbonylated after 2 h reaction time. This behaviour was unexpected in light of previous reports on the reaction mechanism [2] especially as HI reacted to give CH_3I . This gave rise to a more detailed survey of the course of the reaction.

4. Qualitative interpretations

When conducting the experiments with Cr under appropriate conditions, methyl formate generally reacts almost quantitatively to form the desired acetic acid. Only small amounts, if any, of methyl acetate, formic acid, and methanol are present in the reaction mixture. Water is contained in the discharge in low concentration only (e.g., 25 mmol). The collected gas phase consists almost exclusively of carbon monoxide. Hydrogen, carbon dioxide, and methane are present in amounts of a few mmol only at best. Even at partial conversion concentrations of methyl acetate and formic ester in the mixture remain low (less than 10 mol-%; Table 1, example 9). This again contrasts the behaviour of methanol in the Monsanto process supporting the assumption that methyl acetate which unavoidably will form according to reaction (4) reacts further according

Table 2
Initial acetyl group formation ^a

Run no.	Catalyst	Pretreatment of methyl formate ^b	Rate of acetyl formation (mmol/h)
1	RhCl ₃ ·3H ₂ O	none	72
2		none	790
3		–W	66
4		+A (50% b.w.)	86
5		+A (1.2 g)	358
6		–W/ +A (1.2 g)	932
7		–W/ +M (0.5 g)	764
8	[Rh(CO) ₂ Cl] ₂	none	444
9		–W	910
10		–W/ –M	600; 440
11		–W/ +M (0.5 g)	604
12		–W/ –M/ +M (0.5 g)	522
13		+A (1.2 g)	580
14		–W/ +A (1.2 g)	896
15		–W/ –M/ +A (1.2 g)	472

^a Reaction conditions: standard procedure (Table 1, example 1); reaction time: 0.5 h (run no. 2: interval from 0.5 to 1 h).

^b none: technical grade methyl formate; –W: anhydrous methyl formate; –M: methanol (up to 2% in technical grade) removed; +M: methanol added; +A: acetic acid added.

to reactions (7) and (8) instead of (5) and (6) (see below). The latter route may gain importance under less favourable conditions.

Under the same conditions as in example 1 methanol reacted, judging from CO uptake, completely within one hour. The reaction mixture still contained 4% of methyl formate formed by side reaction carbonylation even after two hours. So the assumption of methyl formate conversion to acetic acid taking place via methanol carbonylation requires prior methanol formation by saponification or decarbonylation fitting with kinetics observed. For further clarification short duration experiments have been conducted (Table 2).

In addition following observations have been made:

- (i) No pressure rise by formate decarbonylation occurred whether reaction was fast or slow. No evolution of CO worth mentioning took place at 180°C under conditions which did not give conversion to acetic acid, e.g., under nitrogen atmosphere or in the presence of incomplete catalyst systems.

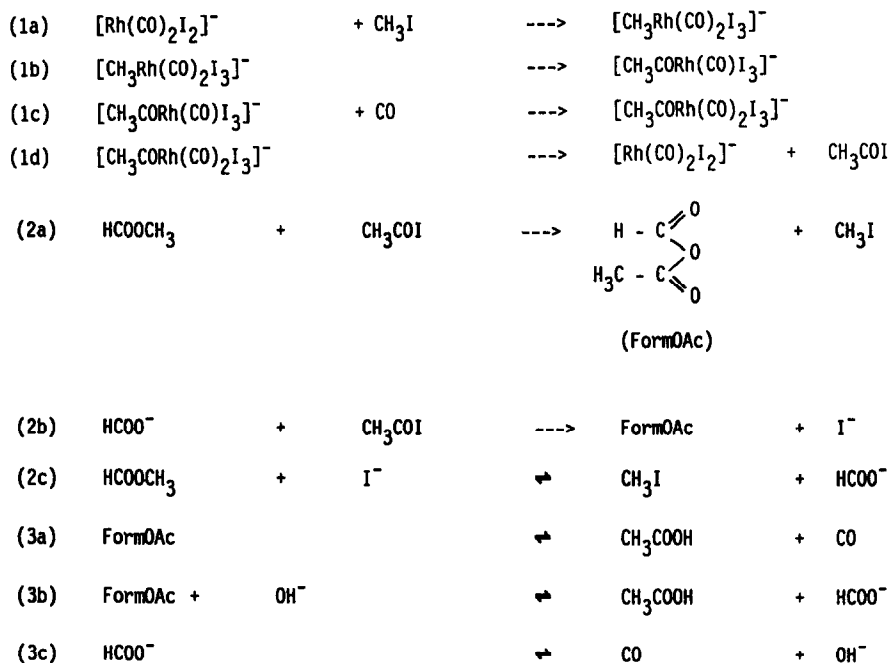
- (ii) Formic acid mixed with an equimolar amount of acetic acid quickly decomposed thermally and catalytically, under 1 bar N₂ as well as 50 bar CO initial pressure, to give CO and water already within the heating-up period. Under conditions typical for methyl formate conversion formic acid apparently is more stable as is shown by its presence in some % concentration during the reaction.

Repeating example 1 with addition of 5 g of water did not give an acceleration. After 45 min a pressure rise up to 85 bar followed by a slow decline to normal reaction pressure occurred. Similar behaviour ought to be effected by the presence of acetic acid but was not observed, either when it was added at the start or during its build-up in the course of the reaction.

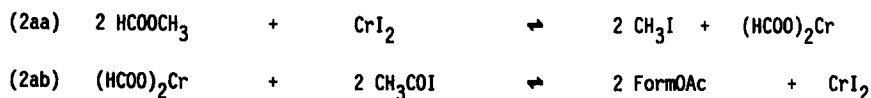
Table 2 demonstrates the influence of water, methanol and acetic acid. Due to time required for the formation of the active species the catalyst metal introduced as a Rh(III) salt displays an induction period with little activity (run no. 1) compared to reaction rate after half an hour from the start (run no. 2). Removal of water contained in technical grade methyl formate (run no. 3) and addition of 50% by weight of acetic acid (run no. 4) had no effect whereas a small amount of acid in technical grade (run no. 5) or particularly in anhydrous methyl formate (run no. 6) effected acceleration. Here methanol had the same effect (run no. 7).

This behaviour can be regarded as a result of solubility of the Rh salt in the initial mixture and of acidity on Rh(I) complex formation. Run nos. 5 and 6 indicate that absence of water is beneficial under conditions which bring about a quick formation of the active species.

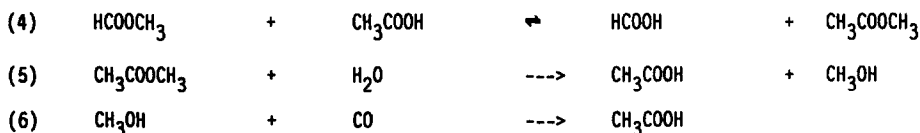
Using a Rh(I) complex which is believed to be of the same valence state as the active form, reaction rate is high from the beginning (run no. 8). Absence of water is clearly beneficial (run no. 9). Presence of small initial amounts of acetic acid in untreated (run no. 13), anhydrous (run no. 14), or methyl formate free of water and methanol (run no. 15) causes little difference to the counterpart run nos. 8, 9, and 10 without acid. Both, the addi-



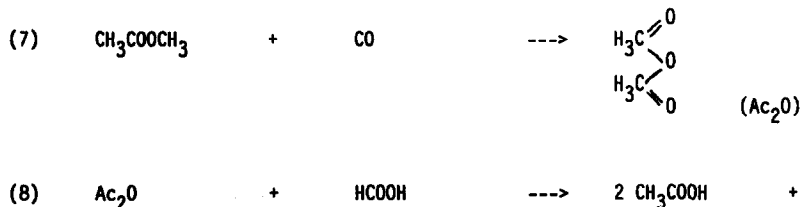
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

On the other hand the formate rearrangement under less preferred conditions which contrary to our findings reported above is accompanied by an intermediate build-up of methyl acetate and formic acid may involve in parallel reaction steps as described earlier.

6. Comparison with the formation of acetic acid by direct carbonylation of methanol

The direct carbonylation of methanol to acetic acid is well described in literature (e.g. [3]). In

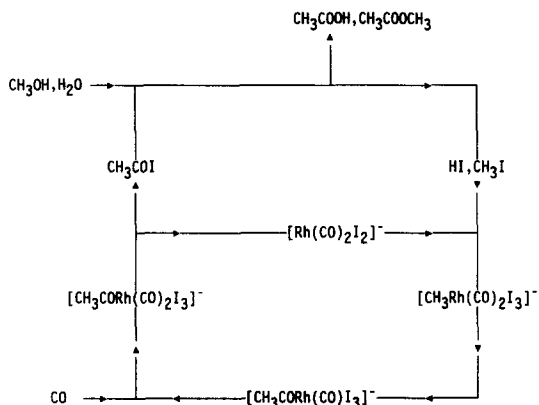
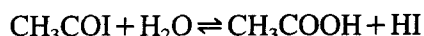


Fig. 2. Mechanism for the Rh catalyzed formation of acetic acid from methanol, water and carbon monoxide.

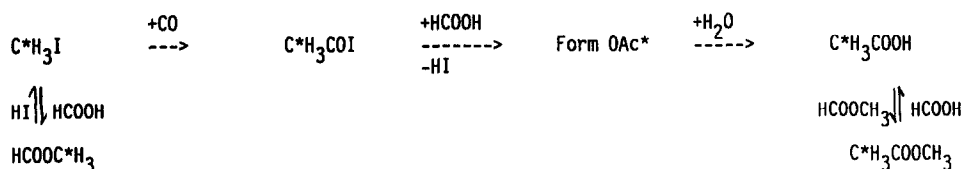
Fig. 2 the generally accepted catalytic cycle and reaction steps are shown.

The important difference when compared with the formation of acetic acid from methyl formate is that considerable amounts of methyl acetate are formed in the course of the reaction, and the presence of water is required to achieve a high reaction rate, acid yield and selectivity. The course of the reaction depending on water concentration is as follows:

at high water concentration:

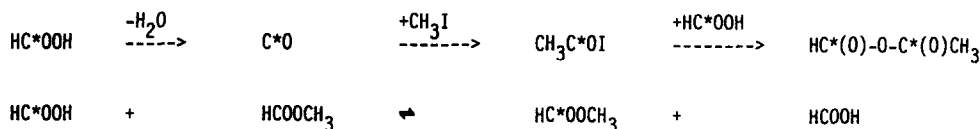


addition of C*H₃I



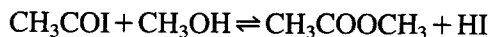
Scheme 6.

addition of HC*OOH



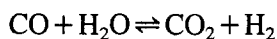
Scheme 7.

at low water concentration:



(comparatively slow further reaction to acetic acid)

In addition the Rh catalyzed water gas shift reaction is occurring: in presence of I⁻



From the results above we deduce that experimental results with carbon C-14 labeled methyl iodide, formic acid, and carbon monoxide published in [2] do not prove a mechanism starting with formate decarbonylation followed by methanol carbonylation.

Data as reported by Bryant et al. (see Table 3) are not compelling for this route but fit as well with reaction mechanisms as suggested by us in Schemes 6–8. Small amounts of C*H₃I as reported for a run with HC*OOH might have been generated by hydrogenation of C*O. This experiment is not a proof for methyl formate decarbonylation. It does not prove formic acid decomposition either as radioactivity can be transferred into formate by transesterification.

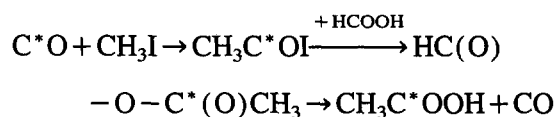
Table 3

Experimental results with carbon-14 labeled components initially present in methyl formate converted to acetic acid in presence of Rh/I from [2]

Run no	Methyl formate conversion	Original carbon-14 component	Amount of original carbon-14 in intermediates/products (%)			
			CH ₃ COOH + C H ₃ COOCH ₃	CH ₃ I	HCOO CH ₃	CO
1	15%	CH ₃ I	89	7	<1	<1
2 ^a	>99%	HCOOH	81	2	3	9
3	>99%	CO	91	0	<1	8

^a This run initially contained 50% acetic acid as solvent.

addition of C*O



Scheme 8.

The relatively high C* content in the products formed in the initial part of the reaction with C*O is easily explained by CO interchange mediated by the catalyst. The ensuing depletion in C*O of the gas phase can occur by reactions not involving formate decomposition.

7. Conclusion

The former statement [2] that rhodium catalyzed and iodine promoted formation of acetic acid from methyl formate under CO pressure proceeds via decarbonylation of the formate and subsequent carbonylation of the methanol generated

[3] does not seem to be conclusive and is not supported by experimental evidence as gained later with the catalyst systems Rh/Li/I [1] and Rh/Cr/I described above. It is more probable that acetic acid is formed via direct carbonylation of methyl formate yielding the mixed anhydride from which the acetic acid is formed.

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