

Homogeneous activation of the C–H bond in formates. Decarbonylation of formates to alcohols

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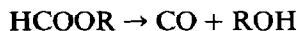
(Received November 24th, 1989)

Abstract

Triruthenium dodecacarbonyl in the presence of a basic phosphine catalyzes the decarbonylation of formates to the corresponding alcohols in high yield and with high selectivity. The reactions involving methyl and ethyl formate require the basic tricyclohexylphosphine. The reaction path is believed to involve oxidative addition of the C–H bond to the ruthenium cluster.

Introduction

The homogeneous organometallic chemistry of alkyl formates is a much growing research area owing probably to potential role of these species as a source of carbon monoxide, thus avoiding gas handling and reducing the cost involved in using carbon monoxide itself.



The decarbonylation process is believed to proceed via oxidative addition of a transition metal to the C–H bond of the formate [1]. However, until recently, no efficient catalytic systems were known. In stoichiometric reactions involving molybdenum [2] or nickel(0) complexes [3], CO is not evolved, but becomes fixed to the metal center as a ligand. Earlier catalysts were based on iridium [4] and rhodium [1, 5], but yields of alcohols were, generally low [4]. Very recently, independent reports from our group and a Japanese group simultaneously announced observation of catalysis of the decarbonylation reaction by ruthenium compounds [6,7]. The other group used the $\text{Ru}_3(\text{CO})_{12}/(\text{CH}_3)_3\text{NO} \cdot 2\text{H}_2\text{O}$ system [6], while we showed that $\text{Ru}_3(\text{CO})_{12}$ in the presence of tributylphosphine could efficiently catalyze the decarbonylation at atmospheric pressure [7]. Exceptions were the lower alkyl (methyl, ethyl) and benzyl formates which were also decarbonylated, but with only a moderate selectivity with respect to formation of the alcohol. We describe here in more detail the transformation of formate esters to carbon monoxide and the

corresponding alcohols. The case of methyl formate is of particular interest because this ester is more increasingly considered as a versatile intermediate for the selective synthesis of important industrial compounds [8,9].

Experimental

Starting materials

Triruthenium dodecacarbonyl and 1,2-bis(diphenylphosphino)ethane were purchased from Aldrich, ruthenium acetylacetonate from Johnson–Matthey, and the other catalysts, as well as tributyl- and tricyclohexyl-phosphine from Fluka. The remaining phosphines were made in this laboratory. The formates were either commercially available or were prepared (i-butyl, 2-methylpropyl, n-pentyl, i-pentyl, n-heptyl, cyclohexyl) by esterification of the corresponding alcohol with formic acid. As an example, formic acid (6 ml) and 2-butanol (7 ml) were placed in a 50 ml round bottom flask and heated under reflux for 24 h. The mixture was added to an excess of a saturated aqueous sodium hydrogen carbonate. When evolution had ceased the organic layer was washed with a saturated sodium chloride and dried over anhydrous sodium sulfate. Distillation gave 2-methylpropylformate with a purity of 98.5%.

Catalytic reactions

In a typical experiment, the formate (20 mmol), the catalyst (0.08 mmol), the phosphine (0.16 mmol), and diglyme (GC standard, 2 mmol) were placed in a stainless steel vessel fitted with a manometer. The vessel was closed, placed on a magnetic stirrer plate and heated to 180 °C. The increase in CO pressure was monitored during 10. The vessel was then cooled and vented and a gas sample taken for analysis. The vessel was opened and the liquid phase removed and analyzed by GC under the following conditions: (i) for the lower formates (C₁ to C₄) Hayesepp S, 2.5 m, diam. 1/8", 80–100 mesh, 50–240 °C, 4 °C/min; (ii) for the other formates, OV 351 10% on Chromosorb PDMCS, 80–100 mesh, 3 m, diam. 1/8", 50–220 °C, 4 °C/min.

Results

Decarbonylation of n-butyl formate was selected as the reference reaction. A series of experiments were carried out in order to establish the effects and the nature of the catalyst and of the added ligand, as well as of other parameters such as temperature and the catalyst/phosphine ratio. The case of methyl formate is considered separately later.

1. Catalyst effect

The effect of the catalytic system is shown in Table 1. The reactivity of n-butyl formate was very low in the absence of catalyst and phosphine (runs 1, 6). The iron, cobalt and the molybdenum catalysts showed low activity even in the presence of tributylphosphine (runs 3–5). It is clear that the reaction is greatly affected by the type of ruthenium catalyst used. Most of them led to very moderate yields of n-butanol (entries 10–13). In contrast Ru₃(CO)₁₂ and Ru(acac)₃ showed a high efficiency; the conversion of formate was 85–90%, with a ca. 70% yield of the

Table 1

Decarbonylation of n-butyl formate. Effects of variation of the catalyst and the phosphine ^a

Run	Catalyst	Phosphine	Conversion (%)	Alcohol, yield(%)
1	none	none	5	5
2	Fe(CO) ₅	PBu ₃	16	11
3	Co ₂ (CO) ₈	none	12	7
4	Co ₂ (CO) ₈	PBu ₃	24	11
5	Mo(CO) ₆	PBu ₃	17	7
6	none	PBu ₃	10	7
7	Ru ₃ (CO) ₁₂	PBu ₃	85	71
8 ^b	Ru ₃ (CO) ₁₂	PBu ₃	82	79
9	Ru(acac) ₃	PBu ₃	90	68
10	RuCl ₃ ·xH ₂ O	PBu ₃	19	8
11	RuCl ₂ (PPh ₃) ₃	PBu ₃	28	17
12	Ru(CO) ₂ Cl ₂ (PPh ₃) ₂	PBu ₃	12	12
13	RuO ₂	PBu ₃	nd	8
14	Ru ₃ CO ₁₂	none	65	39
7	Ru ₃ (CO) ₁₂	PBu ₃	85	71
15	Ru ₃ (CO) ₁₂	PPh ₃	69	45
16	Ru ₃ (CO) ₁₂	dppe	34	34
17	Ru ₃ (CO) ₁₂	Ph ₂ PN(Me)Ph	28	20
18	Ru ₃ (CO) ₁₂	Ph ₂ PN(Me)(C ₆ H ₁₁)	29	22

^a Formate (20 mmol), catalyst (0.08 mmol), phosphine (0.16 mmol), 180 °C, 10 h. ^b Water was added (28 mmol).

alcohol, which was the only liquid produced. The gas analysis revealed CO (95%) and a small amount of CO₂ possibly originating from decarboxylation of the formate [6]. Only a trace of butane was found.

The effect of phosphines was investigated with Ru₃(CO)₁₂ as the catalyst. It is well known that phosphines influence the catalytic activity through steric effects

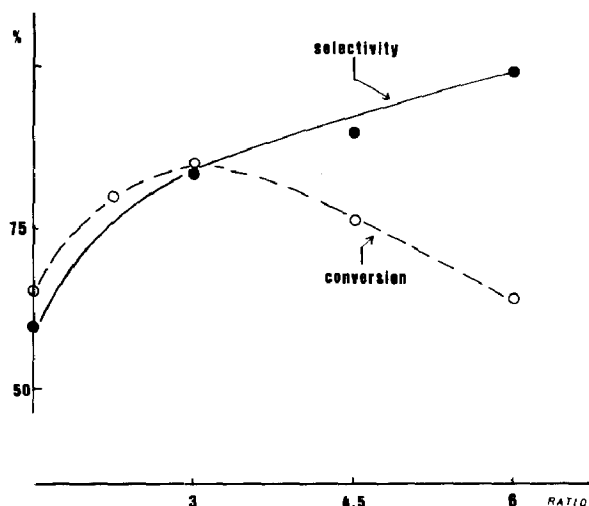


Fig. 1. Decarbonylation of n-butyl formate to n-butanol. Effect of the molar phosphine catalyst ratio (*T* 180 °C, other experimental conditions in text).

Table 2

Decarbonylation of n-butyl formate. Temperature effect ^a

<i>T</i> (°C)	Conversion (%)	Alcohol selectivity (%)
160	50	98
180	85	84
200	95	78

^a Ru₃(CO)₁₂ (0.08 mmol), P(C₄H₉)₃ (0.16 mmol), *t* (10 h).

(ligand cone angle) and through an electronic effects [10] that determine the basicity of the ligand [11].

The catalyst/phosphine ratio is of importance (Fig. 1). Thus conversion of the formate increases with increasing phosphine concentration up to a phosphine/catalyst ratio of 3/1. In contrast, the selectivity progressively increases as the ratio is increased, and with a 9/1 these is 100% conversion of the to n-butanol.

2. Temperature effect

The effect of this parameter is shown in Table 2. The decarbonylation proceeds even at temperatures below 150 °C, though slowly. Higher temperatures promote the reaction, but at the expenses of selectivity. A compromise was reached at a temperature of 170–180 °C, which gave good conversion and selectivity.

3. Extension to the decarbonylation of alkyl formates

The system Ru₃(CO)₁₂/PBU₃ was used to decarbonylate other alkyl formates (Table 3).

It is noteworthy that the activity of the catalyst is almost constant regardless of the alkyl part of the formate, apparently suggesting that the catalytic activity operates, at least in a first step, at the C–H bond of the formate rather than at the C–O bond of the alkoxy moiety. However, there is an induction period that depends on the formate and is characterized by the absence of CO production. For methyl,

Table 3

Activity of Ru₃(CO)₁₂/PBU₃ in the decarbonylation of alkyl formates

Alkyl formate	Activity ^b	Alcohol selectivity (%)
CH ₃	121	49
C ₂ H ₅	107	80
n-C ₃ H ₇	104	90
n-C ₄ H ₉	107	95
i-C ₄ H ₉	117	97
CH(CH ₃)C ₂ H ₅	130	86
n-C ₅ H ₁₁	116	100
i-C ₅ H ₁₁	126	91
C ₇ H ₁₅	115	97
Cyclohexyl	105	92

^a Ru₃(CO)₁₂ (0.2 mmol), P(C₄H₉)₃ (0.6 mmol), *T* (180 °C), *t* (8h). ^b Mol formate reacted/mol catalyst⁻¹.

ethyl and n-propyl formate, there is no detectable induction period. Production of CO starts after 0.3 h for i-propyl formate, 0.5 h for the n-butyl, 6 h for the i-butyl 1 h for the n-pentyl, 3 h for the n-heptyl, and 4 h for the cyclohexyl ester.

The selectivity with respect to the alcohol is high, as we reported previously, except for methyl formate [7]. The side product is CO₂, and alkanes and alkenes are detected only in very small amounts. No dehydrogenation of the alcohol to the corresponding aldehyde occurs under these conditions, which accounts for the excellent selectivity. Comparison of these results with those obtained by the Japanese group [6] makes clear that the simpler catalytic system we used leads to much higher turnover numbers with better selectivity, and is of more general use since it decarbonylates with similar efficiency secondary alkyl formates, and there is no need for a solvent.

4. Decarbonylation of methyl and ethyl formate

As shown in Table 3, methyl formate is not selectively decarbonylated to methanol. Since the C₁ ester is the most accessible and so the most widely used formate, it was important to find a suitable method of improving the selectivity. The efforts were focused on the basicity of the ligand and the medium. Increase in the phosphine: catalyst ratio resulted only in a small increase in the selectivity. Replacing PBu₃ by pyridine had little effect, but combination of the phosphine with pyridine was more successful, and methanol was produced in 70% yield with good selectivity (88%). An even better result was obtained with the more basic tricyclohexylphosphine (PCx₃) (75% yield and 96% selectivity). It should be observed that whatever the nature and concentration of the ligand, the rate of conversion of the formate remains almost constant. In the presence of PCx₃, ethyl formate was also decarbonylated with excellent yield and selectivity (Table 4).

Discussion

An earlier report presented two possible decarbonylation mechanisms for iridium catalysts [4]; one involving oxidative addition and the other formylation of the metal complex. The second alternative was favoured by Alper [4]. IR analysis of the residues in our reactions or of the solution after reaction revealed bands at 2057, 2049, 2013, 1985, 1940 cm⁻¹ for the Ru₃(CO)₁₂/PBu₃ catalyzed reaction, and 2048,

Table 4
Decarbonylation of methyl and ethyl formate^a

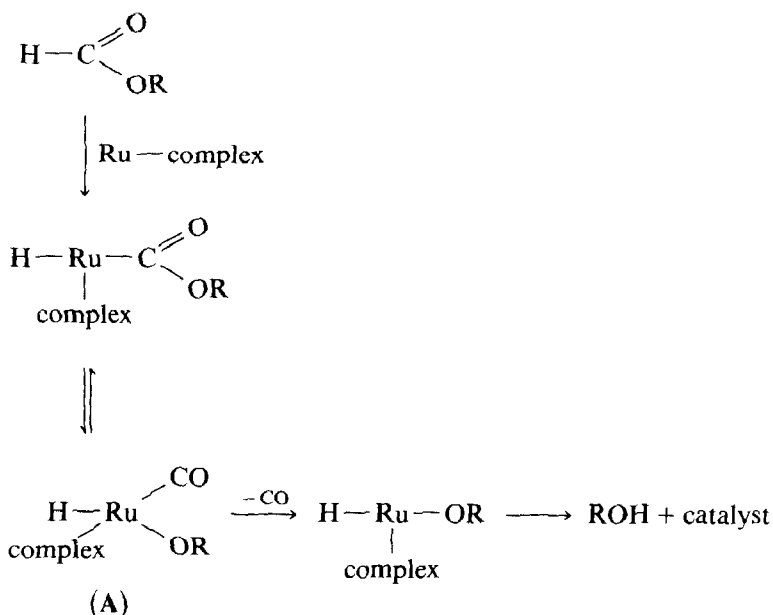
Formate	Ligand ^b (mmol)	Formate conversion (%)	Yield of alcohol (%)
Methyl	PBu ₃ (0.24)	80	40
Methyl	PBu ₃ (1.20)	79	52
Methyl	pyridine (6.20)	78	53
Methyl	pyridine (6.20) + PBu ₃ (1.20)	80	70
Methyl	PCx ₃ (1.20)	78	75
Ethyl	PBu ₃ (0.24)	74	59
Ethyl	PCx ₃ (1.20)	83	83

^a Formate (42 mmol), Ru₃(CO)₁₂ (0.08 mmol), 180 °C, 10 h. ^b PCx₃ = tricyclohexylphosphine.

2015, 1980, 1939 cm^{-1} for the $\text{Ru}(\text{acac})_3/\text{PBu}_3$ system. While some of the bands could arise from $\text{Ru}_3(\text{CO})_{12}$ (2057, 2013 cm^{-1}) [12], there is no evidence for the presence of monomeric $\text{Ru}(\text{CO})_5$ species (2036, 2000 cm^{-1}) [13], and the other bands could possibly be attributed to the complex ruthenium hydride $[\text{HRu}_3(\text{CO})_{11}]^-$ (2015, 1985, 1945 cm^{-1}) [14], which was shown to be the active species in the forward reaction, which however occurred only under high CO pressures [15]. However, the absence of hydrogen as well as the lack of a suitable counter-ion does not support this attribution, and we suggest that the bands arise from a $\text{Ru}_x(\text{CO})_y(\text{PR}_3)_z$ species. When the corresponding reaction was carried out with the $\text{Ru}_3(\text{CO})_{12}/\text{PPh}_3$ system, IR bands were present at 2047, 1996, 1990 and 1960 cm^{-1} , which may arise from a specific complex of the type $\text{Ru}_x(\text{CO})_y(\text{PPh}_3)_z$ [12,16].

The role of phosphines is to modify the character of the metal-carbon bond [17]. The results of Table 1 show that the order of reactivity parallels the order of basicity. Tricyclohexyl-phosphine is more basic (and so a better σ -donor) than tributylphosphine, which in turn is more basic than triphenylphosphine. It also has been shown previously that enhanced catalyst activity is correlated with increased stability of the phosphine, which contributes to the overall stability of the catalyst system [18]. The results with the phosphines used in this work are in accord with this correlation, as well as with a previous observation that an increase in the basicity of the ligand results in an increase in rate of oxidative addition [19,20]. That observation, considered together with our results on the effect of phosphines on the decarbonylation rate, favours the oxidative addition pathway.

We, therefore, suggest that the $\text{Ru}_3(\text{CO})_{12}/\text{PR}_3$ catalyzed decarbonylation of formates involves oxidative addition of the C-H bond in the formate to the



Scheme 1

ruthenium cluster, followed by CO migration and decarbonylation to the alcohol (Scheme 1).

This scheme shows some analogy with that suggested for rhodium-catalyzed C–H bond cleavage in ethyl formate [1]. The existence of an induction period that depends on the alkyl group of the formate suggests that the rate-determining step is the decarbonylation of the ruthenium entity (A). Although at the end of the reaction, polynuclear complexes seem to be present (*vide supra*), it is not possible to decide whether mononuclear or cluster-like species are active catalyst precursors. Catalysis by metal clusters has indeed been established for several processes [21]. In fact, Ru–Ru bond fission occurs less easily than replacement of carbonyl ligands by phosphines [22].

Conclusion

The ruthenium cluster $\text{Ru}_3(\text{CO})_{12}$ in association with a basic phosphine in an appropriate ratio is a very efficient catalytic system for the decomposition of alkyl formates to alcohols and carbon monoxide. Even methyl formate is decarbonylated with high conversion. The result is important in connection with the possible use of formates as generators of carbon monoxide.

Acknowledgments

We acknowledge the skillful assistance by Ms. S. Libs-Konrath and E. Schleiffer with GC analyses and Dr. R. Bender with recording of IR spectra, and thank Dr. B. Dilworth for improvement of the English.

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