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Homogeneous Decarbonylation of Formate Esters Catalyzed by Vaska's Compound

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Vaska's compound, chlorocarbonylbis(triphenylphosphine)iridium(I), can catalyze the decarbonylation of formate esters to alcohols and carbon monoxide. The reaction proceeds at atmospheric pressure and at 160–240 °C, depending on the reaction conditions (i.e., solvent, open vs. closed system).

There has been considerable interest in recent years in the chemistry of formate esters.[2] The conversion of methyl formate to methane and carbon dioxide is particularly favorable from a thermodynamic point of view.[3] A more desirable transformation is the generation of carbon monoxide and an alcohol from a formate ester. Carbon monoxide can, in this manner, be obtained in high purity,[2] and the alcohol can be utilized for subsequent reactions.

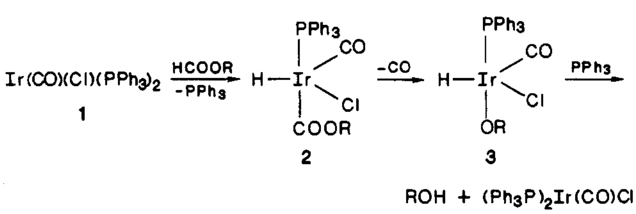
A number of methods exist for the decarbonylation of formate esters. Heterogeneous catalysts such as palladium on carbon[4] and Raney nickel[5] are known but, with one exception, alcohol yields are low. Copper complexes containing an acid anion (e.g., $CF_3SO_3^-$) and carbonyl, phosphine, or phosphite ligands react with formate esters, preferably in the presence of an iodine containing promoter, to give the alcohol and carbon monoxide, but a pressure of 10 atm is required in this case.[6] The decarbonylation of formate esters can also be achieved by using an amidine (e.g., 1,5,7-triazabicyclo[4.4.0]dec-5-ene) or a Lewis base and an epoxide (e.g. triethylamine–propylene oxide). Again, high pressures (63–76 atm) are necessary for this reaction.[7]

It seemed conceivable to us that the decarbonylation of formates could be attained under mild conditions (i.e., atmospheric pressure) using homogeneous catalysis. We now wish to report that Vaska's compound, chlorocarbonylbis(triphenylphosphine)iridium(I), is an effective catalyst for the conversion of formate esters to alcohols and carbon monoxide.

Results and Discussion

When *n*-octyl formate was heated for 48 h at 180 °C, in the presence of Vaska's compound (1), *n*-octanol was obtained in 64% yield, the remainder being recovered starting material. The ratio of substrate to catalyst was 130:1, with the formate functioning as both reactant and solvent. If the reaction is carried out in an autoclave instead of an open system, the yield of alcohol is less and appreciable quantities of *n*-octyl ether, octenes, and octane are formed as well (see Table I for reaction conditions and product distribution). That is, the conversion of *n*-octyl formate to products is greater in a closed than in an open system, but the process is significantly less selective by using an autoclave. It is noteworthy that the yield of octanol decreases with increasing reaction time (i.e., 39% after 6 h; 38% after 10 h; 18% after 23 h), when a closed system is used. To determine whether some of the reaction byproducts arise from subsequent reactions of the formed alcohol, *n*-octanol was exposed to the iridium(I) catalyst [120:1 n-$C_8H_{17}OH/Ir(I)$] at 240 °C for 20 h in an autoclave, giving 4% *n*-octyl ether, 3% of the aldehyde, less than 2% each of octane and octenes, and 61% starting material, with the remainder being unidentified. Mesitylene is a better solvent than *N*,*N*-dimethylformamide for the decarbonylation of *n*-octyl formate, but xylene is superior to both of these solvents. With xylene in a open or closed system, one can obtain octanol in yields comparable with those realized by using neat conditions. The use of an argon atmosphere instead of nitrogen for the closed system is of little consequence in terms of product distribution.

Scheme I



p-Toluenesulfonic acid has a detrimental effect on formate decarbonylation, as does added triphenylphosphine or tri-*o*-tolylphosphine. Similarly, replacement of the triphenylphosphine ligands in Vaska's compound by the more basic methyldiphenylphosphine or by triphenylarsine results in poor conversions of *n*-octyl formate. Other catalysts which are quite ineffective include the dimer of chloro(1,5-hexadiene)iridium, and chlorocarbonylbis(triphenylphosphine)rhodium(I).

The results for the decarbonylation of a series of formate esters, catalyzed by Vaska's compound, are listed in Table II. Alcohols were obtained in quite good yields from formates bearing primary alkyl groups (except methyl formate which affords methanol in low yield). The secondary formates, 2-heptyl and 2-octyl formates, do undergo decarbonylation with elimination products also formed in the case of the octyl system. Benzyl alcohol was obtained in up to 32% yield from benzyl formate, the main byproduct being toluene. The latter is formed in good yield by using the rhodium analogue of Vaska's complex as the catalyst. A byproduct of this reaction is dibenzyl. Neither dibenzyl nor toluene appear to arise via a radical pathway

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Table I. Decarbonylation of *n*-Octyl Formate

cat.	formate/ cat. ratio	solv[a]	reactn time, h	temp, °C	reactn system[b]	yield of octanol, %	recovered octyl formate, %	other products, %
1	130		48	180	O	64	36	
	130		6	240	C	39	41	octyl ether, 4
	130		10	240	C	38	22	octyl ether, 16 octenes, 13 octane, 6
	130		23	240	C	18	4	octyl ether, 13 octenes, 16 octane, 24
	130	I	45	165	O	43	57	
	130	II	48	160	O	23	77	
	130	II	72	160	O	40	60	
	60	III	48	160	O	57	24	octyl ether, 7 octenes, 6
	60	III	10	200	C	53	47	
	60	III	24	200	C	61	13	octyl ether, 5 octenes, 16
	60	III	24	200	C[c]	62	10	octyl ether, 13 octenes, 15
	60	III	48	200	C	48	7	octyl ether, 9 octenes, 28
	60[d]		18	180	O	27	11	octyl ether, 57
	60[d]		36	180	O			octyl ether, 88
	60[e]		48	180	C	16	81	
	120[f]		40	180	C	21	79	
$Ir(CO)(Cl)(PMePh_2)_2$	120		48	180	O	16	70	octenes, 2
$Ir(CO)(Cl)(AsPh_3)_2$	60		48	180	C	11	89	
	60	III	24	200	C	6	94	
$Rh(CO)(Cl)(PPh_3)_2$	120		36	180	C	13	87	
$[(1,5\text{-COD})IrCl]_2$	60	III	48		O	19	75	octyl ether, 3 octanal, 3
	60	III	16	200	C	17	83	
	60	III	24	200	C	19	81	
	60	III	48	200	C	23	77	

[a] I = mesitylene; II = *N,N*-dimethylformamide; III = xylene. [b] O = open system; C = closed system (i.e., autoclave—no applied pressure). [c] Argon atmosphere. [d] Added *p*-toluenesulfonic acid. [e] Added PPh_3 (10:1 ratio of PPh_3/Ir). [f] Added tri-*o*-tolylphosphine (10:1 ratio of phosphine/Ir).

Table II. Decarbonylation of Formate Esters (Neat)

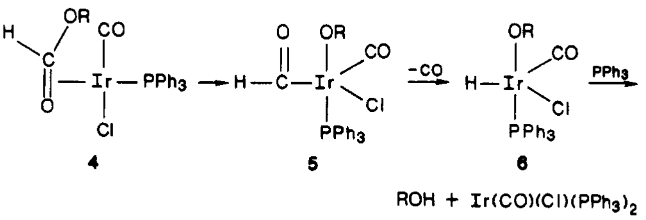
HCOOR, R =	cat.	formate/ cat. ratio	reactn time, h	temp, °C	reactn system[a]	yield of alcohol,[b] %	recovered formate, %	other products, %
CH_3	1	120	72	180	C	8	92	
$n\text{-}C_4H_9$	1	120	48	180	C	42	58	
$t\text{-}C_4H_9$	1	120	24	200	C[c]	26	27	isobutylene, 47
$n\text{-}C_7H_{15}$	1	120	48	180	O	65	35	
$2\text{-}C_7H_{15}$	1	130	48	200	C[c]	41	59	
$n\text{-}C_8H_{17}$	1	130	48	180	O	64	36	
$2\text{-}C_8H_{17}$	1	130	24	200	C	49	30	octenes, 21
$PhCH_2$	1	130	8	180	C	32	32	toluene, 28 benzene, 2 benzaldehyde, 6
	1	130	19	180	C	9	9	toluene, 35 benzyl ether, 12 benzaldehyde, 14 benzene, 11
	$Ir(CO)(Cl)(AsPh_3)_2$	120	24	180	C	14	69	toluene, 10 benzyl ether, 2
	$Rh(CO)(Cl)(PPh_3)_2$	120	24	180	C	5	6	toluene, 63 benzaldehyde, 2 dibenzyl, 20

[a] O = open system; C = closed system (i.e., autoclave—no applied pressure). [b] The alcohols and other reaction products were identified by comparison of spectral data and GC retention times with those for authentic samples. [c] Xylene used as solvent.

since repetition of this reaction in the presence of di-*tert*-butyl peroxide, a good radical initiator, gave benzyl alcohol in 18% yield, benzaldehyde in 13% yield, only traces of toluene, and no dibenzyl (60% recovered $HCOOCH_2Ph$). Similarly, the presence of di-*tert*-butyl peroxide has a detrimental effect on the decarbonylation of octyl formate catalyzed by Vaska's complex (Table I, entry 1). The yield of octanol decreased to 51%, 18% octane was formed, 12% of the formate was recovered, and at least four other low-yield by products were detected as well.

A possible mechanism for the decarbonylation reaction is outlined in Scheme I. Oxidative addition of the formate (C–H bond) to Vaska's compound would result in the formation of the iridium(III) complex (**2**). Decarbonylation of the latter, with ligand migration, would give **3**. Re-

Scheme II



ductive elimination of the latter would afford the alcohol and, in the presence of triphenylphosphine, regenerate Vaska's compound. This mechanism, while reasonable, does not account for the fact that an increase in the basicity of the group V ligand (i.e., PCH_3Ph_2 vs. PPh_3) results in less decarbonylation of octyl formate. Increase in the basicity of the ligand should accelerate the rate of oxidative addition.[8,9] However, oxidative addition of **1** to **2** may not be the rate-determining step.

An alternative mechanism (Scheme II) involves π-complexation of the carbonyl group of the formate to iridium giving **4**, which can then experience alkoxy migration from carbon to iridium affording the formyl complex **5**. Replacement of triphenylphosphine by a more basic ligand may retard alkoxy migration to the metal. The alcohol would result by decarbonylation of **5** to the hydride **6**, followed by reductive elimination.

Finally, there has been considerable interest in the metal-catalyzed conversion of formate esters to carboxylic acids, which is usually referred to as a "rearrangement" or "isomerization" reaction.[3,10-12] For example, Pruett and Kacmarcik described the formation of acetic acid from methyl formate using chloro(1,5-cyclooctadiene)iridium(I) dimer as the catalyst, methyl iodide, and an acid such as acetic or propionic acid. No reaction occurs unless acid and methyl iodide are present, and the reaction does not proceed via decarbonylation of formate to alcohol, followed by carbonylation of the latter to the acid.

In conclusion, Vaska's compound, without any promoter or cocatalyst, is useful for the decarbonylation of formate esters (except methyl formate) to alcohols under quite mild conditions. The reaction is particularly clean when effected in an open system since unreacted formate ester is usually the only byproduct.

Experimental Section

General Data. The formate esters were purchased commercially or synthesized according to a literature procedure.[13] Vaska's compound, $(Ph_3P)_2Rh(CO)Cl$, and $[(1,5\text{-COD})IrCl]_2$ were purchased from Strem Chemical Co. and were used as received. The other iridium catalysts [e.g., $Ir(CO)Cl(AsPh_3)_2$] were prepared by literature methods.[14] Solvents were dried by standard methods.

Gas chromatographic determinations were made on a Varian Vista 6000 gas chromatograph (FID detector) equipped with a 2-m 5% Carbowax 20M (or OV-17) on Chromosorb W column. Varian EM-360 and XL-300 instruments were used for recording nuclear magnetic resonance spectra. Mass spectra were recorded on a VG 5050 micromass spectrometer, and a Perkin-Elmer 783 spectrometer was used for infrared spectral determinations.

General Procedure for the Decarbonylation of Formate Esters. Into a 10-mL round-bottom flask, equipped with a reflux condenser and stirring bar, was placed 6 mmol of the formate ester and 0.039 g (0.05 mmol) of Vaska's compound. The mixture was heated, with stirring, in an oil bath to the temperature, and for the reaction time, indicated in Table I or II. Workup of the reaction was effected by thin-layer chromatography.

When a solvent was used, 2 mL of that solvent was added to the reaction mixture. Reactions effected in a closed system were carried out by using a 100-mL stainless-steel autoclave (Parr Instrument Co.).

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Registry No. $HCOOCH_3$, 107-31-3; HCOOBu, 592-84-7; HCOOBu-t, 762-75-4; $HCOO(CH_2)_6CH_3$, 112-23-2; $CH_3CH(OCOH)CH_2CH_2CH_2CH_2CH_3$, 103884-53-3; $HCOO(CH_2)_7CH_3$, 112-32-3; $CH_3CH(OCOH)CH_2CH_2CH_2CH_2CH_2CH_3$, 5451-60-5; $HCOOCH_2Ph$, 104-57-4; $Ir(CO)(Cl)(PPh_3)_2$, 14871-41-1; $Ir(CO)(Cl)(AsPh_3)_2$, 15682-62-9; $Ir(CO)(Cl)(PMePh_2)_2$, 30669-24-0; $R(CO)(Cl)(PPh_3)_2$, 13938-94-8; $[Cl_15\text{-COD})IrCl]$, 12112-67-3; *n*-octanol, 111-87-5; octyl ether, 629-82-3; octene, 25377-83-7; octane, 111-65-9; octanal, 124-13-0; methanol, 67-56-1; *n*-butyl alcohol, 71-36-3; *tert*-butyl alcohol, 75-65-0; *n*-heptanol, 111-70-6; 2-heptanol, 543-49-7; 2-octanol, 123-96-6; benzyl alcohol, 100-51-6; toluene, 108-88-3; benzene, 71-43-2; benzaldehyde, 100-52-7; benzyl ether, 103-50-4; dibenzyl, 103-29-7; isobutylene, 115-11-7.

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