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REDUCTION OF OLEFINS AND ACETYLENES BY MEANS OF FORMIC ACID AND FORMATES IN PRESENCE OF TRANSITION METALS COMPLEXES.

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Transition metal complexes are known as the effective catalysts of the molecular hydrogen activation and olefins hydrogenation.However catalysis of hydrogen transfer from organic compounds to unsaturated substrates has been studied in less detail.Only the reduction of olefins by alcohols and alcoholates has been described (I,2).From this point of view formic acid and its salts may be rather interesting and promising hydrogen donors, due to the high hydride mobility of C-H hydrogen*.

We found that many transition metal complexes are effective catalysts of reduction of olefins and acetylenes by formic acid and formates.The catalytic activities of various ruthenium, osmium, rhodium, platinum and palladium complexes were investigated.

As seen from Table I the majority of the compounds investigated are effective catalysts of the olefin reduction by formic acid.The triphenylphosphine complexes of ruthenium, rhodium and iridium $(Ph_3P)_4RuCl_2$,$(Ph_3P)_3RhCl$,$(Ph_3P)_2Rh(CO)Cl$, $(Ph_3P)Rh(CO)_2Cl$,$(Ph_3P)_2Ir(CO)Br$,$(Ph_3P)_3Ir(CO)H$,$(Ph_3P)_2IrH_2Cl$ were found to be most active at I00°C.At 60° only $(Ph_3P)_3RhCl$,$(Ph_3P)_2Ir(CO)_2H$,$(Ph_3P)_4RuCl_2$ possess any noticeable catalytic activities.

Addition of alkali metal formates increases the degree of reduction. Thus the mixture of formic acid and lithium formate reduced octene-I to octane quantitatively even at 40° in presence of $(Ph_3P)_3RhCl$.Similar results were obtained with HCOONa and HCOOK additives.In some cases the alkali metal formates alone (without HCOOH) reduced olefins in the presence of a trace of water (see Table I).

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*Coffey (3) observed the reduction of butyraldehyde to the alcohol with formic acid in the presence of transition metal complexes.

The reduction of various olefins and acetylenes (cf. Table 2) could be in some cases employed for preparative purposes.

Formic acid decomposition in the presence of transition metal compounds seems to proceed with formation of intermediate hydride complexes (4).These intermediates could either decompose to form H_2 and CO_2 or react with unsaturated substrate leading to its reduction.A possible pathwey of the reaction described could be represented by following scheme (M-metal, L-ligand):

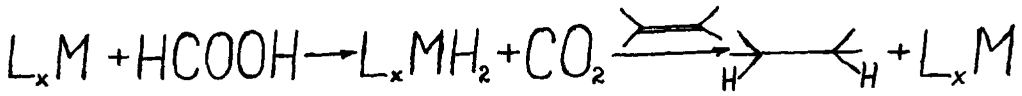

Table I. Reduction of octene-I by means of formic acid and lithium formate.

Catalyst	t°C	Reduction %		
		HCOOH [a]	HCOOH + HCOOLi [b]	HCOOLi [c]
$RuCl_3 \cdot 3H_2O$	60	0	I	I
	I00	I4	60	55
$(Ph_3P)_3RuH(CO)Cl$	60	0	42	2I
	I00	3	7	23
$(Ph_3P)_4RuCl_2$	60	55	I	I
	I00	45	26	27
$(Ph_3P)_4RuH_2$	60	I4	54	20
	I00	I0	5I	I6
$(Ph_3P)_3OsH(CO)Cl$	60	I	I	45
	I00	8	I8	52
$RhCl_3 \cdot 3H_2O$	60	0	I2	20
	I00	I	I4	I3
$(Ph_3P)_2Ir(CO)Cl$	60	I0	I6	I6
	I00	I4	50	4I
$(Ph_3P)_2Ir(CO)Br$	60	I2	26	26
	I00	I00	55	46
$(Ph_3P)_2Ir(CO)J$	60	I	6	2
	I00	29	50	46
$(Ph_3P)_3IrH_5$	60	0	0	0
	I00	I5	9	2
$(Ph_3P)_3Ir(CO)H$	60	0	0	0
	I00	0	0	0

Table I (continued).

Catalyst	t°C	Reduction %		
		HCOOH[a]	HCOOH + HCOOLi[b]	HCOOLi[c]
$(Ph_3P)_2Ir(CO)_2H$	60	I6	I6	5
	I00	52	50	33
$(Ph_3P)_2Rh(CO)Cl$	60	2	63	2
	I00	37	33	2
$(Ph_3P)Rh(CO)_2Cl$	60	I5	58	9
	I00	40	67	42
$(Ph_3P)_3Rh(CO)H$	60	8	27	4
	I00	42	27	8
$(Ph_3P)_3RhCl$	25	-	I5	-
	40	2	I00	-
	60	I5	I00	I5
	I00	50	67	25
H_2PtCl_6+ $SnCl_2$	60	0	5	2
	I00	2	2	2
$(Ph_3P)_3IrH_2Cl$	60	4	0	9
	I00	67	53	22
$(Ph_3P)_3IrHCl_2$	60	0	I2	2
	I00	37	5	I5
$(Ph_3P)_2Ir(CO)HCl_2$	60	0	0	0
	I00	0	6	24
$[(PhO)_3P]_4IrH$	60	0	0	0
	I00	3	38	9
cis-$(Et_3P)_2PtCl_2$	60	0	5	0
	I00	I2	2	I9

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a. Octene-I (I0-I5 mmole), HCOOH and the catalyst (molar ratio 30:I00:I) in I ml. of DMF (or dimetylacetamide) were heated for 3 hr with subsuquent GLC analysis.

b. Molar ratio of octene-I: HCOOH : $HCOOLi \cdot H_2O$: catalyst = 30:I00:30:I.

c. Molar ratio of octene-I : $HCOOLi \cdot H_2O$: catalyst = 30:60:I.

Table 2.

Reduction of olefins and acetylenes by means of formic acid in the presence of $(Ph_3P)_3RhCl$ (at $60^{\circ}C$).

Substrate	Reduction product	Reduction %	
		$HCOOH^a$	$HCOOH + HCOOLi^b$
octene-I	octane	I5	IOO
octene-4	octane	7	IOO
heptene-I	heptane	25	70
cyclohexene	cyclohexane	8	58
hexyne-3	hexane	I2	24
phenylacetylene	ethylbenzene	0	I7

a. I ml. DMF; substrate, HCOOH and catalyst (molar ratio of 30:IOO:I) were heated for 3 hr. with subsuquent GLC analysis.

b. Molar ratio of substrate: $HCOOH:HCOOLi \cdot H_2O$: catalyst =30:IOO:30:I.

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