Synthesis Gas Homologation of Aliphatic Carboxylic Acids

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Summary A new preparative route to aliphatic carboxylic acids is described involving a novel homologation using synthesis gas catalysed by soluble ruthenium species coupled with iodide promoters.

In this paper we disclose a new preparative route to aliphatic carboxylic acids that proceeds *via* homologation using synthesis gas. The direct homologation of carboxylic acids is believed to be a novel reaction. The technique can be applied to the building of aliphatic, linear and branched, carboxylic acids and, in its more general form, involves treatment of lower molecular weight carboxylic acids with CO/H_2 in the presence of soluble ruthenium species, *e.g.*, RuO_2, $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, coupled with iodide-containing promoters such as HI or an alkyl iodide.

$$CH_3CO_2H \xrightarrow{CO/H_2} C_nH_{2n+1}CO_2H \tag{1}$$

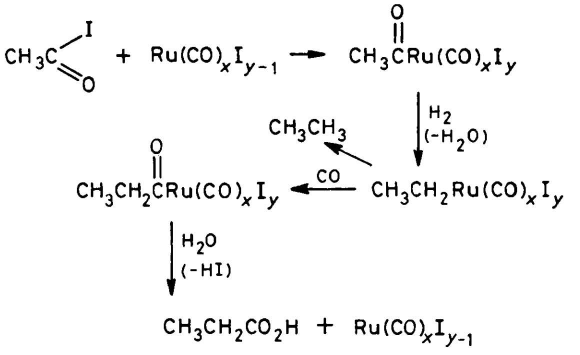
Where acetic acid is the parent acid [reaction (1)], homologation selectively yields the corresponding higher-molecular weight aliphatic carboxylic acids containing one or more additional carbon atoms per molecule. Since acetic acid is itself a 'synthesis gas chemical' derived from methanol *via* carbonylation,[1] this means the higher molecular weight carboxylic acids generated by this new technique may also be built *exclusively* from CO/H_2 without the need for any petroleum-derived coreactant.[2]

Typical preparative data are summarized in the Table for acetic acid homologation. Highest yields of acids are generally achieved with RuO_2–MeI where the total selectivity for propionic, butyric, and valeric acid formation is *ca.* 45% and turnover numbers are typically *ca.* 110 per g atom of Ru. The ruthenium catalyst remains in solution throughout the homologation sequence and the crude liquid products typically display no evidence of the presence of a metal precipitate.

hydrocarbon was always detected. Decreases in reactivity with increases in molecular weight and branching of the acid substrate [Table and the sequence (2)] have also

$$\text{acetic} > \text{propionic} \sim \text{n-valeric} > \text{isobutyric} > \text{trimethylacetic} \tag{2}$$

been reported recently for ruthenium-catalysed carboxylic acid hydrogenation.[3] We conclude that an important step in the homologation sequence is likely to be hydrogenation of the acetyl function, while co-ordinated to the iodoruthenium carbonyl catalyst (Scheme).



SCHEME. Homologation of acetic acid.

TABLE. Carboxylic acid homologation.[a]

Carboxylic acid substrate	Catalyst composition[b]		% Conversion	Principal carboxylic acid products[c]		
	Ru source	Promoter				
CH_3CO_2H	$RuO_2.xH_2O$	MeI	52	$C_2H_5CO_2H$ (37)	$C_3H_7CO_2H$ (6·9)	$C_4H_9CO_2H$ (1·0)
,,	$Ru_3(CO)_{12}$	MeI	70	,, (25)	,, (7·2)[e]	,, (3·2)
,,	$H_4Ru_4(CO)_{12}$	MeI	42	,, (34)	,, (5·5)	,, (<1)
,,	$RuO_2.xH_2O$	EtI	48	,, (37)	,, (3·2)	,, (0·7)
,,	$RuO_2.xH_2O$	HI	50	,, (37)	,, (3·7)	,, (1·0)
$CH_3CH_2CO_2H$[d]	$RuO_2.xH_2O$	MeI	69	$C_3H_7CO_2H$ (21)		
$C_4H_9CO_2H$[d]	,,	,,	67	$C_5H_{11}CO_2H$ (21)[f]		
$(CH_3)_2CHCH_2CO_2H$[d]	,,	,,	43	$(CH_3)_2CH[CH_2]_2CO_2H$ (8)	$C_2H_5C(CH_3)_2CO_2H$ (7)	
$(CH_3)_2CHCO_2H$[d]	,,	,,	45	$(CH_3)_3CCO_2H$ (24)		

[a] Typical operating conditions: 220 °C, 270 atm initial pressure CO/H_2 (1 : 1). [b] Typical reaction charge: ruthenium, 4·0 mmol; iodide, 40 mmol; CH_3CO_2H, 830 mmol. [c] Carboxylic acid yield (mol % in parentheses) estimated from the amount of starting acid converted. [d] Typical reaction charge: $RuO_2.xH_2O$, 2·0 mmol; MeI, 20 mmol; RCO_2H, 245 mmol. [e] Butyric acid, n/iso 5·1. [f] Hexanoic acid, n/iso 4·2.

The versatility of the homologation technique is illustrated also in the Table for other typical linear and branched aliphatic carboxylic acids. In the case of straight-chain acid substrates, such as propionic acid and n-valeric acid, the principal homologated products are those higher acids containing one additional carbon atom per molecule. The linear-chain isomer generally predominates, *i.e.*, n : iso ratios are 4—8 : 1.

Kinetic and spectroscopic studies have provided some insight into the mechanism of this synthesis. Our data reveal similar product distributions using MeI, EtI, and HI promoters (see Table), a positive (but fractional order) dependence of homologation rate upon initial iodide concentration, and no homologation in the absence of iodide. These observations are consistent with a rapid initial formation of acetyl iodide from the acetic acid. During acetic acid homologation we consistently observe ethane as a by-product (plus some propane), and likewise, during the homologation of higher acids, the corresponding

Typical crude product solutions exhibit strong i.r. bands at 2112 and 2047 cm^{-1} characteristic[4,5] of the ruthenium iodocarbonyl ion, $[Ru(CO)_3I_3]^-$. This species in acetic acid appears extremely robust; solution spectra remain unchanged over a wide range of operating conditions. However, at [Ru] >0·2M the neutral complex $[Ru(CO)_3I_2]_2$ may be isolated from the crude product solution as a yellow crystalline solid.

Insertion of CO (into the alkyl–Ru moiety, Scheme) is also an important step in the homologation sequence based upon our rate measurements and ^{13}C enrichment studies. Propionic acid formation is first order in ruthenium concentration and positively dependent upon CO partial pressure for [Ru] in the range 10—80 mM. Labelling experiments and ^{13}C n.m.r. spectroscopy provide confirmation as to the source of carbon for these higher molecular weight acids [reaction (1)]. Starting from acetic acid enriched at the carbonyl carbon, and a 1 : 1 mixture of CO and H_2, the propionic acid product fraction shows significant

^{13}C enrichment only at the methylene carbon [reaction (3)].

$$CH_3\overset{*}{C}O_2H + CO/H_2 \longrightarrow CH_3\overset{*}{C}H_2CO_2H \qquad (3)$$

Still higher molecular weight C_4 and C_5 acid products, containing two or more carbon atoms more than the starting acetic acid, would presumably be formed by completing successive loops of the catalytic cycle.

Previous homologation technology has generally been[6] confined to the homologation of alkyl and benzyl alcohols, and carboxylic acid esters,[4] and the conversion of monocyclic dialkyl ethers into esters and anhydrides.[7]

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