

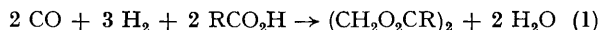
Vicinal Glycol Esters from Synthesis Gas

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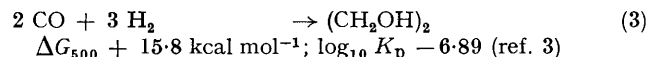
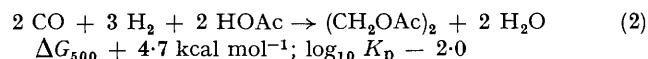
Summary Vicinal glycol esters, such as ethylene glycol acetate esters, are prepared from synthesis gas *via* the use of homogeneous ruthenium catalysis.

VICINAL glycol esters, particularly ethylene glycol acetate esters, have been prepared directly from synthesis gas *via* homogeneous ruthenium catalysis.¹ Aliphatic carboxylic acids, *e.g.*, glacial acetic acid, act both as coreactant (equation 1) and as solvent medium for the CO hydrogenation. The general synthesis [equation (1)] is believed to be novel.^{1,2}



Where ethylene glycol acetate esters are the desired products, glacial acetic acid solutions of ruthenium(III) salts, *e.g.*, ruthenium(III) chloride, in combination with large cationic species, such as quaternary phosphonium and ammonium salts, as well as the alkali metal salts, are the preferred catalyst precursors. Methyl and ethyl acetates constitute the major by-products. Typical preparative data are summarized in the Table for a series of such ruthenium catalyst combinations.

The thermodynamics of ethylene glycol diacetate formation from CO/H₂ [equation (2)] have been estimated to be more favourable than for the comparable direct glycol route³ [equation (3)]. As a consequence, it is not surprising to find that glycol ester syntheses (Table) may generally be conducted under conditions milder than those required for ethylene glycol itself.³ However, at the temperatures



$$1 \text{ cal} = 4.184 \text{ J}$$

necessary to achieve measurable rates of glycol acetate formation¹ (> 180 °C), the reaction is influenced by experimental conditions, particularly: (i) the ruthenium : cation : halogen mole ratio;¹ (ii) the nature of the cationic cocatalyst species (Table); (iii) the total operating pressure, temperature, and [Ru].¹

TABLE. Production of ethylene glycol acetates from synthesis gas:^a $\text{CO} + \text{H}_2 + \text{HOAc} \rightarrow (\text{CH}_2\text{OAc})_2 + \text{MeOAc} + \text{EtOAc}$.

Catalyst precursor	% Acid conv.	Product yield/mmol		
		Glycol acetates ^b	Methyl acetate	Ethyl acetate
RuCl ₃ -8 Bu ₄ POAc	87	38	556	51
Ru(acac) ₃ -8 Bu ₄ POAc ^c	38	5.7	252	18
RuO ₂ -8 Bu ₄ POAc	40	4.8	294	21
RuCl ₃ -10 Bu ₄ PfCl	88	12	498	149
RuCl ₃ -10 Bu ₄ PI	<5	—	—	1.2
RuCl ₃ -10 HpPh ₃ POAc ^e	>80	50	436	47
RuCl ₃ -5 Bu ₄ POAc	85	29	575	44
RuCl ₃ -5 Bu ₄ NOAc	46	5.7 ^d	215 ^d	42
RuCl ₃ -5 Me ₄ NOAc	74	22	491	45
RuCl ₃ -5 (Ph ₃ P) ₂ NOAc	67	1.7	201	137
RuCl ₃ -5 Ph ₄ AsOAc	<5	0.4	13	12
RuCl ₃ -9 Ph ₄ POAc	51	22	425	60
RuCl ₃ -10 CsOAc	15	11	49	10

^a Typical operating conditions: RuCl₃·xH₂O, 3.75 mmol; RuO₂·xH₂O, 4.0 mmol; HOAc, 50 g; 220 °C, 430 atm pressure, CO-H₂ 1:1. ^b Primarily ethylene glycol diacetate + some glycol monoacetate at high conversions. Trace quantities of ethylidene diacetate have been detected. ^c acacH = acetylacetonate. ^d Butyl acetate also present. ^e Hp = heptyl.

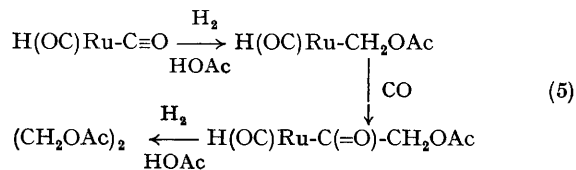
In contrast to rhodium-catalysed glycol synthesis,³ maximum glycol ester formation is favoured for the $\text{RuCl}_3\text{-Bu}_4\text{POAc}$ couple for $\text{P}:\text{Ru} > 1:1$. The effect of glycol acetate formation upon cation structure and size³ (Table) is indicated by equation (4). The glycol acetate: methyl acetate mole ratio is 1:4.5 for the $\text{RuCl}_3\text{-10CsOAc}$ couple.



Glycol acetate formation is believed to involve catalysis *via* solubilized anionic ruthenium carbonyl species. Typical $\text{RuCl}_3\text{-8Bu}_4\text{POAc-HOAc}$ product solutions exhibit the ν_{CO} and ^1H n.m.r. spectral characteristics⁴ of the ruthenium hydrocarbonyl cluster $[\text{HRu}_3(\text{CO})_{11}]^-$, and for syntheses conducted at $[\text{Ru}] \geq 80 \text{ mM}$, $\text{Ru}_3(\text{CO})_{12}$ slowly crystallizes from the product solutions upon cooling. The presence of large cationic species, such as Bu_4P^+ , should aid in stabilizing this anionic ruthenium cluster during the CO hydrogenation sequence. However, the substitution of solvents of high dielectric constant, such as acetic anhydride, that might favour ion-pair separation,⁵ did not significantly increase the productivity of the system or the selectivity for glycol diacetate formation.

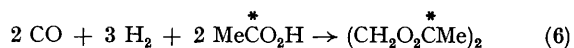
Soluble ruthenium complexes have not in the past readily yielded ethylene glycol from CO and H_2 [equation (3)].^{3,6,7} The role of acetic acid in glycol diacetate formation, apart from thermodynamic considerations, may relate to the influence of acetate ion, as an auxiliary ligand, upon the reactivity of the catalytically active ruthenium centre, together with its importance in the formation of Ru-

acyloxymethyl species⁸ [equation (5)], or Ru-hydroxymethyl⁹ intermediates, during CO hydrogenation. Methyl acetate is unlikely to be an intermediate in glycol diacetate



formation since CO hydrogenation experiments in the presence of MeOAc did not yield the glycol ester. The importance of labile ruthenium-formyl intermediates,¹⁰ *e.g.*, $[\text{Ru}_3(\text{CO})_{11}\text{CHO}]^-$, cannot be ruled out. However, we see no enhancement in glycol ester formation upon the addition of formaldehyde.

¹³C-Enriched acetic acid coreactant has been employed unambiguously to identify the source of carbon for this glycol formation [equation (6)], but for glycol diacetate preparations starting from CO-D_2 or $\text{CD}_3\text{CO}_2\text{D}$, extensive H-D scrambling is observed.



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⁵ L. Kaplan, Amer. Chem. Soc. Meeting, 179, Houston, Paper 16, 1980.

⁶ J. S. Bradley, *J. Am. Chem. Soc.*, 1979, **101**, 7419.

⁷ R. L. Pruett and W. E. Walker, U.S. Pat. 3,833,634/1974.

⁸ Conversion of related Mn complexes bearing the $-\text{CH}_2\text{OC(O)R}$ ligand into ethylene glycol esters by reaction with H_2 or synthesis gas has been reported recently; see B. D. Dombek, *J. Am. Chem. Soc.*, 1979, **101**, 6406.

⁹ R. A. Sanchez-Delgado, J. S. Bradley, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 399.

¹⁰ R. L. Pruett, R. C. Schoening, J. L. Vidal, and R. A. Fiato, *J. Organomet. Chem.*, 1979, **182**, C57.