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Syngas Reactions

IV. Vicinal Glycol Esters from Synthesis Gas[1]

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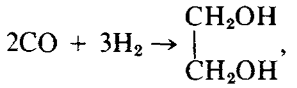
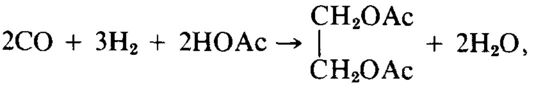
Vicinal glycol esters, such as ethylene glycol acetate esters, are prepared from synthesis gas via homogeneous ruthenium catalysis. Aliphatic carboxylic acids, e.g., glacial acetic acid, act both as coreactant and as ruthenium catalyst solvent for this CO-hydrogenation reaction. Yields and selectivity to glycol ester are substantially improved through the addition of bulky cationic promoters, particularly quaternary phosphonium and cesium cations.

In seeking new routes to preparing ethylene glycol from synthesis gas that no longer require stringent operating conditions (*2*–*9*), it is important to note that the unfavorable thermodynamics of direct glycol synthesis (Eq. (1)) (*10*) can be partially overcome by the alternative approach of generating ethylene glycol diesters, e.g., ethylene glycol diacetate (Eq. (2)) (*11*).



$$2CO + 3H_2 \rightarrow \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}, \tag{1}$$

$$\Delta G_{500} + 15.8\ \text{kcal/mole} \qquad \log Kp\ -6.89,$$



$$2CO + 3H_2 + 2HOAc \rightarrow \begin{array}{c} CH_2OAc \\ | \\ CH_2OAc \end{array} + 2H_2O, \tag{2}$$

$$\Delta G_{500} + 4.7\ \text{kcal/mole} \qquad \log Kp\ -2.0.$$

In view of the more favorable energetics of Eq. (2) it may be possible to achieve selective vicinal glycol ester synthesis under conditions that are considerably milder than those presently required for direct glycol production.

In this paper we describe in some detail the novel synthesis of vicinal glycol esters, particularly ethylene glycol acetate esters, from synthesis gas via homogeneous ruthenium catalysis. Aliphatic carboxylic acids, e.g., glacial acetic acid, act both as coreactant (Eq. (2)) and as solvent for the CO hydrogenation. Of particular note, enhanced glycol ester syntheses may be realized by the addition of bulky cationic promoters, including quaternary phosphonium cations such as tetrabutylphosphonium and heptyltriphenylphosphonium ions as well as cesium salts.

Prior disclosures of this reaction (Eq. (2)) include one preliminary report by us (*12*) plus a more detailed communication (*13*). In the latter case, evidence is presented for a mechanism of ethylene glycol ester formation, catalyzed by unpromoted $Ru_3(CO)_{12}$ in acetic acid, that involves the intermediate formation of ruthenium–formyl and ruthenium–formaldehyde adducts. Our labeling experiments, extensive studies

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[1] For the previous paper in this series see Ref. (*1*).

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concerning the importance of cationic promoter structure and size, the effect of coreactant/solvent media composition, together with rate and spectral measurements, may be rationalized in terms of glycol ester formation via an acyloxymethylene growth reaction.

RESULTS

Glycol Ester Syntheses

During preliminary catalyst screening studies, various ruthenium species, e.g., ruthenium dodecacarbonyl, acetylacetonate, oxide, and chloride, were solubilized in aliphatic carboxylic acids, such as acetic acid, under pressure of synthesis gas (1/1, CO/H_2) for the purpose of generating ethylene glycol esters. Typical product distributions are illustrated in Table 1. Whereas ethylene glycol diacetate is the desired product, methyl and ethyl acetates are the major by-products. Glycol diacetate productivity and selectivity were found to be sensitive to operating parameters such as syngas pressure (*11*), temperature (*11*), and initial [Ru] (*11, 13*), but glycol turnover numbers for these syntheses (Table 1) are low. Consequently, the generation of preparative quantities of vicinal glycol ester by this technique remains difficult.

Two avenues to substantially enhancing the specific activity of the solubilized ruthenium catalysts were considered in this work:

(a) by use of other coreactant/solvent media;

(b) through modification of the ruthenium catalyst.

Summary data for the first approach are provided in Table 2. CO hydrogenations to glycol esters utilizing ruthenium(III) acetylacetonate solubilized in acetic, propionic, and trifluoroacetic acids (Expts. 7–9) indicate there may be a correlation between decreasing pK_a and the quantities of corresponding glycol ester produced. As the acidity of the aliphatic acid increases there is a comparable increase in yield of both vicinal glycol ester and by-product methyl ester. In the case of acetic or propionic acid as coreactant, we find no evidence for the presence of the corresponding esters of propylene glycol, glycerine, or diethylene glycol. It may be noted, however, that ruthenium solubilized in certain other organic (but noncarboxylic) acid solvents of moderate pK_a, e.g., *o*-chlorophenol (Expt. 10), does yield trace quantities of ethylene glycol.

A second approach to enhancing ethylene glycol ester yields and selectivity has been to add certain promoter species to the solutions of ruthenium catalyst. To signi-

TABLE 1

Ethylene Glycol Diacetate From Synthesis Gas[a]

Expt.	Ruthenium precursor	Solvent/ coreactant	Product yield (mmole)[b]		
			Glycol acetate	Methyl acetate	Ethyl acetate
1	$Ru_3(CO)_{12}$	HOAc	0.7	25	0.5
2	$Ru(acac)_3$	HOAc	0.6	20	—
3	$RuCl_3 \cdot xH_2O$	HOAc	—	34	66
4	$RuO_2 \cdot xH_2O$	HOAc	0.7	24	0.5
5	$Ru(CO)_3(PPh_3)_2$	HOAc	0.3	32	3.9
6	$Ru_3(CO)_{12}$–$6PBu_3$	HOAc	—	18	12

[a] Operating conditions: Ru, 2.0 mmole; HOAc, 25 g; 220°C; 430 atm constant pressure; CO/H_2 (1 : 1); 6 hr.

[b] Product yields determined from crude liquid product. Typical gas samples comprised of unreacted CO/H_2, $<2\%$ CO_2, $<0.1\%$ CH_4.

TABLE 2

Ethylene Glycol Esters from Synthesis Gas[a]

Expt.	Ruthenium precursor	Solvent/ coreactant	pK_a	Product yield (mmole)	
				CH_2OOCR $\vert$ CH_2OOCR	CH_3OOCR
7	Ru(acac)$_3$	CH_3COOH	4.76	0.4	30
8	Ru(acac)$_3$	C_2H_5COOH	4.87	0.5	41
9	Ru(acac)$_3$	CF_3COOH	0.25	1.5	106
10	Ru(acac)$_3$	o-ClC_6H_4OH	8.48	Trace[b]	2.1[b]
11	Ru(acac)$_3$	{o-ClC_6H_4OH/ {$Cl_3C_6H_2OH$[c]	 6.00	—	38[b]
12	Ru(acac)$_3$	CH_3COOH/H_2O[d]		0.6	29
13	Ru(acac)$_3$	CH_3COOH/H_3PO_4[e]		Trace	49

[a] Operating conditions: Ru, 1.0 mmole; solvent/coreactant, 50 ml; 220°C; 18 hr; 272 atm (1 : 1, CO/H_2) initial pressure; variable-pressure run.

[b] Products identified as methanol and ethylene glycol.

[c] Solvent composition: o-chlorophenol, 25 g; 2,4,6-trichlorophenol, 25 g.

[d] Solvent composition: acetic acid, 45 ml; water, 5 ml.

[e] Solvent composition: acetic acid, 45 ml; phosphoric acid, 5 ml.

TABLE 3

Glycol Acetates Formation—Effect of Promoter Structure—I[a]

Expt.	Catalyst precursor	Carboxylic acid	Acid conv. (%)	Product yields (mmole)[c]		
				Glycol acetates[b]	Methyl acetate	Ethyl acetate
14	$RuCl_3$–$8Bu_4POAc$	HOAc	87	38	556	51
15	$RuCl_3$–$10HpPh_3POAc$	HOAc	>80	50	436	47
16	$RuCl_3$–$5Bu_4POAc$	HOAc	85	29	575	44
17	$RuCl_3$–$5Bu_4NOAc$	HOAc	46	5.7[d]	215[d]	42
18	$RuCl_3$–$5Me_4NOAc$	HOAc	74	22	491	45
19	$RuCl_3$–$5(Ph_3P)_2NOAc$	HOAc	67	1.7	201	137
20	$RuCl_3$–$5Ph_4AsOAc$	HOAc	<5	0.4	13	12
21	$RuCl_3$–$9Ph_4POAc$	HOAc	51	22	425	60
22	$RuCl_3$–$8Bu_4POAc$[e]	HOAc	30	4.9	238	15

[a] Operating conditions: $RuCl_3 \cdot H_2O$, 3.75 mmole; HOAc, 50 g; 220°C; 430 atm constant pressure; CO/H_2 (1 : 1); 18 hr.

[b] A mixture of ethylene glycol diacetate and monoacetate.

[c] Product yields determined from crude liquid product. Typical gas samples are comprised of unreacted CO/H_2, 5–20% CO_2, <1% CH_4.

[d] Butyl acetate also present.

[e] Reaction time, 2 hr.

TABLE 4

Glycol Acetates Formation—Effect of Promoter Structure—II[a]

Expt.	Catalyst precursor	Carboxylic acid	Acid conv. (%)	Product yields (mmole)		
				Glycol acetates[b]	Methyl acetate	Ethyl acetate
23	$RuCl_3$–10CsOAc	HOAc	15	11	49	10
24	RuO_2–10CsOAc	HOAc	34	11	142	63
25	RuO_2–5Ba(OAc)$_2$	HOAc	22	4.7	116	8.3
26	RuO_2–10NaOAc	HOAc	15	1.9	69	20

[a] Operating conditions: Ru, 4.0 mmole; HOAc, 50 g; 220°C; 18 hr; 272 atm CO/H_2 (1 : 1) initial pressure; variable-pressure run.

[b] A mixture of ethylene glycol diacetate and monoacetate.

ficantly improve the glycol ester yields the promoter need be (*11*):

(a) a large cationic species;

(b) preferably a quaternary phosphonium salt or a salt of a large alkali metal ion.

Table 3 summarizes data from the screening of a number of quaternary Group VB salt promoters coupled with ruthenium(III) chloride in acetic acid coreactant/solvent. Here the selective synthesis of ethylene glycol acetates is demonstrated in up to 50 mmole per pass. This is a near 100-fold improvement in yield over the data provided in Table 1 for the nonpromoted ruthenium salts, e.g., ruthenium(III) acetylacetonate alone (Expt. 2).

Where the promoter is a quaternary, Group VB salt of a weak, organic acid, e.g., an acetate salt, we conclude:

(a) Yields of glycol acetates are generally higher with phosphonium salts than with ammonium salts. Furthermore, the quaternary ammonium salts may be subject to some thermal degradation (Hofmann elimination, e.g., Expt. 17) during the CO hydrogenation sequence.

(b) Highest yields of glycol are realized where the quaternary phosphorus is bonded to alkyl or a mixture of alkyl and aryl radicals, e.g., as in the cases of tetrabutylphosphonium acetate and heptyltriphenylphosphonium acetate (Expts. 14,15). In fact the ruthenium(III) chloride–heptyltriphenylphosphonium acetate couple provides the highest glycol ester yields achieved herein. The glycol acetate : methyl acetate ratio is 1 : 8.7. Turnover frequencies may reach 9.5×10^{-3} s^{-1} for the $RuCl_3$–8Bu_4POAc couple at 220°C and 430 atm total pressure (Expt. 22).

Certain alkali and alkaline-earth metal salts are also suitable promoters for glycol ester synthesis when coupled with ruthenium in acetic acid coreactant/solvent (see Table 4). The cesium acetate–ruthenium(III) chloride couple in particular, produces the highest selectivity to glycol acetates (Expt. 23). In this case the glycol acetate : methyl acetate ratio reaches 1 : 4.5. Glycol ester yields are substantially lower for the spatially smaller sodium and barium promoters (Expts. 25,26).

Because of the operating pressures necessary to effect these glycol ester syntheses (*11*), no detailed kinetic studies have been undertaken in this work. However, it is clear from our productivity and yield data that the ruthenium-catalyzed glycol ester syntheses with quaternary phosphonium salt promoters are particularly sensitive to:

(1) the nature of the cationic promoter species (see Tables 3 and 4);

(2) the ruthenium : cation mole ratio (Fig. 1).

(3) total operating pressure, temperature (*11*), and [Ra] (Fig. 2).

The significance of these findings is discussed infra.

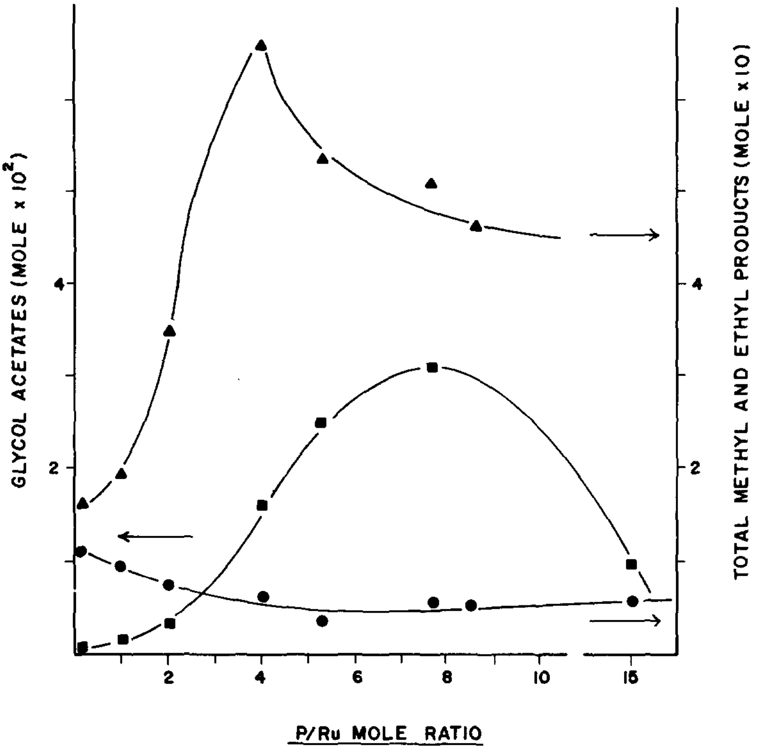


FIG. 1. Ethylene glycol acetate formation vs ruthenium catalyst composition. $AcOCH_2CH_2OAc$ + $HOCH_2CH_2OAc$, ■; MeOAc + MeOH, ▲; EtOAc + EtOH, ●. Operating conditions: Ru, 3.75 mmole; Bu_4POAc, 0 → 56 mmole; HOAc, 50 g; 220°C; 430 atm constant pressure; CO/H_2(1 : 1).

Labeling Studies

A series of deuterium- and ^{13}C-labeling experiments has been carried out to learn more of the mechanism of this glycol ester synthesis and, in particular, to unambiguously identify the source of carbon utilized in glycol formation. Data are summarized in Table 5.

For experiments starting with solutions of $RuCl_3$–$8Bu_4POAc$ solubilized in acetic acid enriched with ^{13}C at the carbonyl function (^{13}C concn: 4.4%), hydrogenation of CO was conducted as outlined in Table 3. The crude liquid product typically contained 4–5 wt% ethylene glycol diacetate product. This material, trapped by preparative GLC, showed ^{13}C enrichment only at the carbonyl function. There was no enrichment of the methylene or methyl carbons. These results are consistent with the stoichiometry of Eq. (3).

For glycol acetate preparations starting from CO plus 99% pure deuterium (CO/D_2, 1 : 1), or for CO hydrogenations catalyzed by $RuCl_3$–$5CsOOCCD_3$ in 99% HOAc-d_4, ^1H NMR analyses of the trapped ethylene glycol diacetate samples showed deuterium incorporation is nonselective within the glycol molecule (see Table 5). Furthermore, scrambling patterns are similar for both the ethylene glycol monoacetate and methyl acetate by-products. We conclude that H–D exchange is rapid within the time frame of the CO-hydrogenation reactions to glycol acetate esters, etc.

DISCUSSION

Vicinal glycol ester production directly from CO/H_2 is a new preparative route to these glycol derivatives (*11–14*). The critical features of this synthesis are:

(1) the ability of homogeneous ruthenium

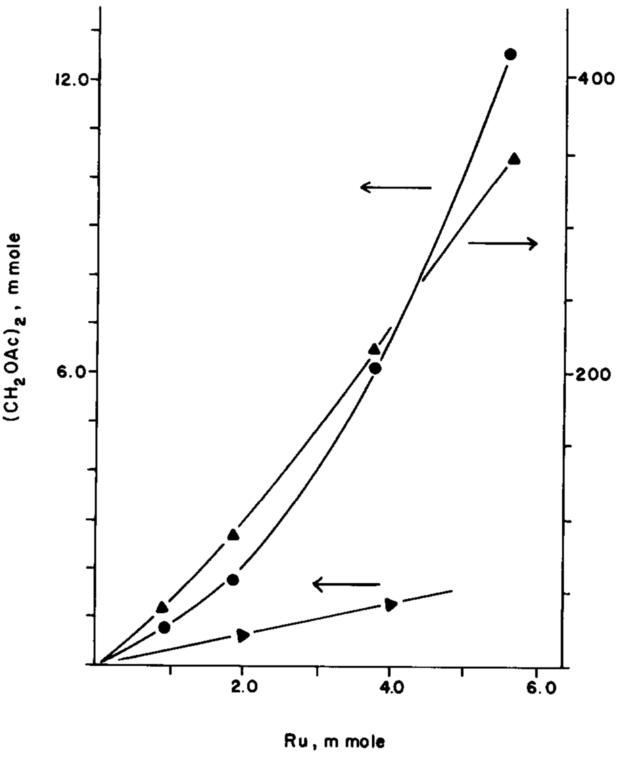
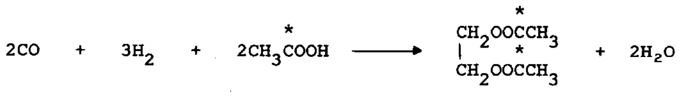


FIG. 2. Ruthenium catalyst composition vs ethylene glycol acetate formation. Ruthenium catalyst precursor: $RuCl_3$–$8Bu_4POAc$: $(CH_2OAc)_2$, ●; MeOAc, ▲. Ruthenium catalyst precursor: $Ru_3(CO)_{12}$: $(CH_2OAc)_2$, ▼. Operating conditions: HOAc, 50 g: 220°C; 430 atm constant pressure: CO/H_2 (1 : 1): 4 hr.

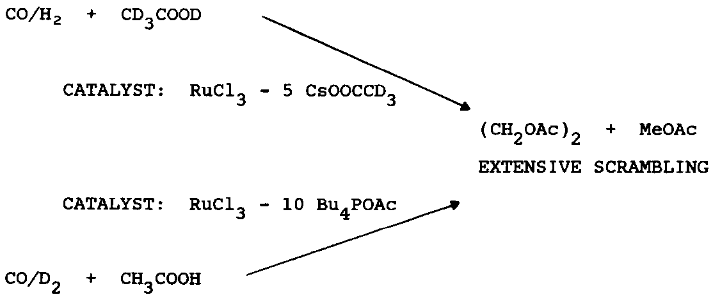
TABLE 5

Carbon-13 and Deuterium Studies



$$2CO + 3H_2 + 2CH_3\overset{*}{C}OOH \longrightarrow \begin{array}{l} CH_2OO\overset{*}{C}CH_3 \\ | \\ CH_2OO\overset{*}{C}CH_3 \end{array} + 2H_2O \qquad (3)$$

CATALYST: $RuCl_3$ - 5 Bu_4POAc



(4)

catalysts to effect reaction, e.g., the formation of ethylene glycol diacetate (Eq. (2));

(2) the substantial improvement in glycol ester yields that may accrue from the introduction of large cationic promoters, particularly certain quaternary phosphonium and alkali metal cations.

Tables 3 and 4 effectively summarize our data concerning the importance of cationic promoter structure and size upon the yield of desired glycol acetates. We conclude that for the alkali and alkaline-earth metal acetate salts, the yields of glycol derivative increase along with cation size in accordance with Eq. (5).

$$\mathrm{Na} < \mathrm{Ba} < \mathrm{Cs}. \qquad (5)$$

For the quaternary ammonium, phosphonium, and arsonium salts, however, the situation is more complicated. Factors other than just the charge/radius ratio are apparently important here in determining the quantity of glycol ester produced. This ordering (Eq. (6)) suggests that these other critical factors include:

(a) the nature of the bonded aryl and alkyl radicals;

(b) the thermal stability of the quaternary Group VB cation;

(c) the polarizability of the cation.

$$(\mathrm{Ph_3P})_2\mathrm{N} < \mathrm{Bu_4N} < \mathrm{Me_4N} < \mathrm{Bu_4P} < \mathrm{HpPh_3P} > \mathrm{Ph_4P} > \mathrm{Ph_4As}. \qquad (6)$$

Glycol ester yields are also particularly sensitive to the initial mole ratios of ruthenium to promoter. Figure 1 illustrates this sensitivity for the $RuCl_3$–Bu_4POAc couple. Incremental increases in Bu_4P^+ concentration up to a P/Ru atomic ratio of ca. 8 : 1 improve the glycol acetate yields far beyond that possible with ruthenium(III) acetylacetonate alone (Table 1, Expt. 2). The optimum Ru/P ratio for glycol formation is ca. 1 : 8 for this particular catalyst combination. This same ratio is, of course, in direct contrast to published data for the homogeneous rhodium-catalyzed synthesis of ethylene glycol (*10*), where the optimum ratio of rhodium to large cationic species is 1 : 0.17. In the case of ruthenium catalysis there are no known, highly charged, anionic ruthenium species corresponding to this 1 : 8 ratio. More likely the same ratio reflects changes in the solvent media properties brought about by the addition of these high concentrations of phosphonium salts. Such a hypothesis finds further credibility in correlations between glycol productivity and [Rn] outlined below.

For solutions of $Ru_3(CO)_{12}$ alone in acetic acid, first-order dependencies of glycol diacetate and methyl acetate formation upon ruthenium concentration have been reported (*11–13*). In those cases where quaternary phosphonium salts are added, however, the yields of glycol diacetate increase more rapidly, and in a nonlinear fashion, with increasing ruthenium concentration. Data in Fig. 2 illustrate this condition for the $RuCl_3$–Bu_4POAc couple at a constant Ru/P mole ratio of 1 : 8. This new, nonlinear, dependence may well be due to

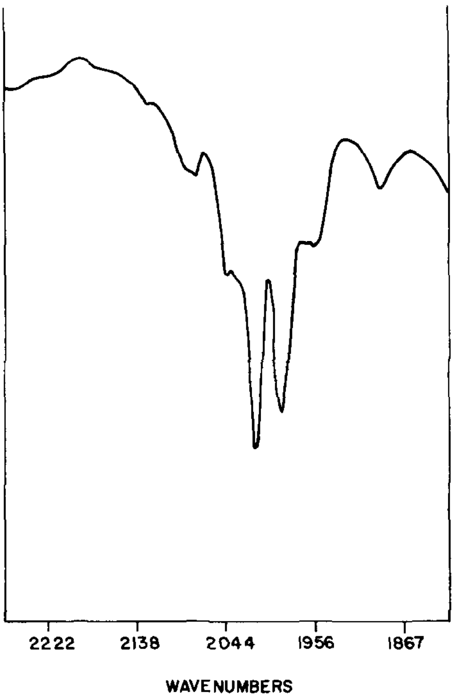


FIG. 3. Typical product solution spectrum; ruthenium catalyst solution, $RuCl_3$–$8Bu_4POAc$/HOAc.

changes in the degree of ion-pair interaction (*15*) between the bulky phosphonium cation and the hydridoruthenium carbonyl anions (e.g., Fig. 3). The addition of large quantities of tetrabutylphosphonium salt will at the same time cause increases in the ionic strength and dielectric constant of the media. It appears unlikely, however, that alterations in the solvent dielectric constant alone could satisfactorily account for the nonlinear dependence of Fig. 2. In related studies, for example, we find the substitution of acetic acid ($\epsilon = 6.15$, Ref. (*16*)) for a solvent of substantially higher dielectric constant, acetic anhydride ($\epsilon = 22$, Ref. (*16*)), does not significantly enhance the glycol diacetate yield (see Table 6, Expts. 27 and 28).

In attempting to raise the glycol ester selectivity and productivity from syngas via the homogeneous ruthenium-catalyzed reaction (Eq. (2)), our initial purpose in adding large cationic species, such as the tetrabutylphosphonium cation, was to stabilize any ruthenium cluster species that may be present during the CO-hydrogenation sequence and which may be responsible for the desired glycol formation. Solution spectra of typical ruthenium-catalyzed glycol syntheses (Table 1) exhibit bands characteristic of a variety of ruthenium carbonyl and hydridocarbonyl (*13*) species. However, reaction solutions containing ruthenium plus large Group VB cations, e.g., $RuCl_3$–$8Bu_4POAc/HOAc$, consistently exhibit ν_{CO} and ^1H NMR spectra characteristic (*17*) of the anionic hydridoruthenium carbonyl cluster, $[HRu_3(CO)_{11}]^-$. A typical product solution spectrum illustrating the strong carbonyl bands of this cluster anion is reproduced in Fig. 3.

It may be noted that for similar preparations conducted where the initial [Rn] ≥ 80 m*M*, the corresponding neutral ruthenium carbonyl cluster, $Ru_3(CO)_{12}$, slowly crystallizes from solution. For glycol syntheses carried out with acetic acid solutions of phosphine-stabilized ruthenium chloride salts, there is a much lower order of glycol productivity (Table 1, Expt. 5), and significant quantities of mononuclear ruthenium complex, *cis*-$(PPh_3)_2(CO)_2RuCl_2$, may be isolated after the CO-hydrogenation sequence.

Labeling experiments with ^{13}C (Table 5) have served to confirm the stoichiometry of the glycol diacetate formation (Eqs. (2,3)) from syngas, but to gain a better understanding of the mechanism of this reaction, the importance of the carboxylic acid coreactant need be better defined. The role of the acetic acid upon glycol diacetate forma-

TABLE 6

Glycol Acetates Formation—Effect of Acetic Anhydride and Formaldehyde[a]

Expt.	Catalyst precursor	Solvent/ coreactant	Acid conv. (%)	Product yields (mmole)		
				Glycol acetates	Methyl acetate	Ethyl acetate
27	$RuCl_3$–$8Bu_4POAc$	HOAc	87	38	556	51
28	$RuCl_3$–$8Bu_4POAc$	$O(Ac)_2$	>99	12	560[b]	56[b]
29	$RuCl_3$–$8Bu_4POAc$	HOAc + HCHO[c]	>99	24	813[d]	37
30	$RuCl_3$–$8Bu_4POAc$	MeOAc	—	10	[e]	37

[a] Typical operating conditions: $RuCl_3 \cdot xH_2O$, 3.75 mmole; HOAc, 50 g; 220°C, 430 atm CO/H_2 (1 : 1) constant pressure, 18 hr.

[b] Plus 189 mmole MeOH; 59 mmole EtOH

[c] Solvent composition: acetic acid, 50 g; paraformaldehyde, 10 g.

[d] Plus 238 mmole MeOH.

[e] Plus 461 mmole MeOH.

tion—apart from thermodynamic considerations—may relate to:

(a) the influence of acetate ion, as an auxiliary ligand, upon the reactivity of the catalytically active ruthenium center;

(b) its importance in the possible formation of intermediate ruthenium–acyloxymethylene species ($Ru–CH_2OOCCH_3$) (*13*, *19*) during the CO-hydrogenation sequence.

The sensitivity of glycol formation to the acidity of the carboxylic acid coreactant has already been noted (Table 2, Expts. 7–9), but apparently Brønsted acids of noncarboxylic nature, when added as solvents, do not promote glycol formation (Expt. 13). Aliphatic carboxylic acids clearly favor the formation of glycol derivatives from synthesis gas (cf. data, Table 2), but their presence is *not* a prerequisite for selective, homogeneous, ruthenium-catalyzed, ethylene glycol synthesis (Eq. (1)) (*20*).

A possible mechanistic scheme leading to the formation of ethylene glycol diacetate and methyl acetate, the major by-product from syngas plus acetic acid—consistent with the data outlined so far—is provided in Fig. 4. It involves initial conversion of a hydridoruthenium carbonyl precursor (possibly a cluster species, viz. Fig. 3) to a ruthenium–acyloxymethylene adduct. Subsequent migratory insertion of CO, followed by hydrogenation would yield the observed ethylene glycol diacetate product. An observed dependence of glycol productivity upon hydrogen and CO partial pressures has been noted here for the $RuCl_3$–Bu_4POAc couple (*11*, *14*), consistent with this mechanistic scheme. The situation is complicated, however, by competing ruthenium-catalyzed water-gas shift (*1*, *18*, *21*) (via Eqs. (7) and (8)) that effectively alters the H_2/CO ratio during the course of glycol formation.

$$CO + 2H_2 + HOAc \rightarrow CH_3OAc + H_2O, \quad (7)$$

$$H_2O + CO \rightarrow H_2 + CO_2. \quad (8)$$

Methyl acetate would be formed via reductive elimination of the ruthenium–acyloxymethylene adduct (Fig. 4). Ethyl acetate, the other major by-product of this synthesis (Tables 1, 3, and 4), is generated through ruthenium-catalyzed homologation (*22*, *23*) of the primary by-product, methyl acetate (Eq. (9)). Although ruthenium-catalyzed acetic acid reduction to ethanol, followed by esterification (Eq. (10)), has been recently demonstrated (*23*) as an alternative source of ethyl acetate, in our syntheses, route (10) is of lesser importance. This conclusion is based upon ethyl ester syntheses conducted in the presence of substituted and higher-MW carboxylic acid coreactants such as trifluoroacetic and propionic acids (*14*), as well as preparations starting with ^{13}C-enriched acetic acid, where ^{13}C enrichment of the product ethyl acetate appears only at the carbonyl carbon (*22*).

$$CH_3COOCH_3 + CO + 2H_2 \rightarrow CH_3COOC_2H_5 + H_2O, \quad (9)$$

$$CH_3COOH + 2H_2 \rightarrow C_2H_5OH \xrightarrow{CH_3COOH} CH_3COOC_2H_5. \quad (10)$$

Other potentially important intermediates in ethylene glycol diacetate formation include coordinated acetate ester, or a derivative thereof, as well as ruthenium formyl species. Although methyl acetate is a major by-product of glycol acetate ester syntheses (Tables 1 and 3), CO-hydrogenation experiments conducted with methyl acetate as coreactant (Table 6, Expt. 30) yielded significantly smaller quantities of glycol derivative. We conclude glycol is

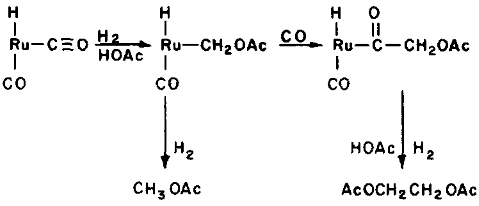


FIG. 4. Mechanism of glycol diacetate formation.

likely to be a primary product of ruthenium-catalyzed CO hydrogenation. Ruthenium carbonyl cluster anions containing the coordinated formyl group, e.g., $[Ru_3(CO)_{11}CHO]^-$ (*24*), as well as ruthenium-coordinated formaldehyde intermediates (*13*), have recently been proposed. In contrast to the latter proposal, however, we find no enhancement in glycol ester formation occurs upon the addition of either formaldehyde, or a formaldehyde precursor, to the Ru-containing acetic acid reaction solutions (e.g., Table 6, Expt. 29).

EXPERIMENTAL SECTION

Synthesis gas was purchased from Big Three Industries in various proportions of carbon monoxide and hydrogen. All ruthenium derivatives, alkali and alkaline-earth metal salts, as well as quaternary ammonium and phosphonium salts, were purchased from outside suppliers. All high-pressure experiments were conducted in 450-ml- and 845-ml-capacity Aminco pressure reactors constructed of 316 stainless steel, fitted with heating and agitation means, and hooked to large, high-pressure, synthesis gas reservoirs. Each reactor was fitted with interchangeable Pyrex glass liners.

The extent of reaction and distribution of products was determined by gas–liquid chromatography using a 6-ft × ⅛-in. column of Porapak QS (60/80 mesh) programmed from 140 to 280°C with 30 cm^3/min He flow. The ethylene glycol ester products, particularly ethylene glycol monoacetate and diacetate esters, were isolated by fractional distillation *in vacuo*, and by GLC trapping, and identified by NMR, FTIR, and elemental analyses.

Typical synthesis. In a typical synthesis, a deoxygenated sample of acetic acid (25–50 g), ruthenium(III) chloride, hydrate (2.0–4.0 mmole), and tetrabutylphosphonium acetate (10.0–60.0 mmole) is charged to the glass-lined pressure reactor. The mixture is flushed with synthesis gas (CO/H_2, 1 : 1), and the reactor sealed, pressured with 136 atm of CO/H_2 (1 : 1), and heated to 220°C with agitation. At temperature, the pressure within the reactor is raised to 430 atm by addition of 1/1 syngas from the large high-pressure reservoir. Further quantities of gas are introduced as required during reaction so as to maintain the pressure at 430 atm.

Upon cooling the reactor to ambient temperature (10–20°C), a clear deep-red liquid product is recovered. No solid fraction is in evidence. The methyl acetate, ethyl acetate, and glycol monoacetate and diacetate fractions are recovered from the crude liquid product by fractional distillation *in vacuo*.

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