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CATALYTIC OXIDATION OF ALCOHOLS TO ESTERS WITH $Ru_3(CO)_{12}$

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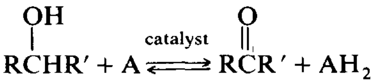
Summary

$Ru_3(CO)_{12}$ is an efficient homogeneous catalyst precursor for the conversion $2RCH_2OH \rightarrow RCO_2CH_2R$. With aliphatic primary alcohols and benzylic alcohols yields and selectivities of ca. 90% are obtained. The reaction requires a hydrogen acceptor molecule; triple bonds and activated double bonds, as well as ketones and aldehydes, function as H-acceptors. The reaction proceeds in two steps, with an aldehyde intermediate which subsequently oxidatively couples with an alcohol to generate an ester. In most cases the aldehyde is present in a steady state concentration implying the presence of an equilibrium system. A disproportionation alcohol ⇄ aldehyde is a component of the above system. A catalytically active intermediate complex, $Ru_2(CO)_6(Ph_2C_2)$, was isolated when Ph_2C_2 was used as an acceptor.

Introduction

The homogeneously catalyzed H-transfer process outlined below (eq. 1) is a well documented reaction [1]. With transition metal complexes as catalysts, primary and secondary alcohols can be oxidized to aldehydes and ketones, respectively. An acceptor molecule A is simultaneously reduced. A variety of organic acceptors, including aldehydes and ketones, can be used. Thermodynamically the reaction depends on the redox properties of the system.



$$\overset{\displaystyle OH}{\overset{|}{RCHR'}} + A \underset{}{\overset{\text{catalyst}}{\rightleftharpoons}} \overset{\displaystyle O}{\overset{\|}{RCR'}} + AH_2 \quad (1)$$

$(R, R' = H, \text{alkyl}, \text{aryl})$

Kinetically, the process requires the intervention of a metal complex capable of transferring H atoms from a donor to an acceptor molecule. The Meerwein-Pondorf-Oppenauer oxidation-reduction reaction exemplifies the reactivity of aluminium alkoxides as catalysts in reaction 1. Among transition metal catalysts a variety of complexes, based mainly on Ru, Rh and Ir, were successfully employed [1].

In a recent communication we described a new type of a homogeneously catalyzed H-transfer reaction [2], which primary alcohols are transformed to esters with a catalytic amount of $Ru_3(CO)_{12}$ in the presence of an H-acceptor (A) (eq. 2). Although this reaction also involves a hydrogen transfer, it differs fundamentally

$$2RCH_2OH + 2A \xrightarrow{Ru_3(CO)_{12}} RCO_2CH_2R + 2AH_2 \tag{2}$$

(R = aryl, alkyl)

from reaction 1 in that it is bimolecular. Formally, reaction 2 is an oxidative coupling of two alcohol molecules to give an ester. Thus, dodecacarbonyl triruthenium is a unique H-transfer catalyst percursor, exhibiting a new type of catalytic activity.

Subsequent to our publication, two reports, also claiming reaction 2 under homogeneous conditions, but with different transition metal catalysts, have appeared in the literature [3,4]. These reports are discussed below.

Discussion

The scope of the reaction

The scope of reaction 2 was examined with several types of alcohols, and the results are presented in Table 1. (For detailed reaction conditions see footnote in Table 1). The reaction under investigation seems to be a general one. Straight and branched chain primary aliphatic alcohols as well as various benzylic alcohols are reactive. With most alcohols the conversions are very good; and prolongation of the reaction leads to practically quantitative conversions of the alcohols. Even neopentyl pivalate, a very hindered ester, is produced in respectable yield, and this can be further improved by prolonging the reaction.

TABLE 1 [a]

EXPERIMENTAL PARAMETERS FOR THE REACTION $2RCH_2OH \rightarrow RCO_2CH_2R$

Alcohol	Time (h)	Conversion (%)	Selectivity (%)	
			Ester	Aldehyde
Propanol	4	93	98	2
Octanol	4	98	99	1
Isobutanol	4	95	99	1
Neopentanol	4	76	97	3
2-Ethoxyethanol	4	56	100	–
Benzyl alcohol	4	96	97	3
Benzyl alcohol [b]	9	83	86	3
4-Chlorobenzyl alcohol	4	63	84	16
4-Methylbenzyl alcohol	4	99	87	13
4-Methoxybenzyl alcohol [c]	4	75	69	25
1,4-Butanediol [d]	6	95	100	–

[a] Reaction conditions: alcohol (7.5 mmol); tolane (7.5 mmol); $Ru_3(CO)_{12}$ (0.05 mmol). Temperature (145°C) under dinitrogen in a closed reactor. [b] Acetone (22.5 mmol) and tolane (0.75 mmol) were used as acceptors. A small quantity of isopropyl benzoate was detected. [c] Bis-(4-methoxybenzyl) ether was detected. [d] The product is γ-butyrolactone.

Excellent selectivities are attained (> 90%) with aliphatic alcohols as well as with benzyl alcohol. Aldehydes of the corresponding alcohols, which are intermediates in the reaction (vide infra), are the main by-products (> 1% by GlC). Although the conversion of 4-methoxybenzyl alcohol is good, the selectivity in the ester formation is poor (bis-(4-methoxybenzyl) ether is also produced). With ethoxyethanol, although the selectivity is good, the reaction is slow.

Tsuji et al. [3], using $PdCl_2$ or $Pd(OAc)_2$ and CCl_4 as an acceptor, recently reported similar ester formation from octanol and benzyl alcohol. Although the yield of octyl octanoate is good (73%), the selectivity in the formation of benzyl benzoate is poor (35%). No further examples were given in the above report.

Murahashi et al. [4], have also recently described an efficient catalytic transformation of alcohol to ester using $H_2Ru(Ph_3P)_4$ as a catalyst precursor. Although they used more severe reaction conditions (180°C; 16–24 h), somewhat lower conversions of the primary alcohols were obtained. Nevertheless, in most cases no hydrogen acceptor was used and liberation of dihydrogen is therefore implied. We could not affect ester formation to an appreciable extent with $Ru_3(CO)_{12}$ in the absence of H-acceptor even at 180°C. The two catalytic systems must obviously be fundamentally different.

Our catalytic system is also reactive with diols, and most of the work with those has been described in two preliminary reports [5,6]. The most selective and, therefore, useful reaction is with 1,4-butanediol, which is quantitatively converted into butyrolactone (Table 1). With acetone as an acceptor the reaction is somewhat slower, but a high selectivity is maintained. While 1,5-pentanediol gives rise to a mixture of δ-valerolactone and a polyester, higher α,ω-diols yield only polyesters. An interesting transformation described below was affected with 2-butyne-1,4-diol, a commercially available inexpensive material. This one-step reaction was affected albeit in a low yield, with $Ru_3(CO)_{12}$ and $H_2Ru(PPh_3)_4$ [6].

Nevertheless, the reaction does not require an external H-acceptor and in fact constitutes an isomerization reaction, which to the best of our knowledge has not been previously reported. If a more efficient H-transfer catalyst can be discovered this type of reaction may turn out to be useful in the direct conversion of 2-butyne-1,4-diol into butyrolactone.

The catalyst

The relationship between the trimetallic catalyst precursor and the active catalytic species is not known. The catalytic activities of several cluster complexes in the oxidation of benzyl alcohol under identical conditions are indicated by the following relative rates: $Ru_3(CO)_{12}$ (100), $H_4Ru_4(CO)_{12}$ (100), $Os_3(CO)_{12}$ (10), $Fe_3(CO)_{12}$ (~ 1). The similar reactivities of the Ru_3 and Ru_4 clusters is noteworthy. Although we employ reaction conditions appropriate for the formation of $H_4Ru_4(CO)_{12}$ from $Ru_3(CO)_{12}$ [7], it is at present impossible to tell whether the former is actually present in the reaction mixture. The IR spectrum during and at the end of the reaction shows a broad, unresolved band in the CO stretching region, and preliminary isolation experiments have revealed the presence of many complexes in the mixture. From visual inspection of the orange reaction mixtures of $Ru_3(CO)_{12}$, tolane, and alcohols, it is concluded that the reaction is homogeneous at all stages. Ruthenium metal was found to be inactive in the reaction under consideration.

Other clusters viz. $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$ as well as $Mn_2(CO)_{10}$, $CO_2(CO)_8$, $Fe(CO)_5$ and $W(CO)_6$ are inactive in reaction 2 at 145°C in the presence of diphenylacetylene.

From the work of Murahashi [4] with $H_2Ru(PPh_3)_4$ and our work with $Ru_3(CO)_{12}$, it appears that although the nuclearity of the catalytic species is not known, both mononuclear and cluster complexes are active catalyst precursors.

The acceptor

Diphenylacetylene (tolane) was used as an acceptor throughout most of this work. It is reduced to a mixture of *cis* and *trans* stilbenes and 1,2-diphenylethane. *Cis*-stilbene is the kinetic product, and in a separate experiment was found to undergo a catalytically induced isomerization with $Ru_3(CO)_{12}$ to give *trans*-stilbene. In most experiments equimolar quantities of tolane and alcohol were used. The further reduction of the stilbenes to diphenylethane is a considerably slower process.

A variety of other organic compounds function as H-acceptors in reaction 2. We have evaluated the relative efficiency of several H-acceptors which are of interest by measuring the initial rate of disappearance of benzyl alcohol. Another parameter of interest in a catalytic reaction is the maximum turnover number, an indicator of catalyst life time. This parameter was determined for reaction 2 by using large excess of alcohol and acceptor and ascertaining their concentration when catalytic activity ceased. The data are presented in Table 2.

Cyclohexanone and acetone exhibit a peculiar behavior. After a short reaction time (ca. 25% conversion of the alcohol), a ruthenium mirror is formed and the reaction stops. However, when a small quantity of tolane is present (10% of alcohol concentration), the reaction mixture stays homogeneous throughout the reaction and, in fact, cyclohexanone becomes a better acceptor than tolane. In such a mixture very little tolane is reduced. We infer that tolane stabilizes the active catalytic species. No such stabilization was obtained with phosphines.

TABLE 2

INITIAL RATES AND TURNOVER NUMBERS FOR THE REACTION $PhCH_2OH \xrightarrow{Ru_3(CO)_{12}} PhCO_2CH_2Ph$

Acceptor compound	Initial rate [a] (M h^{-1})	Turnover [b] number (h)
PhCOCH=CHPh	0.45	1300 (24)
Cyclohexanone	0.22	950 (21)
PhC≡CPh	0.11	305 (31)
Acetone [c]	0.9	630 (38)

[a] Measured as the initial rate of disappearance of $PhCH_2OH$ in 1-methylnaphthalene at 145°C. $[PhCH_2OH] = [\text{acceptor}] = 0.75\ M$; $[Ru_3(CO)_{12}] = 5 \times 10^{-3}\ M$. [b] Maximum number of moles of alcohol consumed per mole of $Ru_3(CO)_{12}$ at the time designated in brackets; the following molar ratio was used: $[Ru_3(CO)_2]/[PhCH_2OH]/[\text{acceptor}] = 1/1500/1500$ without solvent. [c] $[Ph_2C_2]/[Ru_3(CO)_{12}] = 15/1$.

While a slow reaction was observed with 1-octene as an acceptor, (34% conversion at 16 h), there was none with ethylene at 600 psi. Both diethyl maleate and *c,t,t*-1,5,9-cyclododecatriene are reactive but slow acceptors.

Carbon monoxide (600 psi) also fails to oxidize an alcohol in the presence of $Ru_3(CO)_{12}$ and it completely inhibits reaction 2 in the presence of tolane. We infer that there is a preliminary dissociation of CO from a complex. Another interesting acceptor is CCl_4, which must react as follows:

$$2PhCH_2OH + 2CCl_4 \xrightarrow{Ru_3(CO)_{12}} PhCO_2CH_2Ph + 2HCCl_3$$

Evolution of HCl was observed and chloroform was identified by GLC. After 5.5 h the yield of benzyl benzoate was 44%. The presence of HCl catalyzes substantial formation of dibenzyl ether. However, since the reaction was carried out in a closed system, the formation of the ether becomes reversible. Accordingly, we were able to detect the formation and disappearance of dibenzyl ether with concomitant formation of benzyl benzoate. In order to minimize ether formation (and also corrosion), the reaction was carried out in the presence of anhydrous K_2CO_3. The reduction of the C–Cl bond is a good indication of the presence of metal hydrides species in the reaction mixture [8].

Several of the ester-forming reactions described by Murahashi [4], using $H_2Ru(PPh_3)_4$, do not require an H-acceptor, and this implies the liberation of dihydrogen (180°C). As previously stated, we could not effect our reaction in the absence of an H-acceptor even at 180°C. The thermochemistry of ester formation from alcohol (ethanol) is depicted below [8b].

$$2C_2H_5OH \rightarrow CH_3CO_2C_2H_5 + 2H_2 \; \Delta H = 18.8 \text{ kcal mol}^{-1}$$

Obviously, an acceptor molecule will turn the above endothermic process into an exothermic one (heat of hydrogenation). Alternatively, high temperature coupled with a positive entropy will also favor the above reaction. However, since Murahashi [4] did not report dihydrogen formation and since Nishiguchi et al. [9] have reported that heating $H_2Ru(PPh_3)_4$ in the presence of hydrogen donor but in the absence of hydrogen acceptor compounds leads to hydrogenolysis of the P–Ph bond, it is conceivable that the phosphines (12 P–Ph bonds per mol) or even phenyl rings serve as H-acceptors in Murahashi reactions. This may also explain our observation of the inactivity of $Ru_3(CO)_{12}$ in the absence of an H-acceptor.

Mechanism studies

The mechanistic analysis of a catalytic reaction may conceptually and experimentally be divided into the catalyst and the substrate levels with the ultimate goal of unifying them into a single comprehensive scheme. Although our efforts to trace the active catalytic species have not yet been successful, we have accumulated interesting information regarding the mode of substrate transformation which reveals some mechanistic details of the reaction under investigation.

The reaction profiles of the various alcohols were constructed by monitoring (GLC) the concentration changes of all the components. In contrast with the experiments in Table 1, these experiments were conducted in the presence of diglyme as a solvent. Figures 1 and 2 present the data for benzyl alcohol and pentanol. All the alcohols in this study were examined in the same way and were found to exhibit similar behavior.

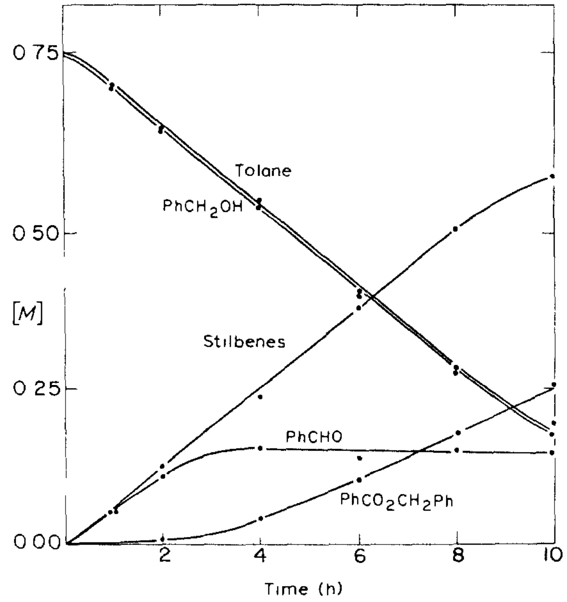


Fig. 1. Initial concentrations: [$PhCH_2OH$] = [tolane] = 0.75 *M*; [$Ru_3(CO)_{12}$] = 5×10^{-3} *M*, in diglyme at 145 ± 1°C.

Two basic conclusions emerge from these data:

(a) Aldehydes are intermediates in the oxidative coupling of alcohols to ester.

(b) The overall transformation of alcohols to ester is a two-stage process.

It will, therefore, be convenient to analyze the two steps separately.

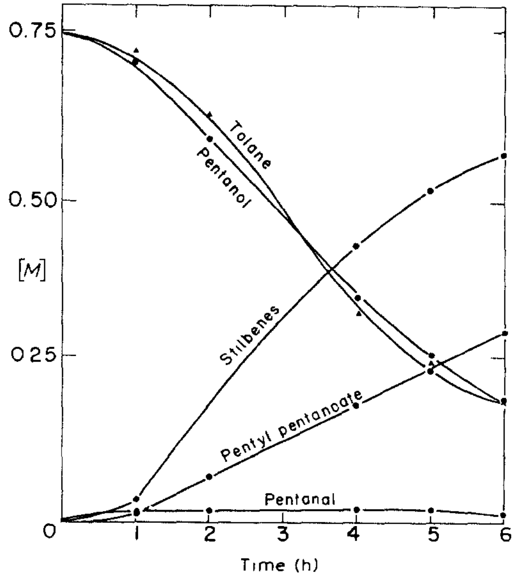


Fig. 2. Initial concentrations: [1-pentanol] = [tolane] = 0.75 *M*; [$Ru_3(CO)_{12}$] = 5×10^{-3} *M*, in diglyme at 145 ± 1°C.

Aldehyde formation

Aldehyde is the first stable product. The following simple stoichiometry was inferred from the various reaction profiles:

$$RCH_2OH + A \xrightarrow{Ru_3(CO)_{12}} RCHO + AH_2 \qquad (3)$$

Figures 1 and 2 indicate that a steady state concentration of the aldehyde is attained and maintained during most of the reaction period. All the alcohols (Table 3) except 4-methoxybenzyl alcohol exhibit similar behavior, each giving rise to a different level of aldehyde concentration. Since ester formation requires one mole of aldehyde (vide infra), the quantity of aldehyde produced at any time is the sum of the observed aldehyde and ester concentrations. In Table 3 are listed the rates of aldehyde formation during its steady state concentration period, and the actual steady state concentration (M). The aliphatic alcohols give rise to a low steady state aldehyde levels (0.02–0.03 M) compared to higher levels (0.12–0.22 M) found for the benzylic alcohols (Table 3).

The variations in the rates of formation the aldehydes (Table 3) are very small. A small retardation in the rates is noted upon increasing the bulk of the three aliphatic alcohols. The next three benzylic alcohols have practically equal oxidation rates. Thus, electronic factors have little effect on the rates of oxidation of alcohols to aldehydes. With 4-methoxybenzyl alcohol a modest rate enhancement is noted, as might have been expected on the basis of its relative oxidation potential [10]. Therefore, it must be concluded that very little charge is generated on the carbinol carbon atom in the transition state of the oxidation reaction. This is also in accord with our findings that benzyl alcohol is oxidized at practically the same rate in diglyme, t-butanol and 1-methylnaphthalene.

At present it is difficult to define other mechanistic details. We have, however, established that with benzyl alcohol the initial rate of oxidation is proportional to the alcohol as well as to the $Ru_3(CO)_{12}$ concentrations. The observed steady state concentration of the aldehyde indicates the establishment of an equilibrium system involving the aldehyde and other intermediates. The nature of this system will be considered.

TABLE 3

RATES OF ALDEHYDE AND ESTER FORMATION AT CONSTANT ALDEHYDE CONCENTRATION

Alcohol [a]	Rates ($M\ h^{-1}$)		(M) [b]
	(Aldehyde)$\times 10^2$	(Ester)$\times 10^2$	
1-Pentanol	5.6	5.6	(0.02)
Isobutanol	4.7	4.7	(0.02)
Neopentanol	2.6	2.6	(0.03)
Benzyl alcohol	3.3	3.3	(0.15)
3-Chlorobenzyl alcohol	2.7	2.7	(0.12)
4-Methylbenzyl alcohol	3.0	3.0	(0.22)
4-Methoxybenzyl alcohol	6.7	1.4	

[a] Initial concentrations: [alcohol] = [tolane] = 0.75 M, $[Ru_3(CO)_{12}] = 5 \times 10^{-3}$ M in diglyme at 145 ± 1°C under dinitrogen in a closed reactor. Concentrations were monitored with GLC using appropriate calibrations. [b] The numbers in brackets are the molar steady state concentrations of the aldehydes.

Ester formation

The aldehyde formed in the first reaction stage may react catalytically to give an ester by one of the following two routes:

$$2RCHO \rightarrow RCO_2CH_2R \qquad (4)$$

$$RCHO + RCH_2OH + A \rightarrow RCO_2CH_2R + AH_2 \qquad (5)$$

Reaction 4 is a Tishchenko type intermolecular disproportionation of aldehydes, classically catalyzed by aluminium alkoxides [11]; however, a recent report claims that $H_2Ru(PPh_3)_4$ also catalyzes reaction 4 with a high degree of efficiency [12]. In reaction 5 the ester is generated by an oxidative coupling of an aldehyde and an alcohol molecule; again, a recent report claims a similar reaction with rhodium complexes [13]. Thus both reactions, 4 and 5, may occur with transition metal complexes. In order to establish the actual route in our case, we carried out a reaction with $Ru_3(CO)_{12}$ in the presence of aldehyde only. No ester could be detected with benzaldehyde both in the absence of benzyl alcohol or its presence in only a small amount; the alcohol may possibly be required to generate the active catalytic species.

We, therefore, conclude that although $H_2Ru(PPh_3)_4$ is an efficient Tishchenko type catalyst for reactions 4, $Ru_3(CO)_{12}$ is incapable of inducing such a reaction and serves as a catalyst precursor in reaction 5.

Figure 3 presents a profile for a reaction starting with a solution of PhCHO (0.375 *M*) and $PhCH_2OH$ (0.375 *M*). Both components disappear at very similar rates to give benzyl benzoate. This behavior can also be considered as evidence for a one-to-one reaction of alcohol and aldehyde to generate the ester. It should, however, be noted that the above reaction does not occur under a steady state aldehyde concentration.

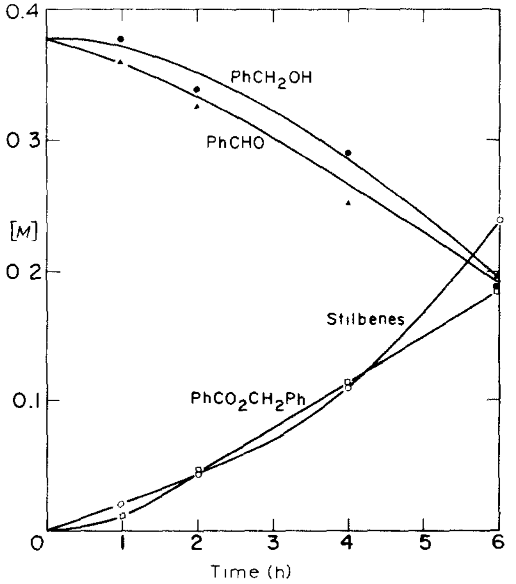


Fig. 3. Initial concentrations: $[PhCH_2OH] = [PhCHO] = 0.375$ *M*; [tolane] = 0.75 *M*; $[Ru_3(CO)_{12}] = 5 \times 10^{-3}$ *M*, in diglyme at 145 ± 1°C.

It is evident from the various reaction profiles that the rates of aldehyde and ester formation are equivalent during the steady state period of the former. This implies that for every ester molecule which is being produced an aldehyde molecule is being formed. Taken together with equation 5, the following relation which has been experimentally established holds true within the experimental error during the steady state period:

$$-0.5\left[\frac{\mathrm{d(RCH_2OH)}}{\mathrm{d}t}\right]=\frac{\mathrm{d(RCHO)}}{\mathrm{d}t}=-\frac{\mathrm{d(RCHO)}}{\mathrm{d}t}=\frac{\mathrm{d(ester)}}{\mathrm{d}t}$$

It is therefore reasonable to conclude that the aldehyde and the ester are formed via a common intermediate. However, the nature of the equilibrium system which keeps the aldehyde concentration constant is not yet clear. We have experimentally established that the ester is produced irreversibly. On the other hand, we have found (vide infra) that the alcohol and the aldehyde present in the reaction mixture undergo a catalyzed disproportionation reaction which does not involve the tolane acceptor:

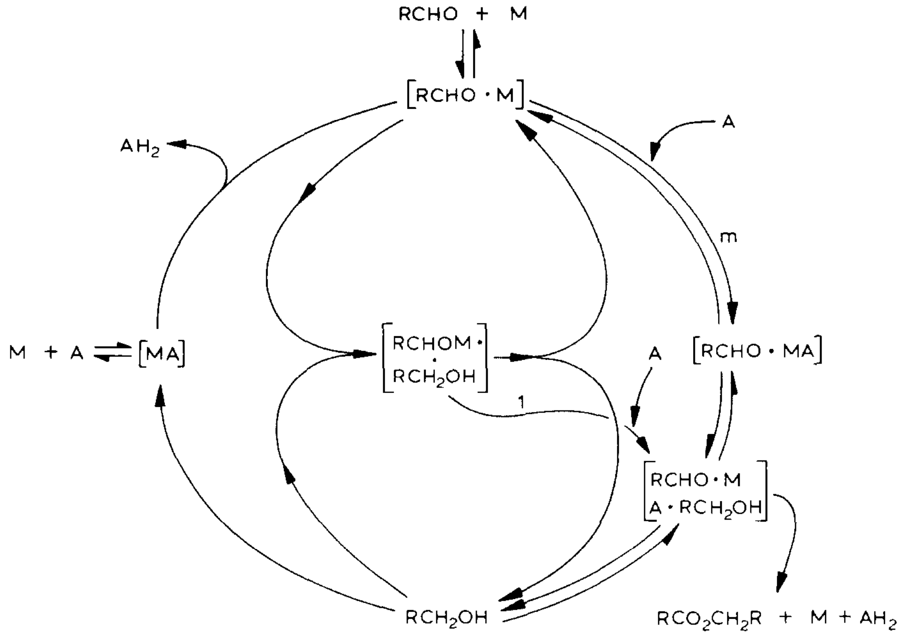
$$\mathrm{RCH_2OH + RCHO \rightleftharpoons RCHO + RCH_2OH}$$

Obviously this reaction is thermally degenerate and therefore can not affect any equilibrium systems. Furthermore from Figs. 1 and 2 it is clear that the aldehyde concentration is not affected by the drastic drop in the alcohol concentration. Therefore, neither the ester nor the alcohol equilibrate with the aldehyde. Furthermore it was found that the initial rates of aldehyde and ester formation are independent of tolane concentration over the range (tolane)/(alcohol) of 0.27 to 4. Recently we have isolated a yellow crystalline complex from a stoichiometric reaction of tolane and $Ru_3(CO)_{12}$ in 1-propanol, performed under our standard reaction conditions. Its IR spectrum and m.p. are identical with those reported by Gambino [14] for $Ru_2(CO)_6(Ph_2C_2)_2$ (to the best of our knowledge no X-ray structure has been determined). Evidently this is the first detectable complex which is formed in the reaction at 145°C. When employed as a catalyst in the ester-forming reaction (from $n\text{-}C_3H_7OH$), the above complex exhibits a reactivity similar to $Ru_3(CO)_{12}$. However, since it disappears at the early stages of the ester forming reaction, it must be a transient intermediate which does not participate in the catalytic cycle of the ester forming reaction. We therefore assume that firstly a reactive ruthenium carbonyl species (M) is formed from $Ru_3(CO)_{12}$ via dissociation of CO. In a second fast step M binds an acceptor molecule (A), and this preceeds the interaction of M with an alcohol molecule:

$$\mathrm{Ru_3(CO)_{12}}\xrightarrow[-\mathrm{CO}]{\Delta}\mathrm{M}$$

$$\mathrm{M + A \rightleftharpoons MA \rightarrow \text{to catalytic cycle}}$$

On the basis of our findings we propose the catalytic cycle depicted in Scheme 1. An aldehyde complex $RCHO\cdot M$, formed from $MA + RCH_2OH$, is a central intermediate in the above catalytic cycle. It is involved in an equilibrium reaction (top of the cycle) which accounts for the steady state concentration of the aldehyde. It should be noted that the above equilibrium controls the effective concentration of M which in turn affects the concentration of MA. The net result is that the rate of the irreversible formation of $RCHO\cdot M$, and consequently RCHO, is controlled by the above equilibrium.



SCHEME 1

RCHO · M is consumed by two additional routes. The inner cycle (Scheme 1) represents the previously mentioned degenerate alcohol–aldehyde interconversion. The oxidation-reduction takes place via a complex depicted in the center of the scheme. It catalyzes a hydrogen exchange between its two bound components and does not require the intervention of another acceptor (vide infra). If this intermediate is capable of binding an acceptor molecule (A), it may lead to ester formation (path 1). Alternatively RCHO · M may bind A (path m) which then, by interacting with an alcohol molecule, generates the ester. These two routes are similar but differ in the order of the acceptor and alcohol complexation with RCHO · M.

Part of the above scheme is still speculative. Current kinetic studies are aimed at solving the remaining problems.

Reversibility of the H-transfer process

It is of interest to elaborate upon the possible reversibility of the aldehyde formation (eq. 3) and ester formation (eq. 5) with $Ru_3(CO)_{12}$ as a catalyst precursor. We have experimentally established that neither of the two reactions is reversible in the presence of stilbenes as H-donors. Also, from the various reaction profiles it is apparent that alcohols, acting as H-donors, are incapable of reducing esters. However, the reversibility of the aldehyde forming reaction, with alcohol as H-donor, would be masked due to the degeneracy of such a process. In order to examine this point we subjected an equimolar mixture of 4-methylbenzyl alcohol and benzaldehyde in the presence of tolane to the catalytic action of $Ru_3(CO)_{12}$. The reaction

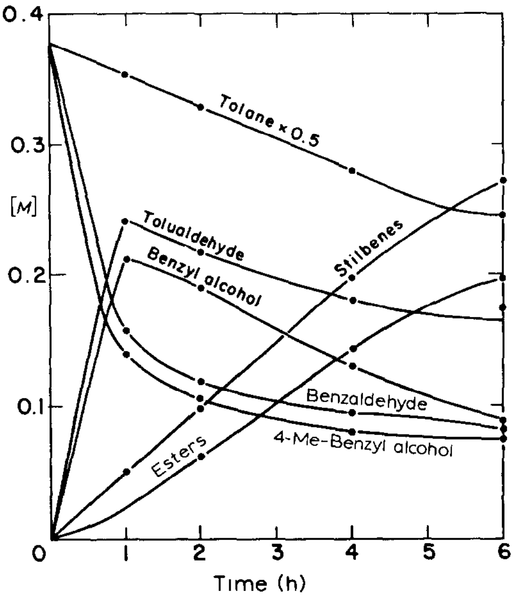


Fig. 4. Initial concentrations: [4-methylbenzyl alcohol] = [benzaldehyde] = 0.375 M; [tolane] = 0.75 M; $[Ru_3(CO)_{12}] = 5\times10^{-3}$ M, in diglyme at 145 ± 1°C.

profile (Fig. 4) indicates that fast disproportionation, which generates a four-component system (eq. 7), takes place. It is also clear that tolane is not involved in this

$$(4)\text{-}CH_3C_6H_4CHO + C_6H_5CH_2OH \overset{K\sim0.3}{\rightleftharpoons} (4)\text{-}CH_3C_6H_4CH_2OH + C_6H_5CHO \quad (7)$$

disproportionation, since stilbene formation corresponds only to the amount of ester which is formed. After ca. 1 h the four-component system reaches an equilibrium ($K \sim 0.3$) (since PhCHO has higher oxidation potential than (4)-$CH_3C_6H_4CHO$, we have anticipated that $K < 1$). Moreover, equilibration continues throughout the ester forming stage as K stays constant (within experimental error). A similar picture is obtained on starting with the other pair, i.e., tolualdehyde and benzyl alcohol. All the four possible esters were produced in this reaction, and identified by comparison with authentic samples.

From the above results we conclude that aldehydes and alcohols can disproportionate in the presence of $Ru_3(CO)_{12}$ serving as a catalyst precursor. Therefore, when starting a reaction with a single alcohol, aldehyde is first formed by an irreversible oxidation of the alcohol with tolane. The alcohol-aldehyde mixture then undergoes a dynamic disproportionation. Being degenerate, it affects neither the alcohol nor the aldehyde concentration. It is also clear that under such conditions the alcohol and aldehyde will never reach thermodynamic equilibrium. We were interested in designing a system in which ester formation will take place from a thermodynamically controlled alcohol-aldehyde concentration. (The advantage of such a system will be discussed later). This can be achieved by replacing the irreversible H-acceptor (tolane) with a reversible one. From examination of the redox potentials and from structural considerations we have selected cyclohexanone,

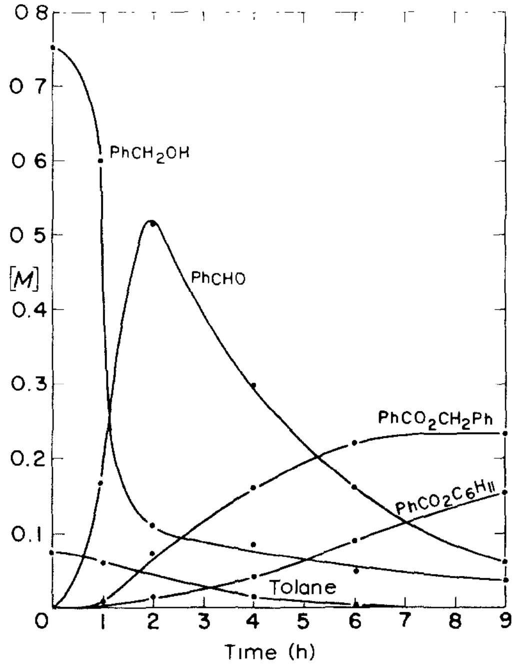
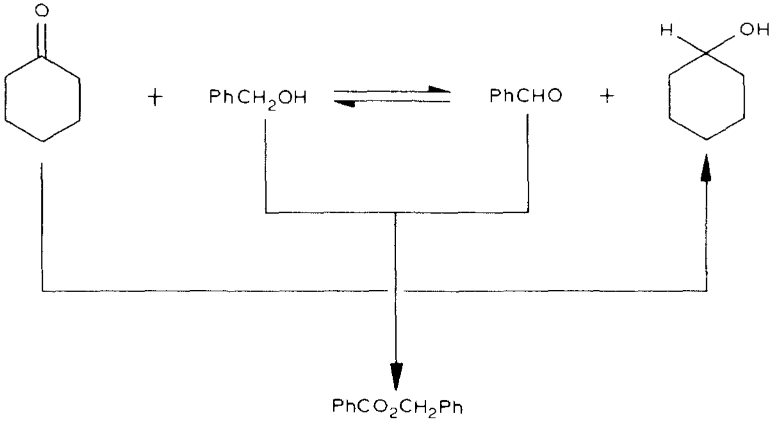


Fig. 5. Initial concentrations: [PhCH$_2$OH] = 0.75 *M*; [tolane] = 0.075 *M*; [Ru$_3$(CO)$_{12}$] = 5×10^{-3} *M*, in cyclohexanone at 145 ± 1°C.

which was also used as a solvent. The catalytic system was stabilized with tolane (vide supra). The reaction profile (Fig. 5) clearly differs from that observed when tolane alone was used (Fig. 1). A thermodynamic equilibrium follows the initial fast surge in the benzaldehyde concentration, and the system is described in eq. 8.
The value of *K* for the four-component system is 0.3 after 2.5 h and 0.25 after 6 h



(8)

(Fig. 5). The concentration ratio (PhCHO)/(PhCH$_2$OH) varies with time (Fig. 5), mainly due to the formation of cyclohexanol in the ester forming step which shifts the equilibrium to the left. Cyclohexyl benzoate is a by-product of this reaction.

The use of cyclohexanone both as a solvent and a hydrogen acceptor is advantageous from the synthesis point of view. In acetone the system behaves similarly but the rate is slower. However, the essential point in using a reversible acceptor is that ester formation takes place from a thermodynamically equilibrating alcohol-aldehyde mixture. Such reaction conditions will prevent a possible situation in which an alcohol is depleted and excess aldehyde remains unreacted. However, one must also consider the lower selectivity of this system due to the competitive formation of the cyclohexyl ester.

Experimental

GLC analyses were carried out on a Hewlett Packard 5830A gas chromatograph. IR spectra were recorded on Perkin-Elmer Grating Infrared Spectrophotometer Model 177, NMR spectra were measured with Bruker WH-90 spectrometer at 90 MHz in $CDCl_3$ solutions and mass spectra were recorded with a DuPont 21-491B spectrometer. All starting materials and solvents were purified and dried according by standard procedures [15]. $Ru_3(CO)_{12}$ was prepared [16] from $RuCl_3 \cdot 3H_2O$.

General procedure for the oxidative coupling of alcohols

The quantities of reaction components and solvents designated in the footnotes of Tables 1, 2 and 3 as well as in the legends of Figs. 1–5 were placed in a stainless steel glass-lined reactor (45 ml). Air was purged with dry nitrogen. The reactor was closed and placed at a thermostated oil bath of 145 ± 1°C. For the construction of reaction profiles, samples for GLC analyses were withdrawn periodically. The GLC analyses were carried out using calibration curves for the various components and are accurate to ±3%; each experiment was carried out in duplicate. Every GLC signal was identified by comparison of the retention times using authentic samples. There is a reasonably good agreement (10–15%) between isolated and GLC yields.

Reaction components were isolated by column chromatography. Good separations were obtained on silica using petroleum ether/CH_2Cl_2 mixtures. The isolated products were identified by comparison with authentic samples.

The effect of triphenylphosphine

Benzyl alcohol (0.81 g), tolane (1.33 g), triphenylphosphine (0.045 g) and $Ru_3(CO)_{12}$ (0.032 g) in 1-methylnaphthalene (10 ml) were heated in a closed glass lined reactor under a blanket of dinitrogen at 145 ± 1°C. After 4 h, GLC analysis (mol %): benzyl alcohol (29), benzaldehyde (71); no benzyl benzoate could be detected.

The use of various acceptors

(a) Benzyl alcohol (0.81 g), $Ru_3(CO)_{12}$ (0.032 g) in 1-methylnaphthalene (10 ml) were placed in a glass lined reactor. The air was purged with CO, and finally the reactor was pressurized to 600 psi of CO. After 6 h, GLC analysis has indicated that no reaction took place. $Ru_3(CO)_{12}$ crystallized from the yellow solution.

(b) The above reaction (a) was repeated in the presence of tolane (1.33 g). GLC analysis has indicated conversion to benzaldehyde (3.6%) after 6 h reaction time. No benzyl benzoate could be detected.

(c) Reaction (a) was repeated with ethylene in place of CO (600 psi). After 6 h, GLC analysis indicated no reaction.

(d) Benzyl alcohol (0.81 g), 1-octene (1.40 g) and $Ru_3(CO)_{12}$ (0.032 g) were treated as in (a). After 16 h at 145°C, GLC analysis revealed (mol %): benzyl alcohol (66), benzaldehyde (17), benzyl benzoate (11), dibenzyl ether (6).

(e) Benzyl alcohol (0.81 g), diethyl maleate (1.29 g) and $Ru_3(CO)_{12}$ (0.032 g) were heated in a closed reactor at 145°C for 21 h. GLC analysis (mol %): benzyl alcohol (35), benzaldehyde (12), dibenzyl ether (1), benzyl benzoate (52).

(f) Reaction (e) was repeated (176°C, 24 h) with *c,t,t*-1,5,9-cyclododecatriene as an acceptor. GLC analysis (mol %): benzyl alcohol (20), benzaldehyde (43), benzyl benzoate (28).

(g) Benzyl alcohol (0.81 g), K_2CO_3 anhydrous (2.08 g) and $Ru_3(CO)_{12}$(0.032 g) in CCl_4 (10 ml) were heated under a blanket of dinitrogen in a closed glass lined reactor at 145 ± 1°C. After 5.5 h a GLC analysis indicated the following composition (mol%): benzyl alcohol (10.5), benzyl benzoate (22), benzaldehyde (37.5) and dibenzyl ether (7.5). Chloroform was detected by GLC.

Isomerization of trans-stilbene

Benzyl alcohol (0.81 g), *cis*-stilbene (0.68 g) and $Ru_3(CO)_{12}$ (0.032 g) in 10 ml diglyme were heated in a closed glass lined reactor at 145 ± 1°C under a blanket of dinitrogen. After 2 h GLC analysis indicated 100% conversion of *cis-* to *trans*-stilbene.

Isolation of $Ru_2(CO)_6(Ph_2C_2)_2$

$Ru_3(CO)_{12}$ (0.5 g), tolane (1.39 g) and n-propanol (0.8 g) were heated in a closed reactor at 145°C under nitrogen for 2 h. The title complex was isolated by chromatography (silica gel; petroleum ether) as yellow crystal, 280 mg. An identical complex (m.p., IR, NMR) was obtained by the procedure described by Gambino et al. [14].

Activity of $Ru_2(CO)_6(Ph_2C_2)_2$

n-Propanol 0.5 g (8.3 mmol), tolane 1.33 g (7.50 mmol) and $Ru_2(CO)_2(Ph_2C_2)_2$ 0.032 g (0.05 mmol) were heated under nitrogen for 4 h at 145°C. GLC analysis: tolane (1.9 mmol) n-propanol (2.7 mmol), propyl propionate (4.8 mmol), propanal (0.8 mmol).

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