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Preliminary communication

RHODIUM(I) CATALYZED COOLIGOMERIZATION OF CARBON MONOXIDE WITH ETHYLENE. DIRECT EVIDENCE FOR A SINGLE MODE OF STEPWISE CHAIN GROWTH*

AYUSMAN SEN** and JEFFREY S. BRUMBAUGH
Chandlee Laboratory, Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802 (U.S.A.)

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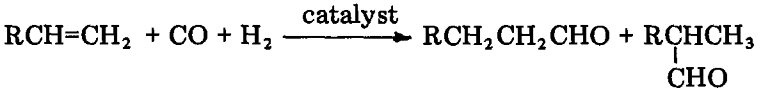
Summary

Rhodium(I) compounds such as $HRh(CO)(PPh_3)_3$ and $ClRh(CO)(PPh_3)_2$, when dissolved in a ROH/HOAc mixture (ROH = MeOH, EtOH), were found to catalyze the cooligomerization of C_2H_4 and CO to a mixture of $H(—CH_2CH_2CO—)_nOR$ and $H(—CH_2CH_2CO—)_nCH_2CH_3$ (n = 1—4). This reaction was found to proceed through a single mode of chain growth involving alternate insertions of CO and C_2H_4 with concomitant alcoholysis and hydrogenolysis of the resulting metal acyls and metal alkyls respectively. The cooligomerization of C_2H_4 and CO was also observed when Me_2CO/H_2O or Me_3COH/H_2O was used as solvent, the exclusive products being the ketones, $H(—CH_2CH_2CO—)_nCH_2CH_3$ (n = 1—4). No reaction was observed in the absence of H_2O.

Catalytic hydroformylation of olefins to aldehydes (eq. 1) is a reaction of considerable practical, as well as scientific, importance [1]. The key intermediate in the mechanism of this reaction is a metal acyl species formed by the successive insertions of olefin and CO into a preformed metal hydride. The final step in the reaction is the conversion of this metal acyl species to the aldehyde by hydrogenolysis (eq. 2) [2]. However, under conditions of



$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2CHO + R\underset{\displaystyle CHO}{\underset{|}{C}}HCH_3 \qquad (1)$$

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*Dedicated to Professor Jack Halpern on the occasion of his 60th birthday.

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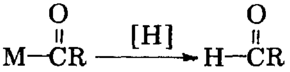
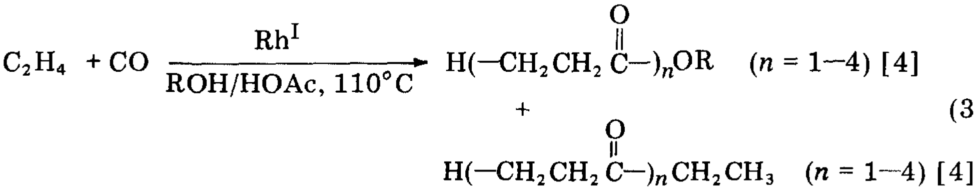


$$M-\overset{O}{\overset{\|}{C}}R \xrightarrow{[H]} H-\overset{O}{\overset{\|}{C}}R \qquad (2)$$

low $[H_2]$ and high [olefin] and [CO], further successive insertions of olefin and CO into the metal—acyl bond should be possible, resulting in the cooligomerization and copolymerization of the olefin with CO. Indeed, several products presumably formed through such a process have been described in the literature [3], although no mechanistic information is available. In this paper, we describe the full spectrum of products formed in the rhodium(I) catalyzed cooligomerization of C_2H_4 and CO (eq. 3), and demonstrate that these products arise through a common mechanistic pathway involving a single mode of chain growth.



$$C_2H_4 + CO \xrightarrow[ROH/HOAc,\ 110^\circ C]{Rh^I} H(-CH_2CH_2\overset{O}{\overset{\|}{C}}-)_nOR \quad (n = 1-4)\ [4]$$
$$+ \qquad (3)$$
$$H(-CH_2CH_2\overset{O}{\overset{\|}{C}}-)_nCH_2CH_3 \quad (n = 1-4)\ [4]$$

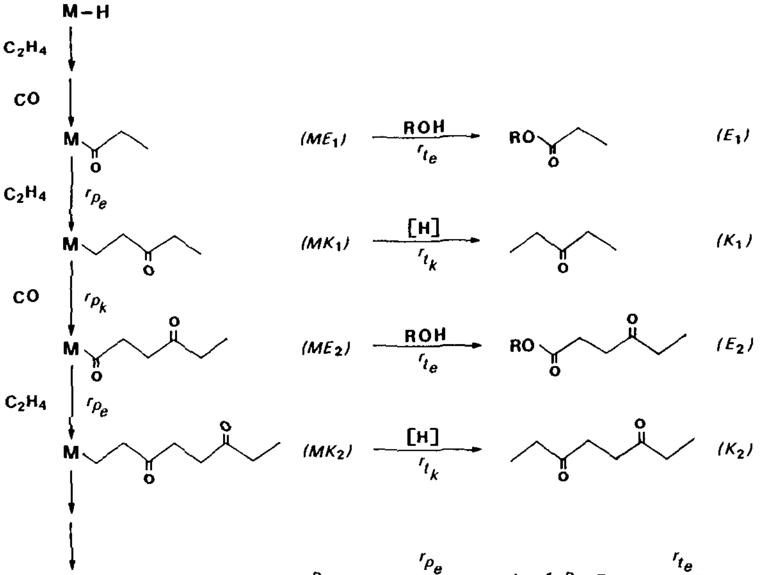
($Rh^I = HRh(CO)(PPh_3)_3$, $ClRh(CO)(PPh_3)_2$;
ROH = MeOH, EtOH)

In a typical reaction, 0.10 g of $ClRh(CO)(PPh_3)_2$ was added to 10 ml of a 1/1 (v/v) mixture of MeOH and HOAc, and this reaction mixture was exposed to C_2H_4 (500 psi) and CO (500 psi) at 110°C for 1 day. At the end of this period, the gases were vented and, following the removal of the Rh containing products, 6.5 g of the organic product mixture were obtained. The overall reaction represented a combined "turnover" of 1350 equivalents (relative to catalyst) of C_2H_4 and CO. After separation of the organic products [6], the following compounds were obtained. $H(-CH_2CH_2CO-)_nOCH_3$: $n = 1$, 1.67 g; $n = 2$, 0.42 g; $n = 3$, 0.088 g; $n = 4$, 0.016 g. $H(-CH_2CH_2CO-)_nCH_2CH_3$: $n = 1$, 2.07 g; $n = 2$, 1.64 g; $n = 3$, 0.48 g; $n = 4$, 0.070 g.

A rational mechanism for this reaction encompasses a single mode of chain growth involving alternate insertions of CO and C_2H_4 (Scheme 1). The esters (E_n) and ketones (K_n) arise by the alcoholysis and hydrogenolysis [7] of the alternately formed intermediate metal acyls (ME_n) and metal alkyls (MK_n), respectively. The metal acyl species are terminated by reaction with ROH (rate = r_{t_e}), and are propagated by insertion of C_2H_4 (rate = r_{p_e}). R_e represents the mole fraction of a metal acyl species that is propagated. Similarly, R_k represents the mole fraction of a metal alkyl species that is propagated. We can now treat this system mathematically in the following way:

n = no. of repeating units of $(-CH_2CH_2\overset{O}{\overset{\|}{C}}-)$
(E_n) = no. of mol of E_n formed
X_n^E = mol fraction of E_n formed

$$(E_1) = (1 - R_e)(ME_1) = (1 - R_e)R_e^{0}R_k^{0}(ME_1)$$
$$(E_2) = (1 - R_e)(ME_2) = (1 - R_e)R_e^{1}R_k^{1}(ME_1)$$
$$(E_3) = (1 - R_e)(ME_3) = (1 - R_e)R_e^{2}R_k^{2}(ME_1)$$



$$R_e = \frac{r_{p_e}}{r_{p_e} + r_{t_e}} \quad ; \quad 1 - R_e = \frac{r_{t_e}}{r_{p_e} + r_{t_e}}$$

$$R_k = \frac{r_{p_k}}{r_{p_k} + r_{t_k}} \quad ; \quad 1 - R_k = \frac{r_{t_k}}{r_{p_k} + r_{t_k}}$$

SCHEME 1. Mechanism for the rhodium(I) catalyzed cooligomerization of CO and C_2H_4.

$$\log[(E_1)/(ME_1)] = \log(1 - R_e) + 0\log(R_eR_k)$$
$$\log[(E_2)/(ME_1)] = \log(1 - R_e) + 1\log(R_eR_k)$$
$$\log[(E_3)/(ME_1)] = \log(1 - R_e) + 2\log(R_eR_k)$$

In general, $\log[(E_n)/(ME_1)] = \log(1 - R_e) + (n - 1)\log(R_eR_k)$, since all the products are ultimately derived from ME_1.

$$(E_n)/(ME_1) = X_n^E$$

Therefore, $\log X_n^E = \log(1 - R_e) + (n - 1)\log(R_eR_k)$ (4)

Similarly, $\log X_n^K = \log(1 - R_k) + \log R_e + (n - 1)\log(R_eR_k)$ (5)

Thus, a plot of the log of the mol fractions of the esters and ketones formed versus $(n - 1)$ should yield two parallel straight lines with a common slope of $\log(R_eR_k)$ and with intercepts of $\log(1 - R_e)$ and $\log(1 - R_k) + \log R_e$, respectively, from which R_e and R_k may be calculated. In reactions where ketones are the sole products (see below), eq. 5 can be simplified to eq. 6 by substituting $R_e = 1$. Eq. 6 is similar to the Schultz—Flory equation [8] which is only applicable to polymerizations involving a single mode of propagation and a single mode of termination. R is identical to the quantity α which is equal to the probability of chain growth in the Schultz—Flory equation [8].

$$\log X_n^K = \log(1 - R_k) + (n - 1)\log R_k \qquad (6)$$

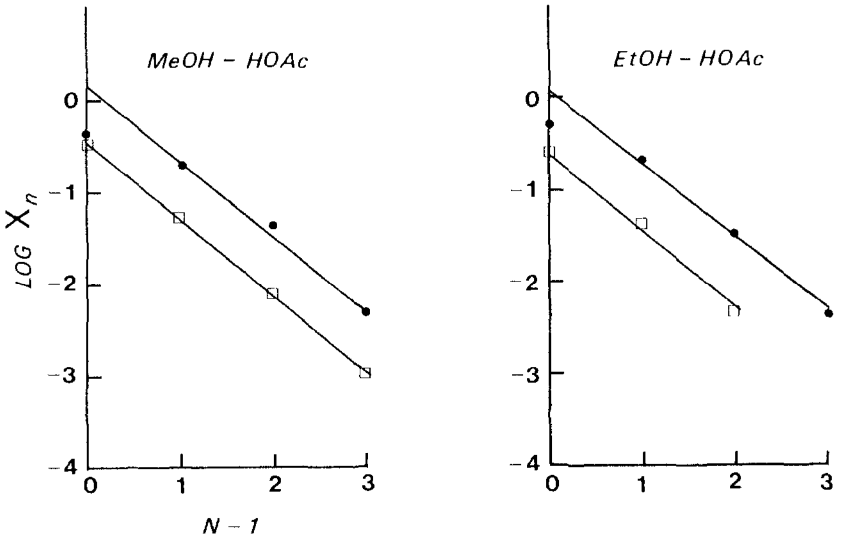


Fig. 1. Plots of logX_n vs. (n — 1) for oligomeric esters (□) and ketones (●). [Rh(Cl)(CO)(PPh$_3$)$_2$] 1 × 10^{-2} *M*. ROH/AcOH = 1/1 (v/v). Reaction temp. 110°C. Reaction time 1 day. Initial pressure: $P_{CO} = P_{C_2H_4}$ = 500 psi.

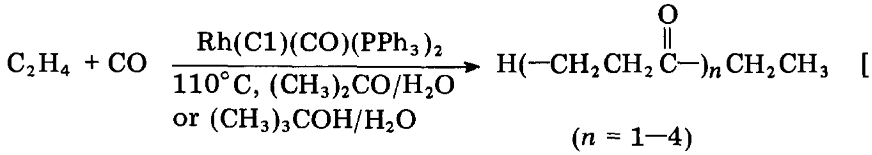
Using ClRh(CO)(PPh$_3$)$_2$ as catalyst, our results in two different solvent systems are shown in Fig. 1. The close agreement with the theoretical prediction indicates that all products arose primarily out of a single mode of chain growth. For reasons not yet clear, the yield of the monoketone was consistently lower than predicted. This indicated a higher propagation rate to termination rate ratio for the corresponding rhodium alkyl species when compared to its higher homologs. The values of R are given in Table 1 [9]. Assuming that the rates of propagation do not differ significantly in the two solvent system [10], our results indicate that the rate of alcoholysis of the metal acyls was ~1.8 times faster in MeOH than in EtOH, presumably due to steric reasons [11]. On the other hand, as expected, the rate of hydrogenolysis of the metal alkyls was independent of the alcohol employed. There was a significant deuterium isotope effect (~2.6) for the rate of alcoholysis of the metal acyls but not for the cleavage of the metal alkyls. Thus, the ratio of ketones to esters formed was significantly higher in MeOD-DOAc than in MeOH/HOAc.

TABLE 1

Catalyst	Solvent	R_e	R_k
Rh(Cl)(CO)(PPh$_3$)$_2$ [a]	MeOH/AcOH [b]	0.72	0.25
Rh(Cl)(CO)(PPh$_3$)$_2$ [a]	EtOH/AcOH [b]	0.82	0.23
Rh(Cl)(CO)(PPh$_3$)$_2$ [a]	MeOD/AcOD [b]	0.87	0.23
Rh(Cl)(CO)(PPh$_3$)$_2$ [a]	Me$_2$CO/H$_2$O [c]	—	0.14
Rh(Cl)(CO)(PPh$_3$)$_2$ [a]	Me$_3$COH/H$_2$O [c]	—	0.13

[a] [Rh^{I}] 1 × 10^{-2} *M*. [b] ROH/AcOH = 1/1 (v/v). [c] Me$_2$CO or Me$_3$COH/H$_2$O = 5/1 (v/v). Reaction temp. 110°C. Initial pressure: $P_{CO} = P_{C_2H_4}$ = 500 psi.

The hydrogen needed for the formation of the ketones may be derived by the dehydrogenation of the alcohol used [12], or from water (formed during the observed esterification of HOAc) by a water-gas shift reaction [13]. The following experiments indicate water to be a viable source of hydrogen. The rhodium(I) catalyzed cooligomerization of C_2H_4 and CO did not occur in pure acetone as solvent; however, addition of water caused the reaction to proceed readily, the products being exclusively the ketones (eq. 7), (no esters were formed since no alcohol was present). Similarly, no reaction was observed in pure t-butanol, but in the presence of water, the ketones were again the sole products (eq. 7). In this case, the esters were not formed because of the inability of the bulky t-BuOH to intercept the intermediate Rh acyls formed in the chain growth sequence [14]. Figure 2 shows a close agreement between the experimental data and eq. 6, indicating that in eq. 7 the products also arose primarily out of a single mode of chain growth. The yield of the monoketone was again lower than predicted (see above). In MeOH/H_2O mixture, as expected, both the ketones and the esters were formed, no reaction being observed in MeOH alone. Thus, at least for these systems, water was the primary source of hydrogen.



$$C_2H_4 + CO \xrightarrow[110^\circ C,\ (CH_3)_2CO/H_2O \text{ or } (CH_3)_3COH/H_2O]{Rh(Cl)(CO)(PPh_3)_2} H(-CH_2CH_2\overset{\overset{O}{\|}}{C}-)_nCH_2CH_3 \quad [4] \qquad (n = 1\text{—}4) \qquad (7)$$

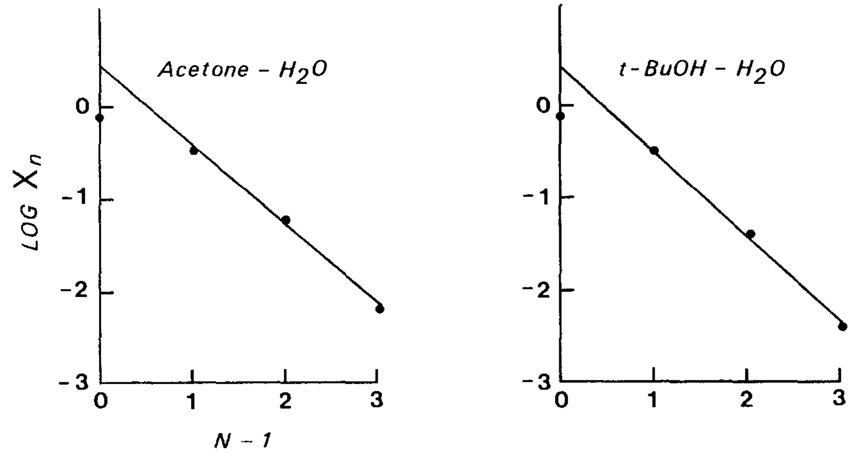


Fig. 2. Plots of $\log X_n^K$ vs. $(n - 1)$ for oligomeric ketones. $[Rh(Cl)(CO)(PPh_3)_2]$ 1×10^{-2} M. Me_2CO or Me_3COH/H_2O = 5/1 (v/v). Reaction temp. 110°C. Reaction time 1 day. Initial pressure: $P_{CO} = P_{C_2H_4}$ = 500 psi.

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3 For a review, see ref. 1(c), p. 215.

4 Spectral data for $\mathrm{H(—CH_2CH_2CO—)}_n\mathrm{OCH_3}$ have been reported [5]. ^{1}H NMR and IR spectral data for $\mathrm{H(—CH_2CH_2CO—)}_n\mathrm{CH_2CH_3}$. $n = 1$: ^{1}H NMR ($\mathrm{CDCl_3}$), δ 2.43 (4H, q, J 7.3 Hz, $\mathrm{CH_3}\mathit{CH}_2\mathrm{CO}$), 1.06 (6H, t, J 7.3 Hz, $\mathit{CH}_3\mathrm{CH_2CO}$); IR (Nujol), $\bar{\nu}$(CO) 1720 cm^{-1}. $n = 2$: ^{1}H NMR ($\mathrm{CDCl_3}$), δ 2.69 (4H, s, $\mathrm{CO}\mathit{CH}_2\mathit{CH}_2\mathrm{CO}$), 2.49 (4H, q, J 7.3 Hz, $\mathrm{CH_3}\mathit{CH}_2\mathrm{CO}$), 1.06 (6H, t, J 7.3 Hz, $\mathit{CH}_3\mathrm{CH_2CO}$); IR (Nujol), $\bar{\nu}$(CO) 1710 cm^{-1}. $n = 3$: ^{1}H NMR ($\mathrm{CDCl_3}$), δ 2.72 (8H, br, $\mathrm{CO}\mathit{CH}_2\mathit{CH}_2\mathrm{CO}$), 2.47 (4H, q, J 7.3 Hz, $\mathrm{CH_3}\mathit{CH}_2\mathrm{CO}$), 1.05 (6H, t, J 7.3 Hz, $\mathit{CH}_3\mathrm{CH_2CO}$); IR (Nujol), $\bar{\nu}$(CO) 1705 cm^{-1}. $n = 4$: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.72 (12H, br, $\mathrm{CO}\mathit{CH}_2\mathit{CH}_2\mathrm{CO}$), 2.48 (4H, q, J 7.3 Hz, $\mathrm{CH_3}\mathit{CH}_2\mathrm{CO}$), 1.07 (6H, t, J 7.3 Hz, $\mathit{CH}_3\mathrm{CH_2CO}$).

5 A. Sen and T.-W. Lai, Organometallics, 3 (1984) 866.

6 The organic products were separated either on a silica gel column or by gas chromatography using a 10% SP-2100 column. For samples separated by column chromatography, quantitative analysis was performed by using ^{1}H NMR spectroscopy. For samples separated by gas chromatography, quantitative analysis was done by comparison with standard samples.

7 At this point, we are uncertain about the detailed mechanism for the conversion of the metal alkyls to the ketones, (see also ref. 2).

8 G. Henrici-Olivé and S. Olivé, Angew. Chem. Int. Ed. Engl., 15 (1976) 136.

9 R_e and R_k are functions of $P_{\mathrm{C_2H_4}}$ and P_{CO} respectively. Therefore, these values should be used for comparisons only.

10 In a closely analogous case, we had demonstrated that for the Pd$^{\mathrm{II}}$ catalyzed cooligomerization of $\mathrm{C_2H_4}$ and CO, the propagation rate in MeOH did not differ significantly from that observed in EtOH [5].

11 A similar observation was also made for the Pd$^{\mathrm{II}}$ catalyzed cooligomerization of $\mathrm{C_2H_4}$ and CO [5].

12 Transition metal catalyzed transfer of hydrogen from alcohols to other substrates is well-documented. For specific examples, see: B.R. James, Adv. Organomet. Chem., 17 (1979) 319.

13 For a recent review, see: P.C. Ford, Acc. Chem. Res., 14 (1981) 31.

14 Similarly, in the analogous Pd$^{\mathrm{II}}$ catalyzed cooligomerization of $\mathrm{C_2H_4}$ and CO, esters were formed with MeOH and EtOH but none was observed when t-BuOH was used as the solvent [5].