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ALTERNATING OLIGOMERIZATION OF ETHYLENE AND CARBON MONOXIDE CATALYZED BY RHODIUM CARBONYL

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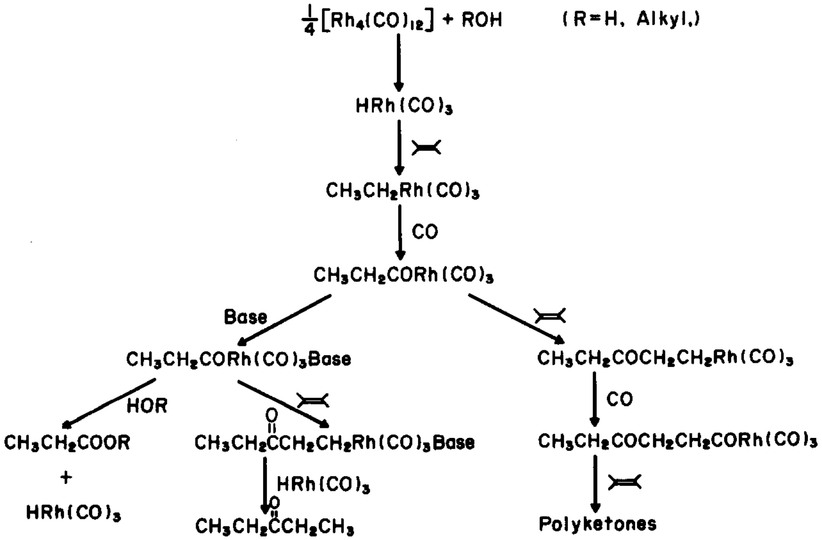
Brubaker and his coworkers have reported the free radical-initiated copolymerization of ethylene and carbon monoxide at superatomospheric pressures (1). Reppe and Magin (2) have found the polyketone formation from ethylene and carbon monoxide in the reaction catalyzed by a large amount of nickel cyano complex.

Now the authors wish to describe the alternating oligomerization of ethylene and carbon monoxide catalyzed by rhodium carbonyl. From the rhodium catalyzed reaction of ethylene with carbon monoxide in acetic acid, water, alcohols or in the mixture of these, polyketones $H(CH_2CH_2CO)_nR$ ($R=CH_3CH_2$, CH_3O and C_2H_5O) were obtained in high conversion rates.

In a typical experiment, ethylene (0.33 mol) and carbon monoxide (2 mol) were introduced into a 100 ml stainless steel autoclave containing a suspension of rhodium oxide (50 mg) in 1:1 mixture of acetic acid and methanol. The reaction was carried out at 130° for 24 hours. The products were purified by distillation and recrystallization. Octane-3,6-dione (26.1 %), undeca-3,6,9-trione (5.5 %), tetradeca-3,6,9,12-tetraone (1 %), methyl homolevulinate (15 %), and a small amount of higher members (n=7, 9) were identified as described below. These compounds show carbonyl stretching vibration at 1700 cm^{-1} in ir spectra and the signals of ethyl group at $\delta=1.0$ (triplet) and $\delta=2.5$ (quartet) and the singlet of methylene groups flanked with two carbonyls at $\delta=2.7$ in nmr spectra. The elemental analyses of the 2.4-dinitrophenylhydrazones agree satisfactorily with the assigned formulas. The degree of polymerization was determined by the nmr integration of terminal methyl protons and methylene protons. The gas remained in the autoclave after completion of the reaction was shown to consist of carbon dioxide (85.2 %), carbon monoxide (3.6 %), ethylene (1.3 %) from the analysis by gas chromatography.

The result that a large amount of carbon dioxide is generated during the reaction denotes that carbon monoxide is catalytically oxidized by the oxygen of solvents, especially by oxygen of water molecules, (3) in a similar mechanism which was shown previously (4).

FIGURE 1



On the basis of these results the formation of rhodium hydride species seems reasonable, for example.

$$[Rh_4(CO)_{12}] + 2CO + 2H_2O \longrightarrow 4HRh(CO)_3 + 2CO_2 \qquad I$$

Water must be supplied in the present case through the formation of ester or through the formation of dimethyl ether suggested by Natta et al. (5).

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O \qquad II$$

The products of these reactions may be explained by Heck's mechanisms (6) as illustrated in Figure 1. The copolymerization may proceed alternatively because of the different nature of carbon-metal bonding in σ-alkyl and σ-acyl groups in the intermediate complexes.

TABLE I

Solvents	Main Products	Yield (%)
CH_3OH (50 ml)	Octa-3,6-dione Undeca-3,6,9-trione Methyl Homolevulinate	14 % 2 % 25 %
CH_3OH (25 ml) CH_3COOH (25 ml)	Octa-3,6-dione Undeca-3,6,9-trione Methyl Homolevulinate	26 % 6 % 15 %
CH_3OH (50 ml) Pyridine (0.1 mol)	Methyl Propionate	58 %
CH_3OH (50 ml) $N(Et)_3$ (0.1 mol)	Diethyl Ketone Methyl Propionate	27 % 4 %
CH_3OH (50 ml) $N(Et)_3$ (0.1 mol) H_2O (0.2 mol)	Diethyl Ketone Methyl Propionate	71 % 4 %

If an organic base, such as pyridine or triethylamine, is added to the solution, the feature of the reaction changes drastically. For example, the above-described reaction, being carried out in methanol containing 0.1 mol of pyridine, gives methyl propionate (50 %) as a main product. If pyridine is replaced to triethylamine (0.1 mol), diethylketone is obtained in 71 % yield and methyl propionate is only 4 % as shown in Table I. The coordination of the added bases to the rhodium atom is probably considered to affect the electronic property of the intermediate complexes.

Examples are as follows: Pyridine has vacant antibonding π-orbitals capable of accepting the electrons of rhodium by back-donation. The pyridine coordinated σ-acyl complex may be easily attacked by nucleophillic OCH_3 group giving methyl propionate, because the electron density on the rhodium atom has been lowered by back-donation.

On the other hand, since triethylamine has not such π-orbitals, the acyl complex may be allowed to react not with OCH_3 but with another ethylene.

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