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A KINETIC STUDY OF PROPYLENE DIMERIZATION CATALYZED BY COBALT DINITROGEN COMPLEXES

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Summary

The kinetics of homogeneous propylene dimerization with the dinitrogen complexes of cobalt $CoH(N_2)(PPh_3)_3$ or $Co(N_2)(PPh_3)_3$ as catalysts under mild conditions can be described by the following rate equation

$$\text{rate} = \frac{k_3K_1K_2[\text{Co}][\text{C}_3\text{H}_6]}{[\text{PPh}_3] + K_1 + K_1K_2[\text{C}_3\text{H}_6]}$$

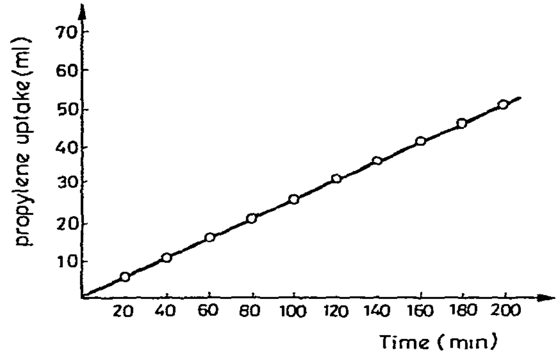
The possible mechanism of the reaction is discussed.

Introduction

Pu et al. [1] have reported that the dinitrogen complex $CoH(N_2)(PPh_3)_3$ catalyses the dimerization of ethylene and propylene. We observed that $[Co(C_2H_4)(PPh_3)_3]_2$ and $Co(N_2)(PPh_3)_3$ also catalyse dimerization of ethylene and propylene, respectively [2]. Since in only a few cases have the kinetics of dimerization reactions been investigated [3], we examined the kinetics of homogeneous ethylene [4] and propylene dimerization in the presence of some cobalt catalysts and this paper reports our results with propylene.

Results

The kinetic experiments were carried out in benzene at temperatures between 10° and 30° and propylene pressures from 400 to 1100 mmHg. The reaction is rather slow, and so the rates refer to the early stages of the reaction. Propylene consumption was followed volumetrically (Fig. 1), and it will be seen that the rate of propylene uptake is constant for several hours. Monitoring of the reaction by gas-liquid chromatography (GLC) revealed no codimerization



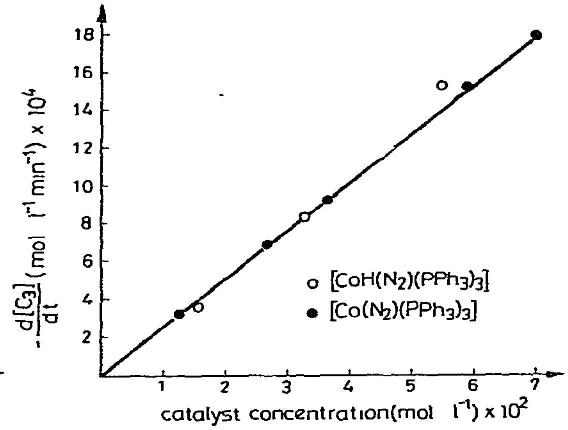


Fig. 1. A typical propylene dimerization experiment catalysed by $Co(N_2)(PPh_3)_3$ Solvent· 10 ml benzene; catalyst concn. 3.66 X 10^{-2} mol l^{-1}; temp. 20°; propylene pressure 1 atm.

Fig. 2. The influence of catalyst concentration on the reaction rate of propylene dimerization. Solvent: 10 ml benzene; temp. 20°; propylene pressure 1 atm.

of propylene with the propylene dimers formed, but a small amount of carbon skeleton fragmentation was detected, probably due to some metathetical reaction. The composition of the reaction products after 3 hours reaction can be seen in Table 1.

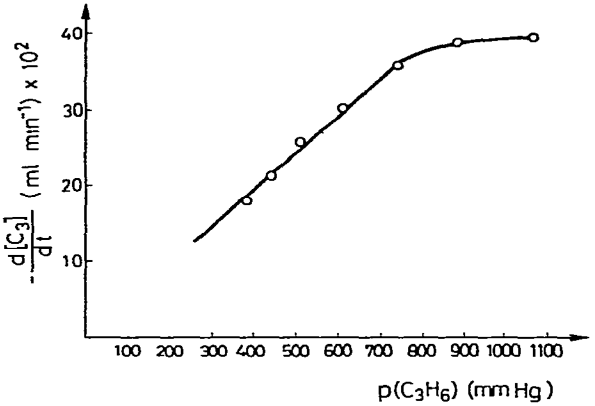
Experiments were reproducible to within ±5%, and the rates were given by the slopes of plots such as that in Fig. 1. Both $CoH(N_2)(PPh_3)_3$ [5] and $Co(N_2)$-$(PPh_3)_3$ [6] were used as catalysts. The dependence of the rate of dimerization

TABLE 1

PRODUCTS OF PROPYLENE DIMERIZATION CATALYSED BY $Co(N_2)(PPh_3)_3$ IN BENZENE [a]

Components	% wt
trans-4-Methyl-2-pentene	17.0
2-Methyl-1-pentene	65.3
2-Methyl-2-pentene	2.3
trans-3-Methyl-2-pentene	0.2
cis-3-Methyl-2-pentene	0.1
2,3-Dimethyl-2-butene	1.4
3,3-Dimethyl-1-butene	2.4
3-Methyl-1-pentene 4-Methyl-1-pentene	2.8
2,3-Dimethyl-1-butene *cis*-4-Methyl-2-pentene	1.2
3-Methyl-1-butene	4.0
2-Methyl-1-butene	2.7
2-Methyl-2-butene	0.6

[a] Reaction time 3 h; solvent 10 ml; catalyst concn. 3.66 X 10^{-2} mol l^{-1}; propylene pressure 1 atm; temp. 20°.



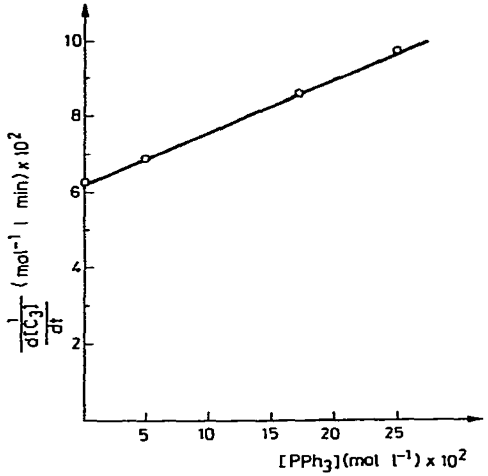


Fig. 3. The dependence of the rate of dimerization of propylene upon the propylene pressure. Solvent: 10 ml benzene; catalyst concn. 5.52 × 10^{-2} mol l^{-1}; temp. 20°.

Fig. 4. The dependence of the reciprocal rate of propylene dimerization on the phosphine concentration. Solvent: 10 ml benzene; catalyst concn. 5.61 × 10^{-2} mol l^{-1}; temp. 20°; propylene pressure 1 atm.

on the catalyst concentration is shown by Fig. 2, in which it can be seen that the same straight line applies to both complexes. This suggests similar mechanisms, and indicates a first order dependence with respect to the cobalt catalyst. Since there is no significant difference between the two dinitrogen complexes in this reaction, $Co(N_2)(PPh_3)_3$ was mainly used, since it is convenient to handle.

Dimerizations at propylene pressures below 700 mmHg gave a linear plot of the reaction rate against pressure with zero intercept. However at higher pressures no influence of the propylene concentration on the reaction rate was observed, as shown by Fig. 3.

Triphenylphosphine inhibits the reaction slightly (Fig. 4). From these results the pre-equilibrium constant K_1 (see Scheme 1) and the degree of dissociation of the phosphine ligand can be calculated (Table 2). As shown by the results, one phosphine ligand is almost entirely dissociated from the catalyst, thus ensuring a coordination site accessible to the substrate molecule.

The effect of temperature is shown in Table 2. The rate constants give a

TABLE 2

THE RATE CONSTANT k_{obs} AT DIFFERENT TEMPERATURES, THE EQUILIBRIUM CONSTANT K_1, AND DEGREE OF DISSOCIATION AT 20°

Temperature (°C)	k_{obs} × 10^2 (mol^{-1} l min^{-1})	K_1 (mol l^{-1})	Degree of dissociation (%)
10	1.92		
20	9.54	0.37	88 [a]
30	29.16		

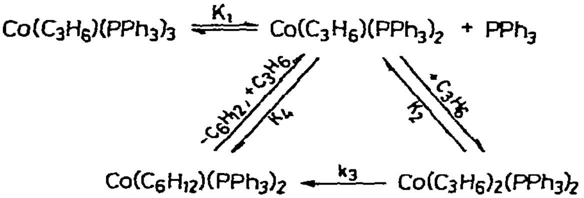
[a] At 5.61 × 10^{-2} mol l^{-1} catalyst concentration.

linear Arrhenius plot, and the following activation parameters were calculated: $\Delta E_a = 22.9$ kcal mol^{-1}; $\Delta H^{\neq} = 22.3$ kcal mol^{-1} and $\Delta S^{\neq} = 13$ cal mol^{-1} K^{-1}.

Discussion

Both $Co(N_2)(PPh_3)_3$ and $CoH(N_2)(PPh_3)_3$ evolved dinitrogen in the presence of propylene and the absorption bands at 1884 cm^{-1} attributable to $\nu(N_2)$ disappeared. In the case of $CoH(N_2)(PPh_3)_3$ the quartet at τ 21.7 ppm in the PMR spectrum also vanished, and a small amount of propane was found among the products, probably formed through a stoichiometric hydrogenation of propylene by the hydridic hydrogen of the complex. The equality of the two complexes in propylene dimerization suggests that after this substitution (and hydride abstraction) both furnish the same catalytically active intermediate species, probably a Co(0)—olefin complex.

SCHEME 1



The kinetic results can be explained in terms of Scheme 1, and the reaction rate can be expressed by eqn. 1:

$$\text{rate} = -\frac{d[C_3H_6]}{dt} = 2\,\frac{d[C_6H_{12}]}{dt} = k_3[Co(C_3H_6)_2(PPh_3)_2] \qquad (1)$$

The concentration of the intermediate cobalt bis-olefin complex is related to the total concentration of the cobalt complexes through K_1, K_2 and K_4. The total amount of catalyst [Co] is expressed by eqn. 2:

$$[Co] = [Co(C_3H_6)(PPh_3)_3] + [Co(C_3H_6)(PPh_3)_2] + [Co(C_3H_6)_2(PPh_3)_2] + [Co(C_6H_{12})(PPh_3)_2] \qquad (2)$$

assuming that none of the species present in solution is dinuclear.

The equilibria 3, 4 and 5

$$K_1 = \frac{[Co(C_3H_6)(PPh_3)_2][PPh_3]}{[Co(C_3H_6)(PPh_3)_3]} \qquad (3)$$

$$K_2 = \frac{[Co(C_3H_6)_2(PPh_3)_2]}{[Co(C_3H_6)(PPh_3)_2][C_3H_6]} \qquad (4)$$

$$K_4 = \frac{[Co(C_3H_6)(PPh_3)_2][C_6H_{12}]}{[Co(C_6H_{12})(PPh_3)_2][C_3H_6]} \qquad (5)$$

can be incorporated into eqn. 2 giving the following equation:

$$[Co] = [Co(C_3H_6)_2(PPh_3)_2]\left\{\frac{[PPh_3]}{K_1K_2[C_3H_6]} + \frac{1}{K_2[C_3H_6]} + 1 + \frac{[C_6H_{12}]}{K_2K_4[C_3H_6]^2}\right\} \qquad (6)$$

In the early phase of the reaction

$$\frac{[C_6H_{12}]}{K_2K_4[C_3H_6]^2} \sim 0$$

so that eqns. 1 and 6 can be combined to

$$\text{rate} = \frac{k_3K_1K_2[Co][C_3H_6]}{[PPh_3] + K_1 + K_1K_2[C_3H_6]} \qquad (7)$$

which rate equation is in agreement with the experimental results.

From the results of the experiments in presence of added triphenylphosphine the extent of dissociation in the first equilibrium of Scheme 1 may be calculated. If no phosphine is added and the propylene concentration is low, eqn. 3 may be rewritten in the following form:

$$K_1 = \frac{[PPh_3]^2}{[Co] - [PPh_3]} \qquad (8)$$

since in this case the amount of $Co(C_3H_6)_2(PPh_3)_2$ may be neglected and $[Co(C_3H_6)(PPh_3)_2] = [PPh_3]$.

If an excess of phosphine, $[PPh_3]_{add}$, is added to the reaction mixture eqn. 8 can be modified to

$$K_1 = \frac{[PPh_3'][\{PPh_3'] + [PPh_3]_{add}\}}{[Co] - [PPh_3']} \qquad (9)$$

where $[PPh_3']$ is the concentration of phosphine set free from the catalyst. The ratio of the rates of uninhibited (r) and inhibited (r_i) reactions at constant propylene concentrations is proportional to the ratio of the concentrations of $[Co(C_3H_6)(PPh_3)_2]$, or to the concentrations of the free phosphine coming from the cobalt catalyst in the two reaction mixtures, as shown by eqn. 10.

$$\frac{r}{r_i} = \frac{[PPh_3]}{[PPh_3']} \qquad (10)$$

On the basis of eqns. 8, 9 and 10 the appropriate free phosphine concentrations $[PPh_3']$ and $[PPh_3]$ and the equilibrium constant K_1 can be calculated. A value of 0.37 mol l^{-1} was found for K_1 at 20°C. The inhibition experiments showed that an excess of added phosphine does not have a big effect on the rate, indicating that the dissociation equilibrium lies well over to the right. At the concentrations used in the experiments this results in a dissociation of nearly 90%, so that most of the cobalt is present in the catalytically active form.

The observed change of the reaction order (from one to zero) with respect to propylene on increasing the olefin concentration may also be explained by eqn. 7 which corresponds with a first order dependence on propylene if

$$[PPh_3] + K_1 \gg K_1K_2[C_3H_6] \qquad (11)$$

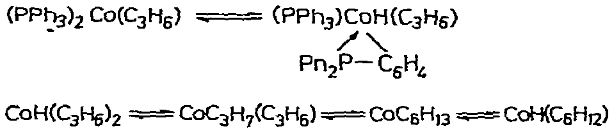
and a zero order dependence on propylene if

$$[PPh_3] + K_1 \ll K_1K_2[C_3H_6] \qquad (12)$$

At high propylene concentrations, when relation 12 is valid, k_3 can be calculated from eqn. 7, and was found to be 3.23×10^{-2} min^{-1} at 20°. At low propylene concentrations, however, relation 11 is valid. Knowing k_3, K_2 can be calculated from eqn. 7 in this case and was found to be 1.67 mol^{-1} l at 20°.

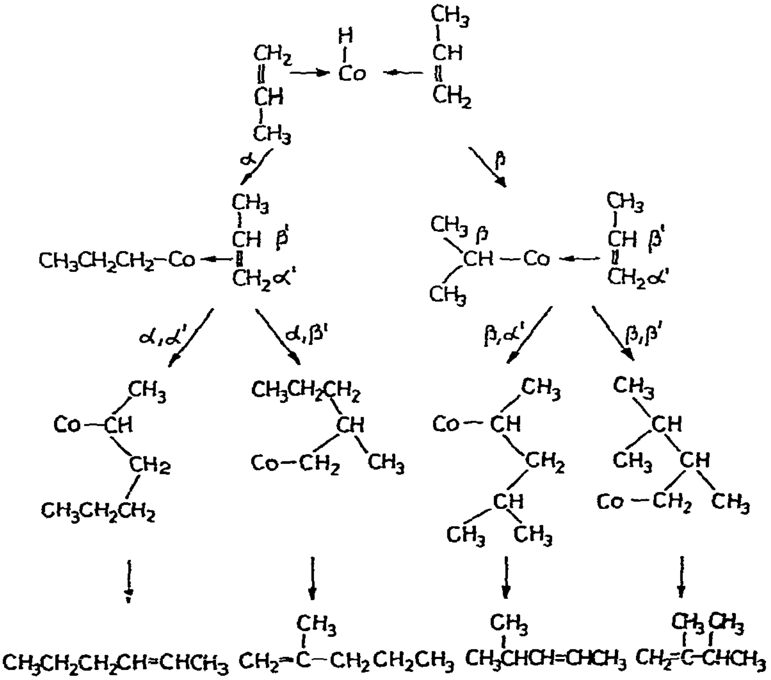
The kinetic results do not give any information concerning the rate-determining step. Since both $CoH(N_2)(PPh_3)_3$ and $Co(N_2)(PPh_3)_3$ show the same activity, the cobalt—hydrogen bond cannot play a role in the reaction mechanism as proposed by Pu et al. This fact, does not, however, exclude reaction through

SCHEME 2



(phosphine ligands omitted)

SCHEME 3



a cobalt hydride. Parshall [7] has shown with $CoH(N_2)(PPh_3)_3$ that the *ortho* C—H bond of the phenyl group undergoes oxidative addition to the cobalt atom. We assume a similar process in our systems as shown in Scheme 2. The cobalt hydride formed in this way may start the catalytic cycle, and the subsequent insertion of coordination olefins into the cobalt—hydride and cobalt—alkyl bonds followed by a β-elimination step ultimately furnishes the dimerized products. The composition of the primary dimeric products is determined by the mode of insertion, as illustrated in Scheme 3. Isomerization with the same catalyst leads to the secondary products found in minor amounts. Obviously the "mixed type additions" designated as $\alpha\beta'$ and $\beta\alpha'$ predominate.

Experimental

$CoH(N_2)(PPh_3)_3$ [5] and $Co(N_2)(PPh_3)_3$ [6] were prepared by known methods. The solvents used were distilled over sodium—potassium alloy under nitrogen. Commercial propylene was purified by bubbling through diethyl aluminium ethoxide after drying with silica gel and P_2O_5. Experiments were carried out in a water thermostatted reaction vessel connected to a thermostatted gas burette.

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