Contribution from the Institute of Organic Chemistry,
University of Chemical Industries, Veszprém, Hungary

Chemistry of Transition-Metal Nitrogen Complexes. IV.[1a] Kinetics and Mechanism of Olefin Isomerization with $Co(N_2)(PPh_3)_3$ as Catalyst[1b]

J. Kovács, G. Speier, and L. Markó

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Hexene-1 is isomerized mainly to cis-*hexene-2 in the presence of $Co(N_2)(PPh_3)_3$. The reaction is second order in catalyst concentration and is strongly inhibited by hexene-2. The migration of the hydrogen atoms is taking place presumably in a dinuclear intermediate.*

Introduction

Reactions of unsaturated hydrocarbons with transition metal complexes as catalysts generally proceed within the coordination sphere of one metal atom, *i.e.* the intermediates of the more or less proved mechanisms were always found to be mononuclear organometallic complexes. This is in contrast to heterogeneous catalytic processes, in which the mechanisms proposed usually use two or more neighbouring metal atoms for activation of the reacting molecules on the metal surface.

We now wish to report on a homogeneous catalytic reaction of olefins which most probably involves a complex containing two metal atoms as the key intermediate.

Experimental Section

Experiments were carried out under Ar in a 50 ml thermostated flask (± 0.25°C) equipped with magnetic stirrer. About 10^{-4} mole $Co(N_2)(PPh_3)_3$[2] was dissolved in 20 ml benzene and 2 ml olefin added through a silicone cap with a syringe. Samples were taken at different time intervals similarly. The reaction in the samples was stopped by addition of acetic acid. Samples were distilled from Na_2CO_3 before analysis by gas chromatography (50 resp. 100 m capillary column, squalane, 40°C).

Results and Discussion

$Co(N_2)(PPh_3)_3$ in benzene solution isomerizes linear C_4—C_{10} 1-olefins to the corresponding 2-olefins (and, to a minor extent also to 3-olefins), mainly to the *cis*-isomer. In the case of n-hexene-1, the rate of isomerisation is second order in cobalt, the influence of olefin concentration, however, is rather complicated. Within one experiment the isomerization is second order with respect to hexene-1, but experiments at different initial concentrations of hexene-1 and hexene-2 show that this is the effect of inhibition by hexene-2, whereas the concentration of hexene-1 has no effect on the initial rate. The hexene isomers are formed at room tmperature in about the following ratio: 55% *cis*-2-hexene, 35% *trans*-2-hexene, and 10% 3-hexene.

The reaction is not inhibited by triphenyl phosphine (concentration range 0-3 moles/mole complex) or nitrogen (pressure range 0.1-1 atm). Following the addition of the olefin to the catalyst solution, gas is rapidly evolved in a quantity showing the displacement of the N_2 ligand by the olefin. This substitution is proved also by the vanishing of the characteristic $\nu_{N,N}$ band of $Co(N_2)(PPh_3)_3$ at 2091 cm^{-1}.

Based on the above mentioned facts the following mechanism is proposed:

$$Co(N_2)(PPh_3)_3 + \text{hexene—1} \xrightarrow{\text{fast}} (\text{hexene—1})Co(PPh_3)_3 + N_2 \qquad (1)$$

$$2(\text{hexene—1})Co(PPh_3)_3 \xrightarrow{\text{slow}} (I) \rightarrow 2(\text{hexene—2})Co(PPh_3)_3 \qquad (2)$$

$$(\text{hexene—2})Co(PPh_3)_3 + \text{hexene—1} \overset{K}{\rightleftharpoons} (\text{hexene—1})Co(PPh_3)_3 + \text{hexene—2} \qquad (3)$$

Equation (1) represents only the formation of the cobalt-olefin complex, the catalytic cycle is represented by equations (2) and (3). (2) is regarded as rate determining step, (3) as a fast pre-equilibrium.

The scheme (1) - (3) gives the rate of isomerization as

$$\frac{-d(\text{hexene—1})}{dt} = k_2[(\text{hexene—1})Co(PPh_3)_3]^2 \qquad (a)$$

To correlate (a) with the experimental observations, the concentration of (hexene-1)$Co(PPh_3)_3$ has to be expressed in terms of hexene and total cobalt complex

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(1) (a) Part III: G. Speier, L. Markó, *J. Organometal. Chem.*, *21*, 46 (1970). (b) Paper presented at the Second Inorganica Chimica Acta Symposium, Venice, August 1969.

(2) G. Speier and L. Markó, *Inorg. Chim. Acta*, 3, 126 (1969).

concentration [Co]:

$$[Co] = [(\text{hexene}-1)Co(PPh_3)_3] + [(\text{hexene}-2)Co(PPh_3)_3] \tag{b}$$

$$K = \frac{[(\text{hexene}-1)Co(PPh_3)_3][\text{hexene}-2]}{[(\text{hexene}-2)Co(PPh_3)_3][\text{hexene}-1]} \tag{c}$$

(b) and (c) give

$$[(\text{hexene}-1)Co(PPh_3)_3] = \frac{K[Co][\text{hexene}-1]}{K[\text{hexene}-1]+[\text{hexene}-2]} \tag{d}$$

From (a) and (d) we get

$$\frac{-d[\text{hexene}-1]}{dt} = k_2\left(\frac{K[Co][\text{hexene}-1]}{K[\text{hexene}-1]+[\text{hexene}-2]}\right)^2 \tag{e}$$

Integrating (e):

$$-\frac{(K-1)^2}{K^2[Co]^2}[h_1] - \frac{2[H](K-1)}{K^2[Co]^2}\ln[h_1]$$

$$\frac{[H]^2}{K^2[Co]^2}\cdot\frac{1}{[h_1]} = k_2t+C \tag{f}$$

were

$$[h_1] = [\text{hexene}-1]$$

$[H] = [\text{hexene}-1]+[\text{hexene}-2] =$ constant (if the amount of hexene-3 formed is neglected)

C = integration constant

This rather complex expression is appreciably simplified by assuming $K \sim 1$. This seems not to be unjustified, as for example the stability constants of $[(\text{olefin-1})Ag]^+$ and $[(\textit{cis}\text{-olefin-2})Ag]^+$ complexes differ only by about 20%.[3] In this case (f) reduces to

$$\frac{[H]^2}{K^2[Co]^2}\cdot\frac{1}{[h_1]} = k_2t+C \tag{g}$$

which, if [H] and [Co] are kept constant (a condition fulfilled within one experiment) is the usual integrated form of a second order kinetic equation. Evaluating C by setting $t = 0$ and $[h_1] = [H]$ (no hexene-2 is present initially), we get

$$\frac{1}{[h_1]} = \frac{K^2[Co]^2}{[H]^2}k_2t + \frac{1}{[H]} \tag{h}$$

Plotting $1/[h_1]$ against t, straight lines are to be expected, with intercept $1/[H]$ and slope

$$tg\alpha = k_{obs} = \frac{K^2[Co]^2}{[H]^2}k_2 \tag{i}$$

Figure 1 shows some of the experimental results. As can be seen, the rate of isomerization is actually second order in [hexene-1] within one experiment. It is also evident that k_{obs} is strongly dependent on [Co].

To verify the $[Co]^2$ term in k_{obs} (cf. equation (i)), the values of k_{obs}, obtained at different catalyst concentrations, were plotted against cobalt concentration in Figure 2. The experimental points fit the expected linear relationship rather well.

Furthermore, k_{obs} should be a function of [H]. This was tested by performing experiments at different initial hexene–1 concentrations or adding hexene–2 at the start to the reaction mixtures and determining the rate of isomerization. If equation (i) is correct, then plotting $\frac{\sqrt{k_{obs}}}{K[Co]}$ against $\frac{1}{[H]}$ should yield a straight line with the slope $\sqrt{k_2}$. Figure 3 shows the result of these experiments.

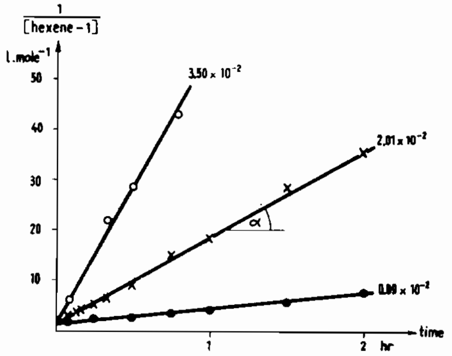

Figure 1. Isomerization of hexene–1 at different catalyst concentrations. Numbers show Co, mole.l^{-1}.

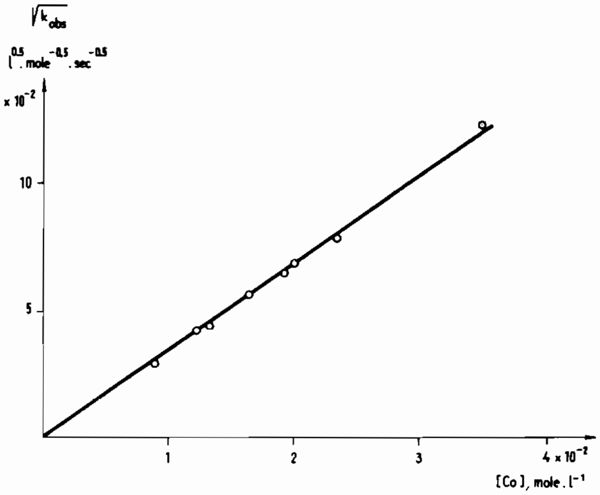

Figure 2. The measured rate constant k_{obs} as a function of cobalt concentration Co.

The experimental data agree with equation (i) and thus support the suggested mechanism. The value of k_2 at 20°C, as obtained from Figure 3 graphically is 6.0 $l.mole^{-1}.sec^{-1}$, which agrees well the arithmetical mean $k_2 = 6.10$ $l.mole^{-1}.sec^{-1}$, calculated from the individual experiments. It should be further stressed in this connection, that the points in Figure 3 were obtained at initial overall hexene concentrations between 0.2 and 1.5 mole.l^{-1} and within these limits with initial ratios of hexene–2 to hexene–1 between 0 and 3, thus represent results obtained under widely varying conditions.

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(3) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, *84*, 4697 (1962).

Figure 3 actually shows, that k_{obs} is decreased by increasing the initial concentration of hexenes. As long as [H] is increased only by an increase of hexene–1, this has no effect on the initial rate of isomerization, *i.e.* the number of hexene–1 moles transformed in unit time. If, however, [H] is increased by adding hexene–2 to the reaction mixture, also the initial rate is strongly diminished, as shown by the following transformation of equation (g).

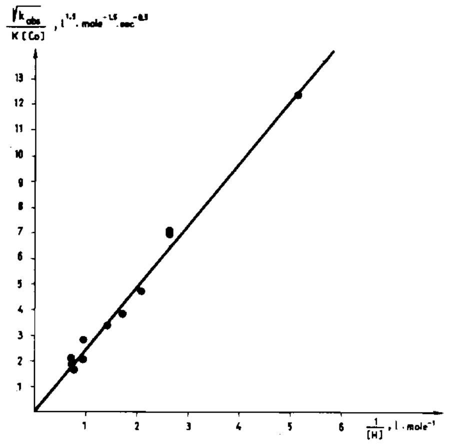


Figure 3. Influence of total hexene concentration H on the measured rate constant k_{obs}.

Let us define

$[h_1]_0$ = initial concentration of hexene—1

$[h_2]_0$ = initial concentration of hexene—2

$$A = \frac{[h_1]_0 + [h_2]_0}{[h_1]_0}$$

$$H = [h_1]_0 + [h_2]_0 = A[h_1]_0$$

Putting this into equation (g) and evaluating C by setting $t = 0$ and $[h_1] = [h_1]_0$ we get a modified form of equation (h):

$$\frac{1}{[h_1]} = \frac{K^2[Co]^2}{A^2[h_1]_0^2} k_2 t + \frac{1}{[h_1]_0} \qquad (k)$$

If now hexene–2 is added to the reaction mixture, A is increased and consequently at a given time $[h_1]$ is increased with respect to experiments without added hexene–2, in agreement with the inhibiting influence of the latter.

The reaction velocity constant k_2 was determined at three different temperatures:

Temperature °C	k_2, $l.mole^{-1}.sec^{-1}$
15	4.26
20	6.10
30	11.6

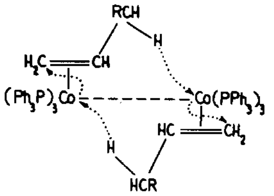
From these data we obtain the following values for the activation parameters:

$$\Delta H^* = 10.100 \text{ cal.mole}^{-1}$$

$$\Delta S^* = -21 \text{ e.u.}$$

Discussion

The quadratic dependence of isomerization rate on catalyst concentration suggests a dimeric complex (I) as the actual intermediate necessary for hydrogen transfer. The values of the activation parameters ΔH^* and ΔS^* are also in accordance with a bimolecular reaction. We therefore propose the structure shown in Figure 4 for intermediate (I).



(I)

Figure 4. Proposed structure of reaction intermediate and probable path of hydrogen transfer.

The tendency for dimerization is not without precedent in $Co(L)(PPh_3)_3$ complexes; the carbonyl derivative (L = CO) is a diamagnetic, dinuclear compound,[4] probably with a Co–Co bond. In the formation of (I), the partly filled orbital in (hexene–1)-$Co(PPh_3)_3$ (which should be a paramagnetic compound) can be used for the formation of a similar Co–Co bond or for the transfer of the hydrogen atom. To which extent this orbital is involved in one of these two functions or both or whether other (filled) orbitals of Co are also taking part, can not be decided at present.

The structure of (I) after migration of the hydrogen atoms is also open to discussion. The olefin ligands may remain on that cobalt atom to which they were originally coordinated, or the transfer of the hydrogens may be accompanied (or followed) by an analogous olefin migration.

Two olefin isomerization mechanisms[5] have been proposed up till now: (a) addition and elimination of a metal hydride and (b) rearrangement through a π-allyl hydride (1,3-shift). The mechanism suggested by our results is a third possibility and may be regarded as the 1,3′-shift of a hydrogen atom.

(4) A. Simon, Z. Nagy-Magos, J. Palágyi, G. Pályi, G. Bor, and L. Markó, *J. Organometal. Chem.*, *11*, 634 (1968).

(5) R. Cramer, *J. Am. Chem. Soc.*, *88*, 2272 (1966), and the literature cited therein.