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KINETIC STUDY ON THE ADDITION OF ETHYLENE TO DI-μ-CHLORO-TETRAKIS(TRIPHENYLPHOSPHINE)DIRHODIUM(I)

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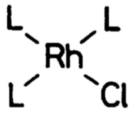
The addition of ethylene to di-μ-chloro-tetrakis(triphenylphosphine)dirhodium(I) is studied by means of a stopped-flow and a rapid-scan spectroscopic method. The reaction is found to proceed in two successive steps: $[RhCl(PPh_3)_2]_2 \xrightarrow[C_2H_4]{k_1} [(C_2H_4)\{RhCl(PPh_3)_2\}_2] \xrightarrow[C_2H_4]{k_2} 2[RhCl(C_2H_4)(PPh_3)_2]$; $k_1 = 2.1 \times 10^2$ and $k_2 = 1.1$ $mol^{-1}dm^3s^{-1}$.

A well-known homogeneous hydrogenation catalyst chlorotris(triphenylphosphine)-rhodium(I) exists in aprotic solvents such as benzene and dichloromethane as a monomer ($RhClL_3$) (1), a reaction intermediate ($RhClL_2$), and a dimer (di-μ-chloro-tetrakis(triphenylphosphine)dirhodium(I), $[RhClL_2]_2$) (2), where L denotes triphenylphosphine.[1,2]

Tolman et al. reported that the dimer (2) reacts relatively slowly with ethylene to produce a monomeric complex (3).[3] In the present study we have found the reaction proceeds in two successive steps: the initial rapid attack of ethylene on the dimer and the subsequent slow reaction.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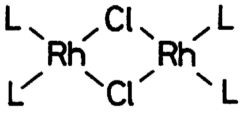
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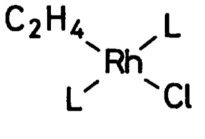
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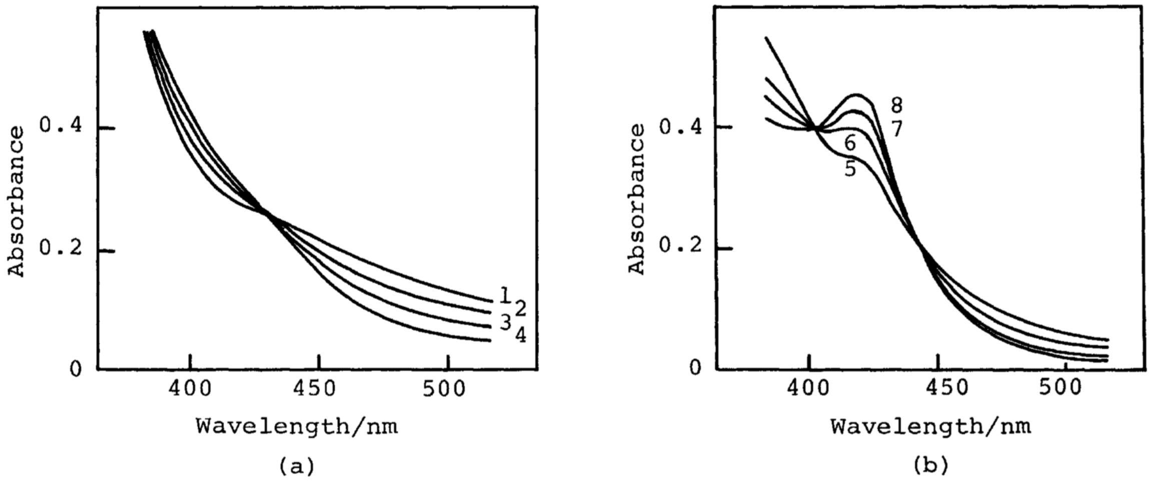
The solution of the dimer (2) was prepared from chloro(ethylene)bis(triphenylphosphine)rhodium(I) (3),[3] which was synthesized according to Osborn et al.[4]

The compound 3 was dissolved in oxygen-free solvent followed by the two freeze-pump-thaw cycles. The spectrum of the resultant solution coincided with that of the dimeric species 2.⁵⁾ Kinetic studies on the addition reactions of O_2 and H_2 also support that the resultant solution contains only the dimeric species.⁵⁾ Benzene was used as a solvent for the stopped-flow measurements and dichloromethane-benzene mixture for the rapid-scan spectroscopy to enhance the solubility of the dimer. The concentration of ethylene was determined by gas-chromatography. The addition rate of ethylene was measured under nitrogen atmosphere with a Union Giken RA-1100 stopped-flow apparatus or an RA-1300 rapid-scan spectrophotometer.

Figure 1 shows the spectral change for the reaction of the dimer 2 and ethylene. Each spectrum was rapidly scanned at appropriate time intervals after the solution of 2 was rapidly mixed with ethylene solution by stopped-flow technique.

At the initial stage, spectrum of the reaction mixture changes rapidly with an isosbestic point at about 430 nm (Fig. 1(a)). Then a relatively slow spectral change occurs with other isosbestic points at 402 and 440 nm (Fig. 1(b)). The final spectrum of the reaction mixture (λ_{max} = 420 nm) coincides with the spectrum of 3.¹⁾



(a) (b)

Fig. 1. Changes of rapidly-scanned absorption spectra during the reaction between $(RhClL_2)_2$ and ethylene. (a) in the first and (b) the second step. Scan speed: (1-4) 300 nm/10 ms and (5-8) 300 nm/50 ms. Recorded at (1) 0, (2) 20, (3) 50, (4) 200 ms, (5) 1, (6) 2.5, (7) 5, and (8) 10 s after mixing. $[(RhClL_2)_2]_0 = 1.4 \times 10^{-4}$, $[C_2H_4] = 7.5 \times 10^{-2}\,mol\cdot dm^{-3}$. At 20 °C. 20%(v/v) Dichloromethane-benzene.

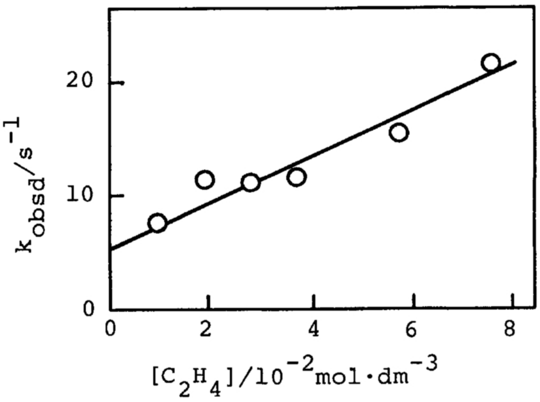


Fig. 2. Plot of k_{obsd} vs. concentration of C_2H_4 in the first step. At 480 nm, 20 °C, and $[(RhClL_2)_2]_0 = 3.6 \times 10^{-5}$ $mol\cdot dm^{-3}$. Benzene.

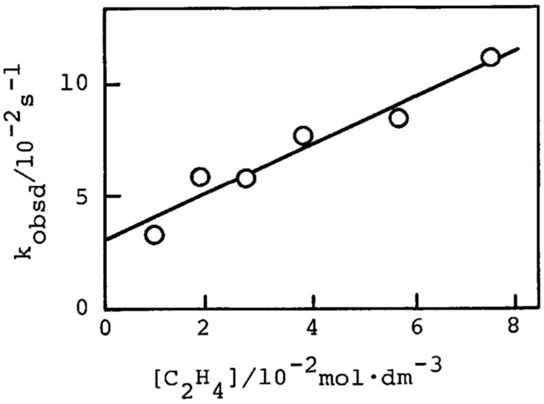


Fig. 3. Plot of k_{obsd} vs. concentration of C_2H_4 in the second step. At 420 nm, 20 °C, and $[(RhClL_2)_2]_0 = 3.6 \times 10^{-5}$ $mol\cdot dm^{-3}$. Benzene.

The rate constants (k_{obsd}) for the first and the second step were determined at various ethylene concentrations by analyzing the stopped-flow signals at 480 and 420 nm, respectively. Figures 2 and 3 show a linear dependence of the k_{obsd} on the concentration of ethylene for the first and the second step, respectively, suggesting the following mechanism,

$$(RhClL_2)_2 \xrightarrow[C_2H_4]{k_1} [(C_2H_4)(RhClL_2)_2] \xrightarrow[C_2H_4]{k_2} 2[RhCl(C_2H_4)L_2].$$

The slopes of Figs. 2 and 3 give $k_1 = 2.1 \times 10^2$ and $k_2 = 1.1$ $mol^{-1}dm^3s^{-1}$, indicating the first step is faster by two orders of magnitude than the second step.

The results clearly indicate that the addition of ethylene to the dimer (2) proceeds in two successive steps. However, fine mechanisms of the reaction is not clear at this moment. The intercepts in Figs. 2 and 3 (5.7 and 0.031 s^{-1}) do not give the reverse rate constants, since the equilibrium lies largely on the side of the product at the concentrations of ethylene in the present study. The large intercepts would suggest the presence of another reaction path with the rate independent of the concentration of ethylene.

Judging from the value of k_1 and k_2, and also from the rate constant of the ethylene addition on the monomer 1,[6)] the first step of the present reaction may be attributed to the reaction between ethylene and the dimer 2 to yield dimeric monoethylene complex

$$(RhClL_2)_2 + C_2H_4 \longrightarrow [(C_2H_4)(RhClL_2)_2],$$

while the second reaction is the attack of ethylene on $[(C_2H_4)(RhClL_2)_2]$

$$[(C_2H_4)(RhClL_2)_2] + C_2H_4 \longrightarrow 2[RhCl(C_2H_4)L_2].$$

The lower value of k_2 would exclude the possibility of the cleavage of both of the chlorine bridges in the first ethylene attack. If both of the chlorine bridges were ruptured in the first step, $RhClL_2$ is produced and consequently the value of k_2 must be large.6)

Acrylonitrile, which is hydrogenated very rapidly than ethylene,7) behaves similarly as ethylene does.

References and Notes

1) C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, J. Am. Chem. Soc., 96, 2762 (1974).

2) Y. Ohtani, M. Fujimoto, and A. Yamagishi, Bull. Chem. Soc. Jpn., 49, 1871 (1976).

3) The compound 3 readily dissociates ethylene to form 2 in benzene (see Refs. 1 and 4).

4) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1966, 1711.

5) Y. Ohtani, M. Fujimoto, and A. Yamagishi, Bull. Chem. Soc. Jpn., 50, 1453 (1977).

6) The reaction mechanism of the ethylene addition on the monomer is

$$RhClL_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RhClL_2 + L$$

$$RhClL_2 + C_2H_4 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RhCl(C_2H_4)L_2.$$

$k_1 = 0.4$ and $k_{-2} = 0.4\ s^{-1}$ (k_{-1} and k_2 are fast)(see Ref. 5).

7) J. P. Candlin and A. R. Oldham, Discuss. Faraday Soc., 46, 60 (1968).

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