BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1457—1460(1972)

Dimerization and Isotopic Mixing of Ethylene by a Palladium Complex Catalyst

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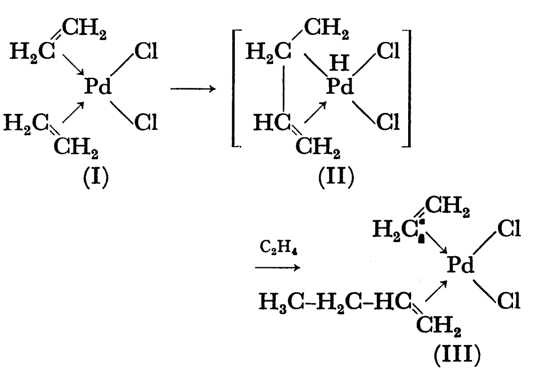
(Received July 5, 1971)

Dimerization and accompanied isotopic exchange of ethylene were studied with dichlorobis(benzonitrile)-palladium(II) complex in benzene solution. Dimerization as well as isotopic exchange take place simultaneously after an induction period, the extent of which is reduced by the presence of hydrogen releasing olefin such as 3-methyl-1-butene. Kinetics of dimerization is of first order in ethylene, but the dimerization rate does not immediately respond to the change in ethylene pressure. The results are interpreted in terms of a preformed palladium hydride complex.

The dimerization of olefin catalyzed by palladium salts has been studied by a number of workers[2–7] since its discovery by Gemert and Wilkinson.[1] Although the catalyst species were varied among palladium chloride or its complex with benzonitrile and di-μ-chlorobis-(ethylene)palladium, *etc.*, the real active species in the dimerization seem to be a monomeric palladium-olefin complex[2] soluble in organic solvents. The following information has been obtained on the dimerization reaction: The rate of dimerization is proportional to concentrations of palladium salt and ethylene.[4] Co-dimerization of ethylene takes place in the presence of other olefin,[6,7] although ethylene is most reactive in the dimerization.[7] There is a remarkable solvent effect.[3,5,7] It is also known that the palladium catalyst catalyzes the isomerization of olefin.[7]

The mechanisms of dimerization so far proposed[2–7] can be summarized into two schemes: (1) A palladium hydride intermediate as adopted for butene isomerization by Cramer and Lindsey is assumed, according to the mechanism proposed by Barlow *et al.*[7] (2) A five co-ordinate hydride complex(II) as an intermediate is assumed according to the mechanism proposed by Ketley *et al.*[2] and is shown in the following. A detailed study was made by Kawamoto, Tatani, Imanaka, and Teranishi[6c] by means of solvent effect and deuterium labeled reactant, styrene-d_3.



On the other hand in the study of the mechanism of ethylene dimerization with nickel oxide-silica catalyst,[9] it was found that a rapid isotopic mixing in ethylene takes place prior to the dimerization and both the isotopic mixing and dimerization are simultaneously poisoned by a very small amount of CO. Since both

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[1] J. T. van Gemert and P. R. Wilkinson, *J. Phys. Chem.*, **68**, 645 (1964).

[2] A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967).

[3] Y. Kusunoki, R. Katsuno, H. Hasegawa, and S. Kurematsu, This Bulletin, **39**, 2021 (1966).

[4] K. Kawamoto, T. Imanaka, and S. Teranishi, *Nippon Kagaku Zasshi*, **89**, 639 (1968).

[5] K. Kawamoto, T. Imanaka, and S. Teranishi, *ibid.*, **91**, 39 (1970).

[6] K. Kawamoto, T. Imanaka, S. Teranishi a) *Kogyo Kagaku Zasshi*, **72**, 1612 (1969); b) This Bulletin, **43**, 2512 (1970); c) *ibid.*, **44**, 1239 (1971).

[7] M. G. Barlow, M. J. Bryant, R. N. Haszeldine, and A. G. Mackie, *J. Organometal Chem.*, **21**, 215 (1970).

[8] R. Cramer and R. V. Lindsey, *J. Amer. Chem. Soc.*, **88**, 3534 (1966).

[9] A. Ozaki, H. Ai, and K. Kimura, Int. Congr. Catal, 4th, Moscow, prepr. **40** (1968); K. Kimura, H. Ai, and A. Ozaki, *J. Catal.*, **18**, 271 (1970).

reactions commonly require an intermolecular hydrogen transfer, the results suggest that the ability of the catalyst to cause the isotopic mixing in ethylene is a requisite for the dimerization catalyst and the dissociation of ethylene to form a nickel hydride is involved in the path way of dimerization.

Thus it is of interest to study the isotopic mixing during the course of dimerization by different catalysts in a homogeneous system. This paper deals with such a study of ethylene dimerization by the benzonitrile-palladium complex.

Experimental

Materials. Dichloro-bis-benzonitrile-palladium(II) complex was prepared by the method of Kharasch.[10] Benzene was treated with metallic sodium prior to distillation in dry nitrogen stream and was preserved and transferred in dry nitrogen. C_2D_4 was prepared by deuterogenation of C_2D_2 at room temperature over a Girdler (58A) Pd catalyst and separated from impurities by means of gas chromatography using a silica gel column. C_2D_2 was obtained by reaction of D_2O with CaC_2 which had been evacuated at 400°C for 150 hr.

Procedures. The reactions were carried out in a small flask with stirring under constant pressure at 36°C. The ethylene concentration in the solvent was confirmed to be proportional to the ethylene pressure. The rate of dimerization was determined from the amount of ethylene absorbed into the catalyst solution. Isotopic analyses were carried out by mass spectrometry with an ionization voltage of 10 eV.

Results

1. The Effect of Ethylene Concentration on the Rate of Dimerization. Ethylene dimerization by the palladium complex is much slower in benzene than in polar solvents,[6] but benzene was chosen as solvent because the slow reaction was convenient for studying the effects of reaction conditions. Figure 1 shows the time course of absorption of ethylene where 0.5 mmol of $PdCl_2(\phi CN)_2$ complex was used. In the initial period, 0.5 mmol of ethylene which is equimolar to the amount of catalyst is absorbed to form the ethylene complex. The amount of initial absorption is independent of ethylene pressure as shown by runs A and B. The absorption due to the dimerization begins after a few hours of induction period, which decreases with the increase in ethylene pressure. The rate of absorption increases with time and attains a steady value about 15—18 hr after the introduction of ethylene into the reactor. The steady rate of absorption is taken as the rate of dimerization of ethylene.

The reaction product was exclusively butenes with a composition of 1-butene 4%, *cis*-2-butene 36%, and *trans*-2-butene 60% which is close to the value corresponding to the equilibrium of isomerization.

According to Kawamoto *et al.*,[4] the kinetics of the dimerization by $Pd_2Cl_4(C_2H_4)_2$ complex in dioxane is as follows:

$$\text{Rate} = k[\text{Pd complex}]^{1.0}[C_2H_4]^{1.0} \qquad (1)$$

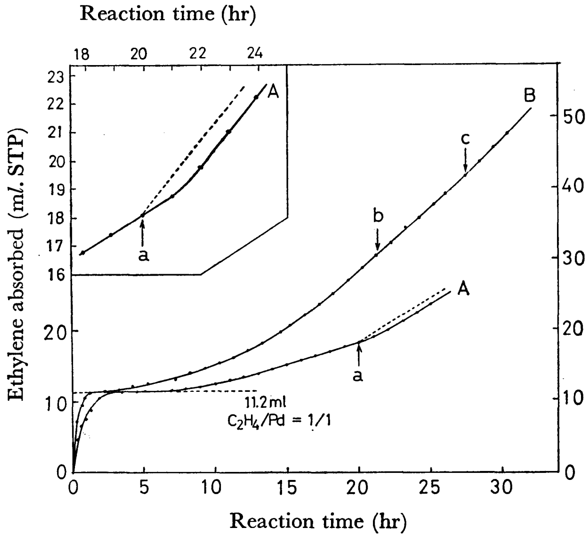

Fig. 1. Time course of ethylene dimerization by $PdCl_2(CN)_2$ catalyst (0.5 mmol) in benzene (50 m*l*) at 36°C under following pressures.
A: 168 mmHg changed to 579 mmHg at a
B: 596 mmHg changed to 131 mmHg at b
and to 596 mmHg at c.

The present results is in line with this equation with respect to ethylene concentration as deduced from the results in Fig. 1, where about 3.5 times difference in the ethylene pressure causes a 3.0 times difference in the steady rate. Proportionality with the concentration of Pd complex was confirmed by separate runs.

A further study of the kinetic behavior of the dimerization was made by a pressure jump method as shown at point "a", Fig. 1, where the ethylene pressure was jumped up to about 3.5 times the initial level. However, as we see from the magnified scale, there is no immediate response in the reaction rate, which stays at the initial value for about 1 hr before beginning to increase and attains another steady value about 3 hr later. The response is further delayed in the case of pressure drop (point "b") where the ethylene concentration is reduced to about three tenths. The reaction rates in the following 6 hr is completely unchanged and the pressure jump up to the previous value made again after 6 hr (point "c") causes little change in the rate of absorption. This slow response of the reaction rate to the sudden change in ethylene pressure was further confirmed by repeated changes in the range of 131 to 600 mmHg which corresponded to ethylene concentration of 2.14×10^{-2} to 9.64×10^{-2} mol/*l*. This result demonstrates that the apparent first order kinetics with respect to ethylene does not directly reflect the kinetic nature of the rate determining step for the ethylene dimerization.

2. Isotopic Exchange between Olefins. A mixture of C_2H_4 and C_2D_4 was introduced into the reaction vessel under the reaction conditions of dimerization, and the isotopic distribution in the remaining ethylene was followed by intermittent analyses. Figure 2 shows the time course of individual isotopic species. It is clear that the palladium complex is activated for the isotopic exchange after a while of induction period and that ethylene exchanges one hydrogen atom at a time. It is

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[10] M. S. Kharasch, R. C. Seyler, and T. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).

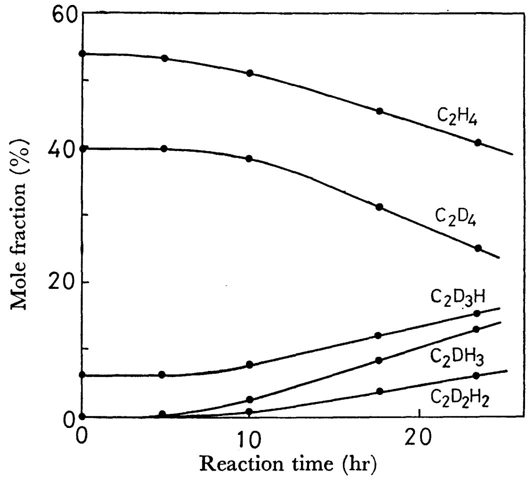


Fig. 2. C_2H_4–C_2D_4 exchange reaction by $PdCl_2(\phi CN)_2$ (0.5 mmol) in benzene (50 m*l*) at 36°C.

noteworthy that the induction period for the exchange is in agreement with that for the dimerization. That is, both reactions set in simultaneously. This demonstrates that a common active species, possibly a hydride, is responsible for the two reactions. It is also suggested that the hydride might be formed by reacting with ethylene.

3. *The Effect of added Olefin on the Rate of Ethylene Dimerization.* If the dimerization is promoted by a hydride complex whose hydrogen is provided by ethylene, the rate of dimerization would be enhanced by the presence of an olefin whose hydrogen is readily dissociated. Thus the runs of ethylene dimerization were carried out in the presence of olefins which were mostly about equimolar to the amount of catalyst. The results are shown in Table 1. It is revealed that the hydrogen-releasing olefins such as 3-methyl-1-butene and 1-butene give rise to a decrease in the induction period with the extent increasing with the amount of added olefin. This decrease in the induction period is accompanied by a remarkable increase in the rate of ethylene dimerization in the case of 3-methyl-1-butene which is known to be most liable to release its hydrogen. The extent of enhancement is nearly proportional to the amount of 3-methyl-1-butene added. *trans*-2-Butene which is less liable to release hydrogen gives rise to no decrease in the induction period. In view of this fact, the rather small extent in the enhancement by butene-1 as compared with the decrease in the induction period may be due to the isomerization of added 1-butene to 2-butene.

TABLE 1. EFFECTS OF ADDED OLEFINS ON THE EXTENT OF INDUCTION PERIOD AND RATE OF DIMERIZATION AT 36°C AND 150 mmHg OF ETHYLENE PRESSURE

Added olefin	(mmol)	Induction Period (hr)	Rate of Dimerization (m*l* STP/hr)
None		15—20	~0.9
1-Butene	0.05	17	0.9
1-Butene	0.2	10	0.95
1-Butene	0.5	8	1.0
1-Butene	0.8	5	1.1
trans-2-C'_4	0.6	17	~0.9
3-Me-1-C'_4	0.14	7	1.4
3-Me-1-C'_4	0.6	5	2.8

C'_4: butene, Me: methyl

Product analyses showed no formation of codimer or dimer of the added olefin. This is reasonable because the amount of added olefin is rather small, and ethylene is most reactive in dimerization among olefins.[7]

Discussion

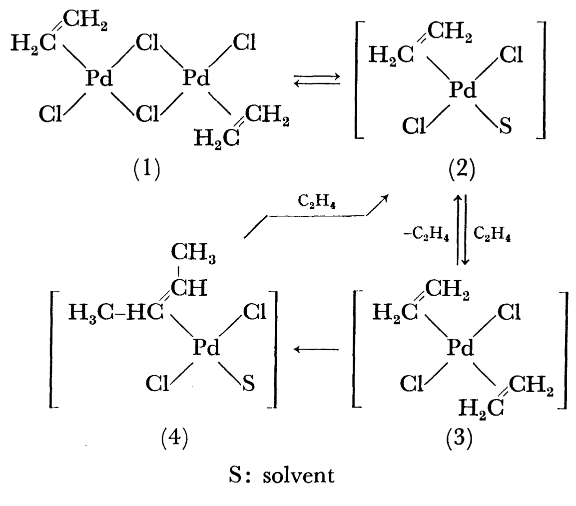
The results are summarized as follows. (1) Although the rate of ethylene dimerization is consistent with the first order kinetics with respect to ethylene, the response of the rate to the ethylene pressure change is considerably delayed.

(2) The palladium-benzonitrile complex is activated after a while of induction period for two reactions simultaneously, ethylene dimerization and isotopic exchange in ethylene.

(3) The presence of hydrogen-releasing olefin decreases the extent of induction period and enhances the rate of dimerization without formation of codimer.

The observed delay in the response to pressure change seems to be caused by the step responsible for the induction period. The delayed response and the apparent first order kinetics can be understood if the equilibrated concentration of active intermediate formed in the induction period is proportional to ethylene pressure and the steady rate of dimerization is proportional to the concentration of this active intermediate.

The kinetics of ethylene dimerization by palladium complex in dioxane has been interpreted in terms of the following scheme:[4]



S: solvent

where a steady state of dimerization is attained by cyclic reactions (2)→(3)→(4)→(2), steps (3)→(4) being rate-determining. However, this scheme is inadequate for the present case because it is inconsistent with the delayed response.

Kawamoto *et al.*[6c] proposed a mechanism with a hydride shift between coordinated olefins, on the basis of a tracer study of codimerization of styrene-d_3 with light ethylene. However, we found that the isotopic exchange between reacting olefins takes place ahead of the dimerization. Since this kind of exchange cannot be ignored in the case proposed by Kawamoto *et al.*, the interpretation of the tracer work seems to be open to question.

On the other hand the results (2) and (3) suggest that a palladium hydride complex whose hydrogen is provided by olefin is responsible for the ethylene dimerization. The observed effects of added olefin could not be due to the formation of codimer. Since 3-methyl-1-butene which is most effective both in decreasing the induction period and enhancing the rate of dimerization is admittedly liable to liberate its tertiary hydrogen, the observed effects of added olefin can be interpreted to be formation of an active hydride complex which catalyzes both the dimerization and the isotopic exchange. The scheme implies that the hydride complex responsible for the dimerization is necessarily preformed by a reaction of the palladium complex with olefin. The ready isomerization of 1-butene as demonstrated by the attainment of isomerization equilibrium in the dimerization product is also consistent with the presence of preformed hydride complex. In the case of five-coordinate hydride scheme[2] or concerted hydride shift scheme[6c] for dimerization, a separate scheme is required for the isomerization and isotopic exchange, whereas the preformed hydride can account for all of three reactions in terms of palladium alkyl intermediate,[7,8] as follows:

$$\begin{tikzcd}
 & \mathrm{PdD} + \mathrm{C_2D_3H}\ (\text{exchange}) & \\
\mathrm{Pd\text{-}H} + \mathrm{C_2D_4} \arrow[r] & \mathrm{Pd\text{-}C_2D_4H} \arrow[u] \arrow[r, "\mathrm{C_2H_4}"] & \mathrm{Pd\text{-}C_2H_4\text{-}C_2D_4H}
\end{tikzcd}$$

$$\longrightarrow \mathrm{Pd\text{-}H} + \mathrm{C_4H_4D_4}\ (\text{dimerization})$$

$$\mathrm{Pd\text{-}H} + 1\text{-}\mathrm{C_4H_8} \longrightarrow \mathrm{Pd\text{-}C_4H_9} \longrightarrow$$

$$\mathrm{PdH} + 2\text{-}\mathrm{C_4H_8}\ (\text{isomerization})$$

If the preformed hydride is necessary for the dimerization, the observed induction period should be ascribed to the slow formation of the hydride complex from olefin. The delayed response of the dimerization rate to pressure change is reasonable if the equilibrium concentration of hydride complex is proportional to olefin concentration. Thus the mechanism of hydride formation is important. The present results seem to suggest a dissociation of olefin to form a hydride. The palladium hydride is known to exist[11] although it is unstable.

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11) E. H. Brooks and F. Glocking, *J. Chem. Soc., (A)*, **1967**, 1030.