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The Dimerization of Ethylene Using Palladous Chloride as the Catalyst

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The dimerization of ethylene was carried out using palladous chloride as the catalyst. Acetic acid, ethylene dichloride, ethylene tetrachloride, benzene, chlorobenzene, triethyleneglycol, acetic acid esters, chloroform, cyclohexane and ethanol were employed as the reaction solvents, and the effects of these solvents on the reaction were investigated. The best yield of butylene (about 1500 mol.% to palladous chloride) was obtained, when acetic acid was used as the solvent; the yield decreased gradually following the above order of solvents until, when ethanol was used as the solvent, it yielded only 96 mol.%. However, in all solvents dimerization was carried out predominantly, and only a few higher polymers were obtained. It is very interesting that the solvent effect mentioned above was different from the effect of solvents in the isomerization of olefin when metal carbonyl was used as the catalyst. To explain these results, a hydride ion-shift mechanism has been proposed.

Recently, many reports have been published on the polymerization or isomerization of olefins, using Ziegler-Natta catalysts or metal carbonyls.[1] In these reactions the intermediate formation of a π-complex between olefin and catalyst was assumed. The present study will deal with the dimerization of ethylene using palladous chloride, which easily forms a complex with ethylene and which gives butylenes in a fairly good yield. Although the dimerization proceeded with few side reactions, the effects of solvents on this reaction were comparatively great. Some solvents, e. g., acetic acid or halogenated hydrocarbons, led to excellent yields of the dimerization products, whereas others, e. g., ethanol, led to lower yields. The maximum yield of butylenes (about 1500 mol.% to the palladous chloride based on the ethylene) was obtained in the case of the acetic acid solvent.

From these results it may be considered that this dimerization reaction is similar to a Friedel-Crafts-type reaction.

Results and Discussion

The experimental conditions are shown in Table I, while the results are summarized in Table II; it is clear from Table II that the highest yield of butylenes is obtained when acetic acid is used as a solvent, and that the yield decreases in the order of the solvents as they are listed in this table, from dichloroethane to ethanol. It may generally be said that the ratio of butylene-2 to butylene-1 decreases with the decrease in the yield of butylenes.

As a by-product, a small amount of hexene was detected in every case; octene or isobutyl chloride was also detected in some cases. However, when an acetic acid ester was used as a solvent, the formation of isobutyl chloride was remarkable. The fact that, in an ethanol solvent, small amounts of ethyl vinyl ether and acetal were detected by gas chromatography, agrees with the observations by Stern and Spector,[2] and Moiseef et. al.[3]

As has been described above, the dimerization of ethylene proceeds predominantly with a palladous chloride catalyst; the formation of higher olefins is negligible. The relation between the yield of butylenes and the kind of solvent is quite contradictory to Mannel's results[4] on the isomerization of olefin with a metal carbonyl catalyst; Mannel obtained good results by using methanol, ethanol, acetone and benzene solvents, while he regarded acetic acid, carbon tetrachloride and acid chlorides as unsuitable solvents. As the mechanism of these isomerizations, the formation of the so-called π-en-yl-type complex by way of a proton shift from a π-complex may be described. Huettel[5] has already pointed out that the hydrogen

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[1] E. Lutz, *J. Am. Chem. Soc.*, **83**, 2551 (1961); J. Rose, *J. Chem. Soc.*, **1960**, 60; B. Franzus, *J. Am. Chem. Soc.*, **81**. 1514 (1959); J. Harris, *J. Org. Chem.*, **25**, 633 (1960); J. Sauer, *J. Am. Chem. Soc.*, **79**, 2659 (1957); L. Meriwether, *J. Org. Chem.*, **26**, 5155, (1961); G. Hata, *Chem.* & *Ind.*, **1965**, 223.

[2] E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, **1961**, 370.

[3] I. I. Moiseef, M. N. Vargaftik and Ya. K. Syrkin, *Doklady Akad. Nauk U. S. S. R.*, **133**, 377 (1960).

[4] T. A. Mannel, *J. Org. Chem.*, **27**, 3941 (1962).

[5] R. Huttel, J. Kratzer and M. Bechter, *Chem. Ber.*, **94**, 766 (1961).

TABLE I. REACTION CONDITIONS

Solvent	React. temp. °C	React. time hr.	Note
Acetic acid	70—100	4.5	additional C_2H_4 43 kg./cm$_2$
Dichloroethane	70— 90	9.0	
Tetrachloroethane	80— 95	4.5	
Benzene	85—100	7.0	additional C_2H_4 61 kg./cm$_2$ (twice)
Chlorobenzene	70— 90	3.0	
Triethylene glycol	95—100	2.5	
Methyl acetate	80—100	3.0	
Butyl acetate	80—100	3.0	
Chloroform	100—150	4.0	
Cyclohexane	110—200	4.5	
Ethanol	100—200	6.0	

$PdCl_2$: 8.8 g. (0.05 mol.), solvent: 40 c.c.,
C_2H_4: 60 kg./cm^2 (initial pressure at room temperature)
Numbers on the left in the temperature column indicate the temperature at which absorption of ethylene began.

TABLE II. EXPERIMENTAL RESULTS

Solvent	Butylene yield		Ratio b)		By-products c)
	g.	% a)	C_4H_8-1	C_4H_8-2	
Acetic acid	20.8	1488	12	88	Hexene
Dichloroethane	13.0	930	9	91	—
Tetrachloroethane	11.9	852	5	55	Hexene, Octene, Isobutyl chloride
Benzene	8.0	552	12	88	Hexene, Isobutyl chloride
Chlorobenzene	8.7	620	6	94	Hexene, Isobutyl chloride
Triethylene glycol	6.1	436	9	91	—
Methyl acetate	6.7	480	9	91	Isobutyl chloride (3.8 g.)
Butyl acetate	5.4	390	7	93	Isobutyl chloride (5.0 g.)
Chloroform	5.2	372	21	79	Hexene
Cyclohexane	3.4	244	12	88	Hexene
Ethanol	1.4	96	38	62	Ethyl vinyl ether, Acetal

a) Calculated as follows: $\dfrac{\text{mol. of butylene produced} \times 2}{\text{mol. of } PdCl_2 \text{ used}} \times 100$

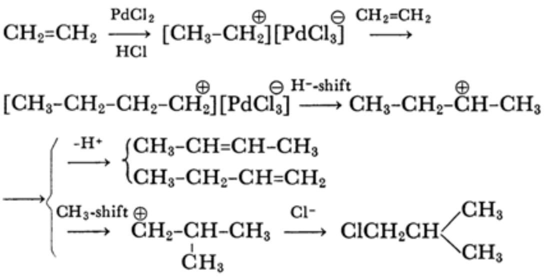
b) Given as percentage of respective peak area in gas chromatography.

c) The amounts of by-products are generally too small to be determined quantitatively.

chloride from Zeise's salt was eliminated and that a complex of another type was formed as:

$$(C_nH_{2n} \cdot PdCl_2)_2 \rightarrow (C_nH_{2n-1} \cdot PdCl)_2 + 2HCl$$

In our experiments the formation of hydrogen chloride was clearly detected. Therefore, considering the Friedel-Crafts-type reaction caused by a palladous chloride - hydrogen chloride system, as in the case of aluminum chloride, these dimerization reactions may be explained as:



$$CH_2{=}CH_2 \xrightarrow[HCl]{PdCl_2} [CH_3\text{-}\overset{\oplus}{CH_2}][\overset{\ominus}{PdCl_3}] \xrightarrow{CH_2=CH_2}$$

$$[CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{\oplus}{CH_2}][\overset{\ominus}{PdCl_3}] \xrightarrow{H^-\text{-shift}} CH_3\text{-}CH_2\text{-}\overset{\oplus}{C}H\text{-}CH_3$$

$$\longrightarrow \left\{ \begin{array}{l} \xrightarrow{-H^+} \left\{ \begin{array}{l} CH_3\text{-}CH{=}CH\text{-}CH_3 \\ CH_3\text{-}CH_2\text{-}CH{=}CH_2 \end{array} \right. \\ \xrightarrow{CH_3\text{-shift}} \overset{\oplus}{C}H_2\text{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}\text{-}CH_3 \xrightarrow{Cl^-} ClCH_2CH{<}{CH_3 \atop CH_3} \end{array} \right.$$

Although the reaction may be explained by the proton - shift mechanism in the case of a metal carbonyl catalyst, the hydride-ion-shift mechanism seems adequate for a palladous chloride catalyst, considering that the effects of solvents on the reaction are quite opposite. Moreover, the fact that the yield of butylene decreases upon a decrease in the dielectric constant of solvents agrees with Pepper's work.[6] However, such polar solvents as acetic acid or ethanol, which have a cocatalytic character in themselves showed either an exceptionally large or an exceptionally small yield of butylene. On the other hand, esters would have a peculiar solvent effect, resulting in a remarkable yield of isobutyl chloride.

Experimental

Apparatus.—A stainless-steel autoclave equipped with a magnetic stirrer was used.

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[6] D. C. Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949).

Reagents.—Palladous chloride: A commercial product of an extra pure grade was used.

Ethylene: Commercial ethylene in a cylinder was used.

Solvents: Commercial solvents were purified and dried as usual before use.

Palladous chloride (8.8 g.; 0.05 mol.) and 40 ml. of solvent were charged into the autoclave and compressed to 60 kg./cm^2 (at room temperature) with ethylene. The autoclave was stirred at room temperature for about half an hour to dissolve the ethylene in the solvent sufficiently, heated to a desired temperature, and again stirred during the reaction. Table I summarizes the reaction conditions for each solvent.

In these cases where a violent absorption of ethylene was observed, additional ethylene was charged in. After the reaction had ended, the autoclave was cooled to room temperature, the pressure read, and the autoclave was again heated to about 50°C while being stirred in order to expel the gaseous products. The gas was passed through cold a trap cooled with dry ice - methanol and a washing bottle containing distilled water to absorb the hydrogen chloride, and then collected in a gas holder. The liquid condensed in the cold trap was vaporized at room temperature after it had been weighed and they collected in another gas holder. The gases were analyzed by gas chromatography (T. C. P. column, 3 m.; temperature, 40°C.; H_2 flow rate, 17.5 cc./min.).

The liquid product was separated from the catalytic residue by filtration and distilled. The distillates were analyzed by gas chromatography, using such proper column packing materials as tricresyl phosphate, polyethylene glycol, and dinonyl phthalate.