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PALLADIUM CHLORIDE CATALYZED DECOMPOSITION OF VINYL ACETATE IN ACETIC ACID
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Moiseev et al. have described the reaction of ethylene and palladium (II) chloride in acetic acid containing sodium acetate to form vinyl acetate. While investigating this preparation in our laboratory, we encountered the formation of considerable amounts of acetaldehyde by-product along with the desired ester. Since anhydrous conditions were employed, the acetaldehyde could not have resulted from an ethylene-palladium chloridewater type reaction. A study of the nature of this side reaction was therefore undertaken, and we have now determined that palladium (II) chloride catalyses the cleavage of vinyl acetate to acetaldehyde and acetic anhydride in an acetic acid-sodium acetate medium. Mention of the palladium chloride catalysed hydrolysis of vinyl acetate has been made by Smidt².

When a mixture of vinyl acetate (0.10 mole), palladium chloride (0.005 mole), and sodium acetate (0.10 mole) in 60 ml. of glacial acetic acid was stirred for 1 day at 45-50°, fifty-five percent (0.055 mole) of the vinyl acetate was converted to acetaldehyde (0.048 mole identified by gas-liquid chromatography and by its 2,4-dinitrophenylhydrazine derivative) and acetic anhydride (0.05 mole identified by gas-liquid chromatography). No additional organic products were evidenced. Appropriate blank experiments were

I. I. Hoiseev, H. N. Vargaftik, and Ya. K. Syrkin, <u>Doklady Akad. Nauk.</u>
 S. S. S. R. 133, 377 (1960).

^{2.} J. Smidt, et al., Angew. Chem. 71, 176 (1959).

carried out. These showed palladium chloride to be the effective catalytic reagent present. When equivalent quantities of mercuric chloride, zinc chloride, or hydrogen chloride were employed in place of palladium chloride, none of the vinyl acetate was destroyed. In the absence of added sodium acetate, negligible conversion to acetaldehyde occurred. By refluxing a solution of acetic acid, sodium acetate, and palladium chloride containing benzene (to form an assectrope with water), it was shown that palladium (II) chloride does not catalyse the formation of acetic anhydride and water from acetic acid.

Significantly, no ethylidene diacetate was detected in the reaction solution³. Only if it had reacted rapidly to form acetaldehyde and acetic anhydride, could ethylidene diacetate have been a reaction intermediate. It was discovered, however, that ethylidene diacetate does not react at all when subjected to the conditions under which the vinyl ester decomposes. Thus, it would appear that the vinyl acetate cleaves directly to acetaldehyde. The work of Jeffrey and Satchell⁴ suggests the unliklihood of ketene as an intermediate. The following reaction sequence may be formulated to account for this reaction.

(1)
$$CH_3 - COOCH = CH_2 + PdCl_2 \longrightarrow CH_3 COOCH = CH_2
PdCl_2 $O - CH_3 - CH_2 = CH_3 - COOCH = CH_2 + CH_3 - COOCH = CH_3 - COOCH = CH_2 + CH_3 - COOCH = CH_3 - COOCH = CH_2 + CH_3 - COOCH = CH_2 + CH_3 - COOCH = CH_3 - C$$$

(3)
$$0 \xrightarrow{-} \text{CH} \xrightarrow{\text{CH}_2} \xrightarrow{\text{CH}_3\text{COOH}} \xrightarrow{\text{HOCH}} = \text{CH}_2 \xrightarrow{\text{O}} \xrightarrow{\text{CH}_3\text{CHO}} \xrightarrow{\text{PdCl}_2} \xrightarrow{\text{PdCl}_2} + \text{CH}_3\overset{\text{O}}{\text{C}} \xrightarrow{\text{O}} \xrightarrow{\text{O}} \xrightarrow{\text{O}} \xrightarrow{\text{CH}_3\text{CHO}}$$

^{3.} R. L. Adelman, J. Org. Chem. 14 1057 (1949).

^{4.} E. A. Jeffrey and D. P. N. Satchell, Chem. and Ind. 1444 (1960).