Palladium(II)-catalysed Formation of Propene from Ethylene and Acetic Anhydride–Hydrochloric Acid Solution

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A RECENT report of the production of propene from ethylene catalysed by palladium chloride in the presence of fluoride salts in nitrilic solvents[1] prompts us to communicate a related reaction in which fluorides and nitrilic solvents are not necessary.

During our studies of olefin oxidation,[2,3] we found that when ethylene is treated with palladium chloride in acetic anhydride–acetic acid solvent in the presence of hydrochloric acid, a rapid contraction of the gas is observed with formation of substantial amounts of propene and butenes.† Butene formation is expected;[4,5] propene formation is surprising.

During the reaction the solution was orange and clear, but rather rapid precipitation of elemental palladium occurred as in a "clock" reaction and the reaction then ceased.

Mass spectrometric analysis of the gas after reaction, in volume % was: propene, 15·2; butenes, 5·7; ethylene, 77·4; *ethane, 1·3;* carbon dioxide, 0·3; carbon monoxide and propane, not detected. G.l.c. analysis confirmed the presence of propene and butenes, the latter being a mixture of but-1-ene and *cis*- and *trans*-but-2-enes in their thermodynamic equilibrium composition.

Propene was not formed in the absence of palladium chloride or acetic anhydride, or when the hydrochloric acid was neutralized with lithium acetate.

The amount of propene produced was of the same order of magnitude as the palladium(II) charged [about 2 moles of propene per mole of palladium(II)]. This could indicate that reduction of palladium(II) is involved in the propene-forming reaction but this has not been proved. Moreover, the butenes and propene account for less than 20% of the ethylene consumed. Palladium precipitation and the fact that the propene accounts for only a portion of the reacted ethylene make the quantitative study of this very peculiar reaction difficult.

Results of experiments with tagged reactants to establish the origin of the propene carbon atoms are awaited before we attempt to answer mechanistic questions.

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† Typical conditions: $PdCl_2$ (4×10^{-3}M), HCl (0·11M), HOAc (0·7M), Ac_2O solvent; ethylene fed by demand from a reservoir. Reaction time 10 min., 80°, atmospheric pressure.

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