The Palladium Chloride-catalysed Reaction of Ethylene and Sulphur Dioxide

By HARVEY S. KLEIN

(*Shell Development Company, Emeryville, California* 94608)

MUCH information is available on the transition-metal catalysed reactions of carbon monoxide and unsaturated organic compounds, but corresponding reactions with sulphur dioxide have not been investigated. However, some inorganic complexes of sulphur dioxide are known which are completely analogous to carbon monoxide complexes of transition metals.[1] We report the $PdCl_2$-catalysed reaction of sulphur dioxide and ethylene.

When ethylene and sulphur dioxide are heated in the presence of a benzene suspension of $PdCl_2$, ethyl *trans*-but-2-enyl sulphone is formed.

$$3CH_2{=}CH_2 + SO_2 \xrightarrow[70^\circ]{PdCl_2}$$

$$CH_3{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CH\overset{t}{=}CH{\cdot}CH_3$$

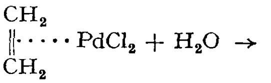
6 Moles (*ca.*) of product are formed per gramme atom of $PdCl_2$. The reaction terminates with precipitation of palladium metal. The product was identified by spectral and elemental analysis and the structure was established by an independent synthesis:

$$CH_3{\cdot}CH_2{\cdot}SO_2Cl + CH_2{:}CH{\cdot}CH{:}CH_2 \xrightarrow{Cu_2Cl_3}$$

$$CH_3{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2CH\overset{t}{=}CH{\cdot}CH_2Cl \xrightarrow[Pd/C]{H_2}$$

$$CH_3{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CH\overset{t}{=}CH{\cdot}CH_3$$

Small amounts of ethyl vinyl sulphone were detected in the reaction mixture. Although ethyl vinyl sulphone reacts with ethylene under the reaction conditions to give ethyl butenyl sulphone, it may be a by-product involved in an equilibrium step (V ⇌ VI in the Scheme) rather than a true intermediate. The mechanism of the reaction may involve hydride species which can originate *via* an oxidation–reduction reaction, involving water present in the reaction system. Under rigorously anhydrous conditions no reaction occurs. The $[Pd^0]$ formed may exist as an ethylene complex



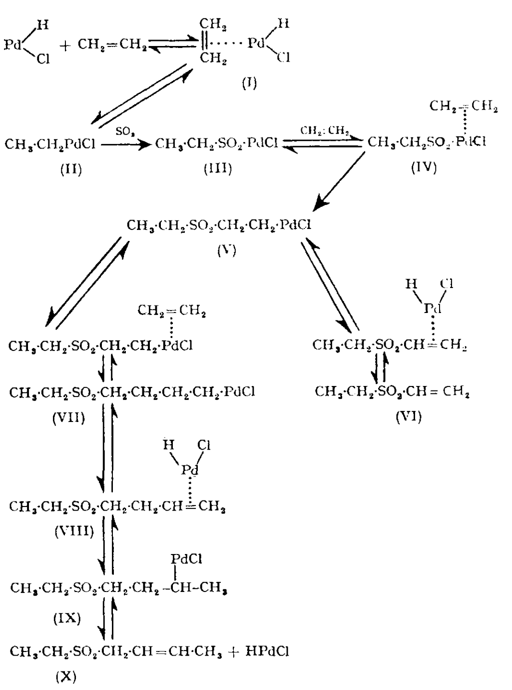
$$\begin{matrix}CH_2\\ \| \cdots PdCl_2\\ CH_2\end{matrix} + H_2O \rightarrow$$

$$MeCHO + 2HCl + [Pd^0]$$

$$[Pd^0] + HCl \rightarrow HPdCl$$

which then adds HCl. The formation of metal hydrides by addition of HCl to complexes having π-bonded ligands appears to be a general reaction.[2] The reaction of the ethylene–palladium chloride complex with water to give acetaldehyde is apparently inhibited by sulphur dioxide since ethyl butenyl sulphone and ethyl vinyl sulphone are the major products when the reaction occurs in water. The overall reaction course is as follows:

SCHEME



Whenever a butylpalladium complex (VII) is formed the reaction is terminated by dissociation to a butenyl species (VIII) which undergoes rapid isomerisation to the thermodynamically more stable *trans*-but-2-enyl isomer (X). Compounds with internal double bonds do not react further with ethylene.

The sequence of insertion steps (I—VI) postulated for the formation of the intermediate ethyl vinyl sulphone (VI) is similar to that in the reported formation of diethyl ketone from ethylene, carbon monoxide, and cobalt hydrocarbonyl in the presence of a reducing agent.[3]

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[2] M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115.

[3] J. H. Staib, W. R. F. Guyer, and O. C. Slotterbeck, U.S.Pat. 2,864,864/1958.