

340. *The Activation of Palladous Chloride by Metal Ions in the Homogeneous Hydrogenation of Ethyl Crotonate.*

By E. B. MAXTED and S. M. ISMAIL.

Small quantities of 1% solutions of palladous chloride have been used as a hydrogenation catalyst. Acetates of copper, nickel, zinc, silver, mercury, cadmium, sodium, and calcium, and chlorides of copper, nickel, cobalt, aluminium, magnesium, cerium, and chromium, as 10^{-4} M-aqueous solutions, were used as promoters at $30^{\circ}/1$ atm. For the solutions studied, the catalyst could be activated, in that the hydrogenation took place at a rapid rate at this relatively low temperature and pressure. With the most active metal ion, sodium, the activity was as much as 6—7 times that of palladous chloride alone.

UNTIL 1938, when Calvin¹ found that cuprous acetate or salicylaldehyde, in quinoline solution, catalysed the reduction of quinoline by molecular hydrogen, hydrogenation catalysts, almost without exception, were solids. Since then, various authors^{2,3} have investigated this system intensively. Flynn and Hulburt⁴ found that ethyleneplatinum chloride was reduced by hydrogen at temperatures as low as -70° . Tulupov³ showed that olefinic compounds could be hydrogenated in the presence of ions. We have shown that the addition of metal ions exerts a strong promoting influence in the catalytic hydrogenation of ethyl crotonate with palladous chloride in homogeneous solutions. Sixteen different salts were tested, and it was established that the metal ion is the activator rather than the anion.

EXPERIMENTAL

All the reagents were of ordinary laboratory grade, and were used as purchased, except for magnesium chloride and zinc acetate, which were analytical-reagent grade.

A small quantity (equivalent to 35.5 mmoles of palladium) of a 1% aqueous solution of palladous chloride was added, in a reaction pipette, to various quantities of metal solutions with ethyl crotonate (1 ml.), and 95% absolute alcohol (5 ml.) was used as solvent. The reaction pipette was cooled in an ice-bath and was then connected to a hydrogen reservoir under atmospheric pressure. The apparatus was flushed 8—10 times with high-purity hydrogen by repeated evacuation with an oil pump and subsequent admission of fresh hydrogen. Calcium chloride traps were used to absorb moisture. The hydrogenation was carried out by shaking the pipette at a rate of 520 revolutions per minute in a thermostat-bath at 30° . The measure of activity was taken as the volume of hydrogen absorbed in the first ten minutes of the reaction.

A typical activation curve is shown in Fig. 1, 0.6 ml. of a 10^{-4} M-solution of nickel acetate, with the standard charge being studied. The absorption of hydrogen is rapid for the first 10 min.; it falls off slowly for the next 5 min., and then more rapidly as the reaction approaches completion. For this reason, the rate-determining steps were subsequently measured for only the first 10 min.; this may be regarded as the preliminary rate.

In Fig. 2, relative activities of copper and nickel acetate and chloride are shown, each point on the curves representing a separate experiment. For each pair of salts having the same metal, the most active points in the curves occur with approximately the same amounts of the metal, irrespective of the anion, showing that the activity is due to the metal ion. In Figs. 3 and 4, the curves rise gradually with an increasing amount of the metal ions. The addition of further amounts of metal ions becomes less effective, in the sense that there is an unnecessary crowding of the metal ions, and the rate of hydrogenation accordingly rises to a limiting value and subsequently falls. Basic lead acetate did not have any activity. The activities at their peak

¹ Calvin, *Trans. Faraday Soc.*, 1938, **34**, 1181.

² Wilmarth and Barsh, *J. Amer. Chem. Soc.*, 1953, **75**, 2237; Weller and Mills, *ibid.*, p. 769; Wright and Weller, *ibid.*, 1954, **76**, 3345; Halpern, Harrod, and James *ibid.*, 1961, **83**, 753; Smidt, Hafner, Jira, Sicher, Sedlmeir, and Sabel, *Angew. Chem.*, 1962, **74**, (3), 93.

³ Tulupov, *Zhur. Fiz. Khim.*, 1957, **31**, 519; *ibid.*, 1958, **32**, 727.

⁴ Flynn and Hulburt, *J. Amer. Chem. Soc.*, 1954, **76**, 3393.

points decrease in the sequence: sodium acetate, zinc acetate, mercuric acetate, cobalt chloride, cupric chloride, cupric acetate, magnesium chloride, cadmium acetate, silver acetate, chromic chloride, aluminium chloride, nickel acetate, calcium acetate, nickel chloride, cerous chloride.

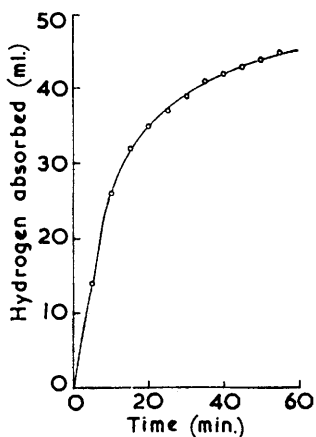


FIG. 1. Activation curve for palladous chloride with nickel acetate as promoter.

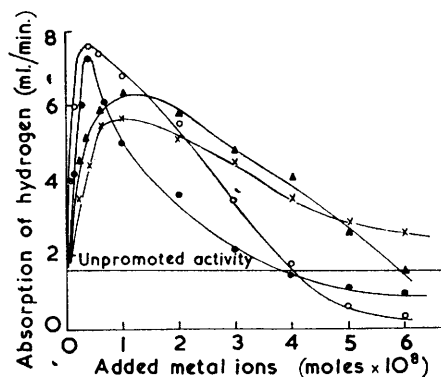


FIG. 2. Activities of: ● copper acetate, ○ copper chloride, ▲ nickel acetate, and × nickel chloride.

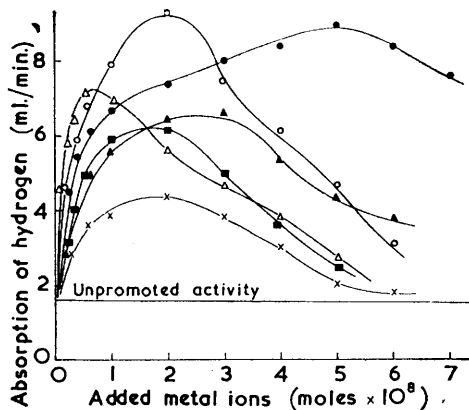


FIG. 3. Activities of: ■ Ca^{2+} , Δ Ag^+ , ○ Na^+ , ▲ Al^{2+} , × Ce^{3+} , and ○ Zn^{2+} .

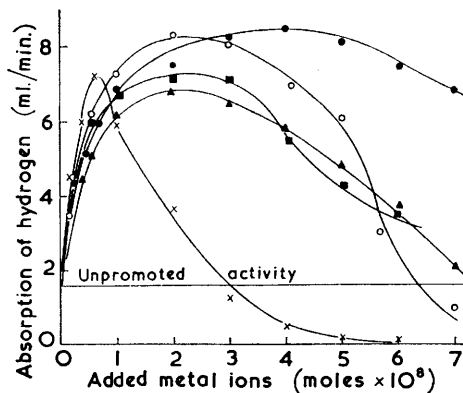
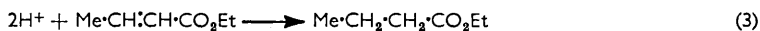


FIG. 4. Activities of: ○ Co^{2+} , ■ Mg^{2+} , ▲ Cr^{3+} , × Cd^{2+} , and ● Hg^{2+} .

DISCUSSION

A known quantity (equivalent to 35.5 mmoles of palladium) of palladous chloride alone absorbed 16.8 ml. of hydrogen in 10 minutes, after an induction period of 10–15 seconds. As the reaction proceeds, a grey spongy precipitate of metallic palladium black begins to form from what was previously a clear amber solution, and the solution does not remain homogeneous during the hydrogenation. It was thought that perhaps the metallic palladium acts as a powerful heterogeneous catalyst. However, the metal produced during the hydrogenation was not catalytically active, since the rate of hydrogenation continually decreased as the reaction proceeded. This evidence suggests that the reaction is truly homogeneous, and the catalytic properties of palladous chloride can be accounted for by the properties of the individual atoms rather than by some macroscopic property of the solid metal catalyst.

The mechanism for this reaction is of the form:



It is possible that the dissociation of the hydrogen molecule occurs during reaction (1); the combination of the hydride ion with Pd^{2+} occurs to form PdH^+ , while a proton combines with a molecule of water. Alternatively, one hydrogen atom may combine with the metal ion and one with the ethyl crotonate molecule, thus forming a radical.

In general, there is some uncertainty with respect to the nature of the species present in these systems, and it is difficult to elucidate the reaction mechanisms in detail. Calvin and Wilmarth⁵ interpreted this in terms of a decrease in the energy required to promote electrons from the full $3d$ shell to empty upper orbitals.

DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY,
THE UNIVERSITY, BRISTOL.

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⁵ Calvin and Wilmarth, *J. Amer. Chem. Soc.*, 1955, **75**, 1301.