Oxidation of Ethylene over Palladium and Palladium-Gold Alloys

UNTIL recently, nearly all successful catalysts used for the partial heterogeneous oxidation of ethylene contained silver as the active component¹. In 1962, however, Kemball and Patterson² reported that ethylene could be oxidized to acetic anhydride and acetic acid over evaporated palladium films, and several applications have since then appeared in the patent literature³. Kemball² suggested that the partial oxidation products (which amounted to only about 3 per cent of the total) were formed by a path parallel to that for the complete oxidation to carbon dioxide. Acetaldehyde was proposed as the intermediate in the partial oxidation reaction, but none was detected, presumably because of its rapid oxidation to acetic anhydride. The purpose of the present work was to isolate and identify the proposed intermediate, and to determine whether higher selectivities might be obtained under more favourable reaction conditions.

A differential reactor was used in which the reactants were circulated rapidly over the catalyst at temperatures where the conversion in each pass was less than 1 per cent. The products were removed continuously from the gas phase by a U-tube trap maintained at -135°C . In a typical experiment, 2 g of palladium sponge (99.95 per cent palladium, less than 10 p.p.m. silver, less than 15 p.p.m. chlorine; surface area, $0.2\text{ m}^2/\text{g}$) were reduced in hydrogen at 500°C and then evacuated for 17 h at this temperature. A standard reactant mixture, containing 43 torr of ethylene and 100 torr of oxygen, was admitted to the reaction system and the gases circulated until about 30 per cent of the ethylene had reacted. The initial rates were close to zero order with respect to ethylene (in the range 10–47 torr) and 0.7 order with respect to oxygen (in the range 25–260 torr). The partial oxidation products, which represented 30–40 per cent of the ethylene oxidized, included acetaldehyde, acetic anhydride and acetic acid. The products were analysed by gas-liquid chromatography and identified by comparison with authentic compounds.

Acetaldehyde was confirmed by the following additional tests: (a) it had the correct retention time on a second (different) gas-liquid chromatography column (where a small quantity of ethylene oxide was also identified); (b) a positive test was obtained with fuchsin aldehyde reagent; (c) its mass spectrum corresponded to that of acetaldehyde. Depending on reaction conditions, acetaldehyde represented 1–20 per cent of the partial oxidation products.

The selectivity (percentage partial oxidation) was almost independent of temperature. In one series of experiments, it increased from 33 per cent at 109°C to 38 per cent at 78°C . These values, which are within our experimental error, indicate that the apparent activation energies of the two parallel reaction paths, if they exist, differ by less than 2 kcal/mole.

Unexpectedly, the selectivity was influenced by changes in oxygen pressure, increasing from 25 per cent to 43 per cent as the pressure was increased from 25 to 259 torr. This result can be explained if complete oxidation involves ethylene adsorbed associatively on adjacent metal atoms, while partial oxidation occurs on single sites. Alternatively, adjacent vacant metal atoms may effect complete oxidation by making possible the dissociative chemisorption of ethylene. The selectivity was not affected by changes in ethylene pressure between 10 and 47 torr.

The idea that the concentration of active sites for complete oxidation might be diminished by adsorption of oxygen led us to look for other ways of increasing the selectivity. Because gold was not a catalyst for this reaction, it was reasoned that the concentration of dual sites would be diluted in a palladium-gold alloy. This should favour partial oxidation. A poorly alloyed sample containing 18 atom per cent palladium was prepared by

reducing the mixed chlorides (obtained by evaporating a solution to dryness). Several experiments with this catalyst yielded selectivities as high as 70 per cent. Experiments with homogeneous alloys (verified by X-ray), prepared by reducing the metal salts with hydrazine, indicated that the selectivity reached a maximum at about 20 atom per cent palladium. Analyses showed, however, that samples prepared by reducing the metal salts with sodium borohydride were severely contaminated with sodium and boron. Our experience in this connexion makes us suspect the validity of using alloy catalysts prepared in this way to investigate the effects of alloying on catalytic properties, because these impurities drastically reduced both the rate and selectivity of the oxidation reaction. It is hoped that work now in progress will make it possible to interpret these results.

Fig. 1. Effect of temperature on rate.

The initial rates were measured over palladium as a function of temperature over the range 71 – 102°C using the standard mixture of reactants. The Arrhenius plot is shown in Fig. 1. From the slope of this line, an apparent activation energy of 20 kcal/mole was calculated, and the initial rate could be expressed as

$$[d(\text{C}_2\text{H}_4)/dt]_{t=0} = 10^{24.6 \pm 0.1} \exp \left[-\frac{20,000 \pm 2,000}{RT} \right] \text{ molecules/sec/cm}^2$$

The activation energy was about 6 kcal/mole greater than that found by Kemball and Patterson² for evaporated films. This discrepancy is outside our experimental error and may be attributed to the differences in catalyst preparations and reaction conditions. In particular, the reaction was first order in ethylene at the lower pressures used by Kemball and Patterson.

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² Kemball, C., and Patterson, W. R., *Proc. Roy. Soc., A*, **270**, 219 (1962).

³ Holtzrichter, H., Kronig, W., and Frenz, B., U.S. Patent 3,275,680 September 27, 1966.