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NOTES

Reaction Products in the Silver-Catalyzed Oxidation of Ethylene

The silver-catalyzed oxidation of ethylene has been the subject of many investigations in the past 20 years and these have been adequately reviewed by Margolis (*1*) and by Voge and Adams (*2*). In none of these investigations have any final products other than ethylene oxide, carbon dioxide, and water been reported, although several well defined chemical intermediates have been postulated by various workers.

We recently initiated a program of study of silver-catalyzed oxidation reactions by, *inter alia,* the pulse micro-catalytic gas-chromatographic technique, using oxygen both as a carrier gas and as a reactant. The preliminary results obtained for the oxidation of ethylene over pure silver and a silver–calcium alloy are sufficiently novel to report at this time, prior to completion of the kinetic studies.

In a typical experiment, a pulse of ethylene (1×10^{-7} to 4×10^{-6} moles) is injected into a stream of oxygen flowing at a constant pressure of 1180 mm Hg and a constant flow rate of 50 ml at STP per minute, through a catalyst loop containing pure silver or a silver–calcium alloy, and the products are analyzed by passage through two chromatographic columns at suitable temperatures (Porapak R at 80°C for ethylene oxide separation and Porapak Q at ice temperature for carbon dioxide–ethylene separation), and then through a thermistor detector. The silver was Cominco 5N silver powder and was presintered and reduced in hydrogen at 500°C before use; the surface area is known to be approximately 0.3 m^2/g, and the amount of silver used was of the order of 0.5 g. The silver calcium alloys were prepared as powders by the method already described (*3*), and are known to have surface areas of the order of 0.6 m^2/g: the amounts of catalyst used are again approximately 0.5 g, depending on their activity. Reaction temperatures were in the range 200–350°C and the conversion of ethylene could be varied from 0–100%. The relative yields of the various products is a function of temperature and catalyst, but generally the ratio of CO_2:EtO production falls in the range of 4:1 to 10:1.

In addition to peaks due to unreacted ethylene, carbon dioxide, and ethylene oxide, a negative peak is observed, immediately following the ethylene oxide peak. This peak has been identified as being due to formaldehyde by the following methods: (A) Methanol injected into the oxygen stream instead of ethylene yields a peak due to carbon dioxide, and a negative peak with the same retention time as the negative peak previously mentioned. (B) Formalin, when injected into the oxygen stream, but bypassing the catalyst, yields an identical peak. (C) The chromotropic acid test (*4*), when run on the collected effluent of many ethylene oxidation reactions, gave a positive result for formaldehyde. (D) The thermal conductivity of formaldehyde is greater than that of oxygen, which is of course a prerequisite for a negative peak (*5*). The yield of formaldehyde appears to be strongly dependent on the degree of sintering of the catalyst and noticeably decreases as a catalyst is aged.

Although the experimental conditions used here are extreme compared to normal synthesis conditions, possibility for the

production of formaldehyde will have to be considered in any mechanistic interpretation of the kinetic studies. These experiments are continuing and will be reported in detail at a later date.

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Reaction of Buta-1,3-diene over a Carbon-Supported Cobalt Oxide Catalyst

The homogeneous gas phase dimerization of buta-1,3-diene is a well-known reaction and has been extensively studied. At short contact times in glass vessels at 300°C the main product is the Diels-Alder adduct 4-vinylcyclohexene (*1*) while under prolonged exposure to temperatures of 500°C and above a profusion of secondary reactions occurs leading to the formation of aromatic and unsaturated alicyclic compounds (*2*). Relatively little attention appears to have been given, however, to the solid catalyzed reactions of gaseous butadiene at elevated temperatures and we wish to report here some results obtained using a charcoal supported cobalt oxide catalyst. Materials of this type have recently been used as mono-olefin dimerization catalysts (*3–6*) and dienes have been shown to interact with them at low temperatures (*3*). No studies of this interaction at high temperatures have previously been reported.

EXPERIMENTAL METHODS

The charcoal used in the catalyst preparation was a BDH granular coconut shell charcoal with an ash content of 4.26% reduced to 0.92% by leaching with 48% hydrofluoric acid (*3*). Catalysts were prepared somewhat after the manner of Schultz *et al.* (*3*) by washing the charcoal with concentrated (0.880) ammonium hydroxide solution, drying under vacuum, impregnating with an aqueous solution of cobalt nitrate hexahydrate (BDH AnalaR), drying again, and then heating in a stream of dry nitrogen at 400°C for 30 min. Decomposition of cobalt nitrate to the oxide began at about 130°C. Catalysts were prepared in this way having a cobalt oxide concentration of 5 and 15%.

Reactions were carried out by passing gaseous butadiene (Matheson Research Grade) at atmospheric pressure and at a measured rate through a fixed bed containing 8 g of catalyst maintained at 300°C in a glass reactor supported in a furnace. The effluent gases were passed through a water condenser and then into a system of gas burettes which enabled measurements to be made of their rate of flow. Liquid products were analyzed using a Pye 105 gas chromatograph fitted with a 10-m squalane column maintained at 136°C. Satisfactory gas analyses were obtained with a 2-m tetraisobutene column maintained at 0°C in a Perkin-Elmer F.11 instrument.