NOTES

Postreactor Reactions during Ethylene Oxidation over Silver

In recent years it has become increasingly evident that postreactor reactions, homogeneous (gas phase) as well as heterogeneous (wall catalyzed), may complicate the interpretation of experimental data from the oxidation of hydrocarbons over heterogeneous catalysts (1, 2). Propylene oxidation reactions have received much attention with regard to this subject. Keulks and coworkers (3, 4) demonstrated that during the oxidation of propylene to acrolein over bismuth molybdate catalysts in a glass reactor acrolein underwent a number of homogeneous reactions in the postreactor section to yield acetaldehyde, formaldehyde, ethylene, CO_2, and H_2O. Homogeneous reactions between propylene and O_2 were also observed and found to produce acetaldehyde, acrolein, methane, formaldehyde, propylene oxide, CO, CO_2, and H_2O. In addition to these homogeneous reactions a surface-initiated homogeneous reaction was also identified which resulted in the conversion of propylene to propylene oxide in the postreactor volume. The influence of postreactor reactions upon other hydrocarbon oxidation reactions has not been investigated as thoroughly. In the present investigation the influence of postreactor reactions upon the product distribution from the oxidation of ethylene to ethylene oxide over silver catalysts was examined.

The silver catalysts were prepared by reacting KOH and $AgNO_3$, washing the precipitate in distilled water, carrying out reduction at 205°C in flowing hydrogen for 4 hr, and sieving to ~1-mm particles. The BET surface area of the silver catalysts was determined to be 0.27 m^2/g. The silver particles were placed in a 10-cm^3 fixed-bed reactor possessing a 1-cm diameter without further pretreatments. The gases used in this study were: C_2H_4 (Matheson—C. P. grade—99.5%), O_2 (Linde—high purity—99.99%), He (Linde—high purity—99.995%), and C_2H_4O (MG Scientific Gases—5% C_2H_4O/95% He). The reactant flow rates were controlled by Vactronics valves and metered with Tylan flowmeters at 130 kPa. The reactor was immersed in a fluidized sand bath for temperature control, and the reactor temperature was monitored with several thermocouples along its axis. The reactor containing the silver catalyst could be bypassed via a parallel reactor packed with 1-mm glass beads. The reactor effluent was sent to a HP-5830A gas chromatograph for analysis. A Porapak Q column was used for product separation and identification. The line from the reactor to the gas chromatograph was kept warm by heating tapes to prevent the condensation of water and oxygenated hydrocarbons. The connecting line consisted of ¼-in. 304 stainless-steel tubing and was 42 in. long; a thermocouple was placed 18 in. before the gas chromatograph. The residence time of the reactor effluent in the connecting line was approximately 6 s. The temperature of this postreactor volume was controlled with a Variac.

The changes due to the postreactor reactions during the oxidation of ethylene over the silver catalyst were monitored as a function of the postreactor temperature. The oxidation of ethylene over the silver catalyst was studied at 235°C with the line from the reactor to the gas chromatograph initially maintained at 155°C. The only reaction products observed under these conditions were C_2H_4O, CO_2, and H_2O; the ethylene conversion was 22% and the ethylene oxide selectivity was 73%. Increasing the temperature of the postreactor section,

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while maintaining the temperature of the reactor packed with the silver catalyst at 235°C, altered the product distribution as shown in Fig. 1. A postreactor temperature of 250°C did not alter the product distribution, but temperatures in excess of 340°C had a pronounced effect upon the reaction products. At the higher temperatures the ethylene oxide concentration dramatically decreased while the concentrations of CO_2 and H_2O (not shown in Fig. 1) increased. Two new reaction products, H_2CO and CH_3CHO, were also formed at high temperatures. The ethylene concentration in the effluent was almost constant throughout the range of temperature investigated, and decreased only slightly with temperature.

Similar results were obtained over a wide range of C_2H_4 and O_2 partial pressures. These results suggest that C_2H_4O was solely responsible for the observed postreactor reactions and new products.

The postreactor reactions of C_2H_4O and C_2H_4 were individually examined to ascertain that only C_2H_4O underwent reactions in the postreactor zone. During this set of experiments the gaseous mixture of interest was diverted to a parallel reactor packed with glass beads and also maintained at 235°C prior to entering the postreactor section. The only postreactor reaction products from a C_2H_4, O_2, and He mixture were H_2O (not shown) and CO_2 (presented in Fig. 2). The ethylene molecule was rela-
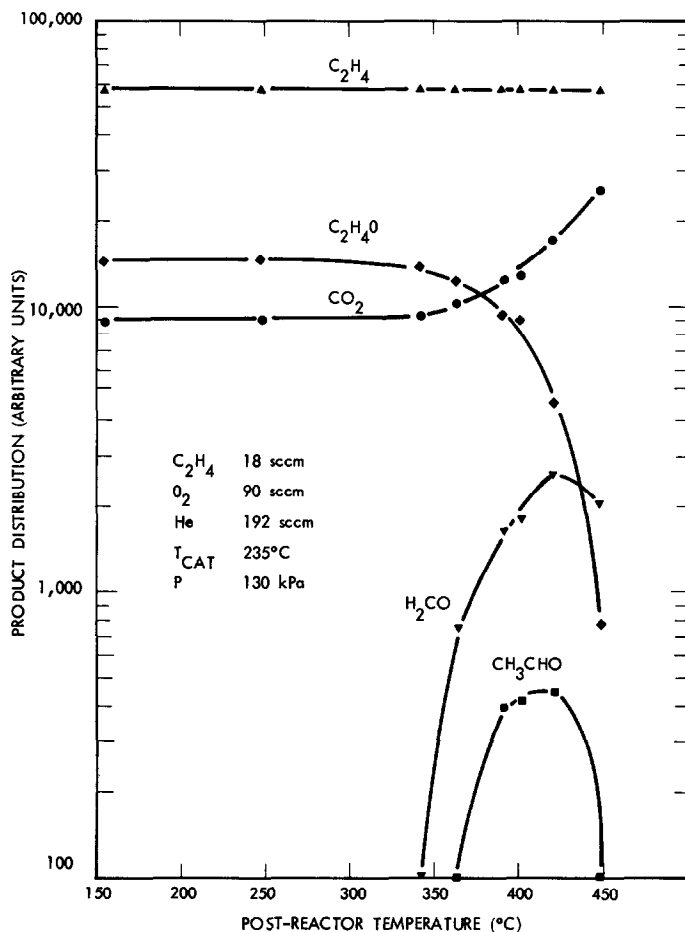

FIG. 1. Influence of the postreactor temperature upon the product distribution from ethylene oxidation over silver.
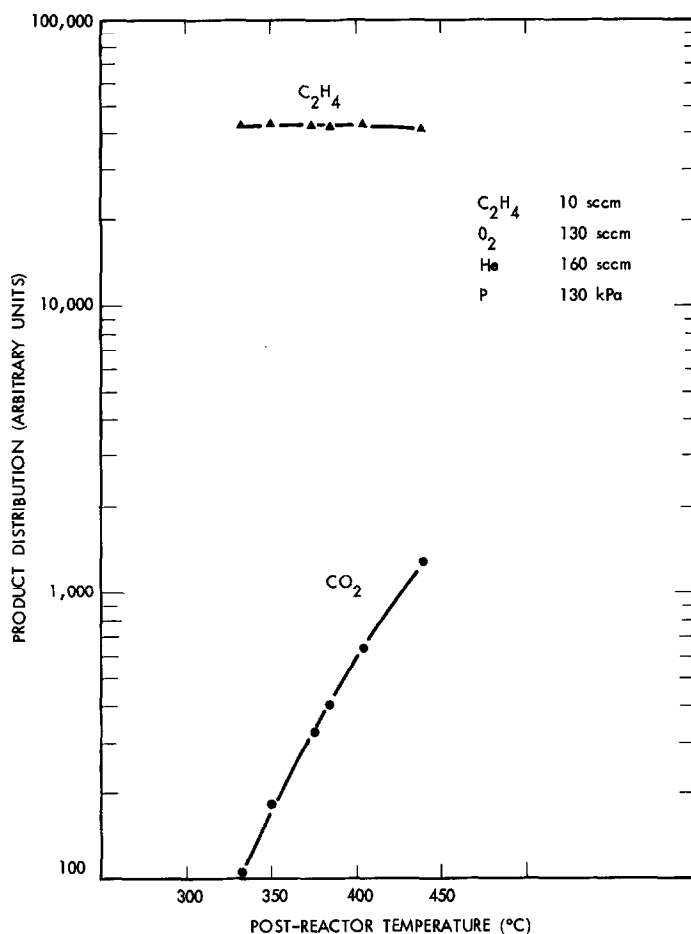
FIG. 2. Influence of the postreactor temperature upon C_2H_4-O_2-He mixture.

tively unreactive under these conditions achieving a conversion of ~1.5% at 440°C. The C_2H_4O, O_2, He mixture was quite reactive at these elevated temperatures in the postreactor section and reacted to produce CO_2, H_2O, H_2CO, and CH_3CHO. The product distribution is shown as a function of temperature in Fig. 3. The C_2H_4O conversion was ~80% at 444°C, and the maxima in the concentrations of H_2CO and CH_3CHO in the effluent were obtained at ~400°C. The product distribution at 400°C was 73% CO_2, 19.5% H_2CO, and 7.5% CH_3CHO. Oxygen exerted a pronounced influence on the reactivity of C_2H_4O and its product distribution in the postreactor volume. Removal of O_2 and substitution of additional

He so that the total flow rate was maintained constant at 400°C decreased the conversion of C_2H_4O to ~5%, dramatically reduced the concentrations of CO_2 and CH_3CHO, and eliminated the presence of H_2CO. These experiments demonstrate that the postreactor reactions originate with C_2H_4O and are accelerated by O_2.

The present experiments demonstrated that during ethylene oxidation over silver catalysts in a stainless-steel reactor the ethylene oxide product can undergo postreactor reactions to yield aldehydes, carbon dioxide, and H_2O. The maxima in the concentrations of CH_3CHO and H_2CO suggest that aldehydes are intermediates in the overall decomposition of ethylene oxide.
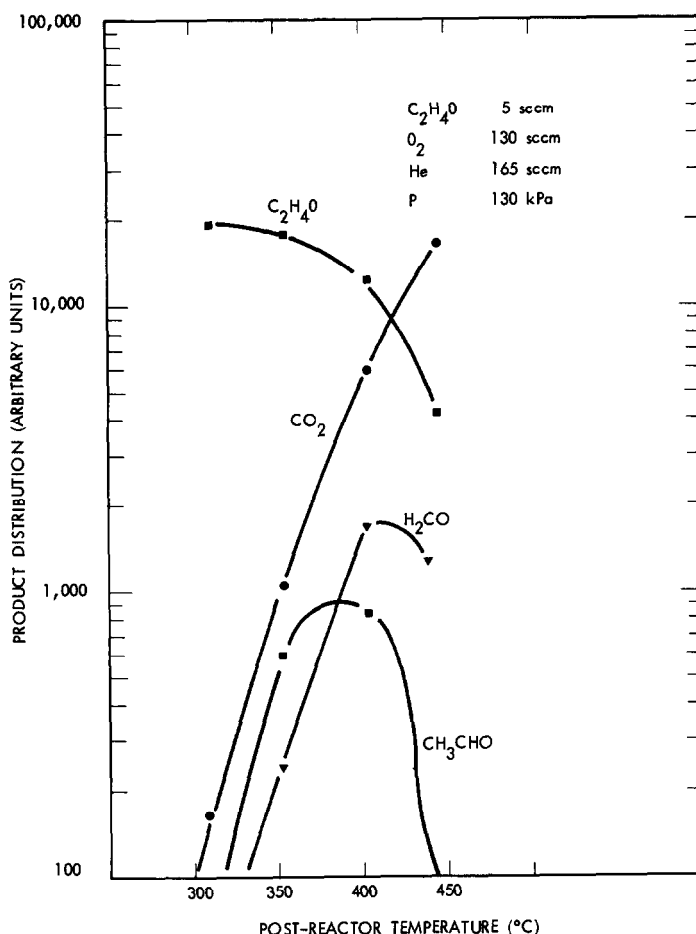
FIG. 3. Influence of the postreactor temperature upon $C_2H_4O-O_2$-He mixture.

This product slate is very different from that observed from the homogeneous pyrolysis of ethylene oxide in the absence of oxygen (5, 6). The major products observed from the homogeneous pyrolysis of ethylene oxide are CH_3CHO, CO, CH_4, C_2H_6, and H_2. The homogeneous pyrolysis of ethylene oxide is thought to proceed via an internal isomerization reaction to yield an excited CH_3CHO molecule which can either collide with a third body to lose excess energy and be stabilized or decompose unimolecularly to methyl and formyl radicals. Subsequent reactions of the radicals lead to the production of CO, CH_4, H_2, and C_2H_6. The different product slate in the present study is due to the presence of oxy-

gen and the participation of the stainless-steel wall. The absence of CH_4, H_2, and C_2H_6 in the present experiment is not unexpected since oxygen participates in homogeneous radical reactions to form CO_2 and H_2O, and the stainless-steel wall also readily oxidizes radicals, CO, and H_2 at these temperatures. The presence or absence of CO could not be confirmed since its retention time on the Porapak Q column was identical to that of O_2. The homogeneous pyrolysis of ethylene oxide yields only a small amount of H_2CO, but the present investigation showed that in the presence of oxygen H_2CO is a major product. One probable pathway to H_2CO formation is the homogeneous reaction between

oxygen radicals and methyl radicals. The present experiments further demonstrated that oxygen was a promoter for the decomposition/isomerization of ethylene oxide since the reaction was very slow in its absence. Thus, the presence of oxygen and the stainless-steel wall greatly enhance the conversion of ethylene oxide relative to that observed in homogeneous pyrolysis experiments (5, 6).

The present observations that ethylene oxide can react to form aldehydes and CO_2 via gas-phase homogeneous and wall-catalyzed heterogeneous reactions has important implications as to the reaction conditions that should be used for the oxidation of ethylene to ethylene oxide over silver catalysts. Although these homogeneous/heterogeneous reactions dominate the product distribution at temperatures that are higher than normally encountered during the oxidation of ethylene over silver catalysts they can proceed to a limited extent at lower temperatures. Laboratory stainless-steel reactors should not be operated above 300°C since the product distribution will be altered by the homogeneous/heterogeneous reactions. Stainless-steel multitubular reactors are employed commercially to carry out this reaction and the presence of hot-spot temperatures exceeding 300°C would be expected to have an adverse effect on the ethylene oxide yield and produce aldehydes. Interestingly, small amounts of formaldehyde (~0.1%) and acetaldehyde (~0.1%) are found in the effluent from commercial reactors and must be separated from the ethylene oxide product (7). The simultaneous appearance of formaldehyde and acetaldehyde in the effluent from these commercial reactors suggests that the aldehydes may originate from the above-mentioned homogeneous/heterogeneous reactions. The oxidation of ethylene over silver catalysts is often also investigated in recycle reactors to minimize heat and mass transfer gradients, but these stainless-steel reactor systems operate with large resi-

dence times. The long residence time of the reaction products in such reactor systems would be expected to enhance the decomposition of ethylene oxide and aldehyde production at the higher temperatures of operation. The present observation that small amounts of aldehydes can be formed from homogeneous/heterogeneous reactions of the reaction products in stainless-steel reactors also has important implications for the interpretation of the mechanism of ethylene oxidation over silver.

Many investigators have repeatedly claimed that aldehydes are intermediates for the combustion of ethylene and ethylene oxide during ethylene oxidation over silver, but are observed at most in trace quantities under typcial reaction conditions because they are readily oxidized to CO_2 and H_2O (8–13). This view has been strengthened with the observation that ethylene oxide can isomerize to acetaldehyde over silver between 200 and 300°C (7, 8, 10, 12). The isomerization reaction is accompanied by the production of C_2H_4 and CO_2, deposition of a carbonaceous residue on the silver surface, and on one occasion the production of acetic acid and crotonaldehyde (13). Formaldehyde is not a product of this heterogeneous reaction of ethylene oxide. As a result of these earlier observations several mechanisms for the combustion of ethylene oxide were proposed that proceeded through aldehyde intermediates. Twigg, (8) proposed that formaldehyde is the intermediate for the combustion of ethylene

$$C_2H_4 + 2O_{ads} \rightarrow$$

$$2H_2CO \xrightarrow{4O_{ads}} 2CO_2 + 2H_2O \quad (1)$$
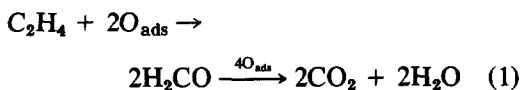
and acetaldehyde is the intermediate for the combustion of ethylene oxide

$$C_2H_4O \rightarrow CH_3CHO \xrightarrow{5O_{ads}}$$
$$2CO_2 + 2H_2O. \quad (2)$$
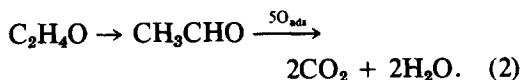
The ethylene oxide combusiton mechanism was also proposed by subsequent investigators (9–13). However, Kenson and Lapkin

(11) and Force and Bell (12) also proposed that acetaldehyde is an adsorbed intermediate for the direct oxidation of ethylene to CO_2

$$C_2H_4 + O_{ads} \rightarrow C_2H_4O_{ads} \rightarrow$$
$$CH_3CHO_{ads} \xrightarrow{5O_{ads}} 2CO_2 + 2H_2O. \quad (3)$$
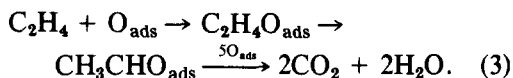
The present observation that small amounts of acetaldehyde and formaldehyde can also be produced by gas-phase homogeneous and wall-catalyzed heterogeneous reactions demonstrates that aldehydes do not necessarily have to originate from reactions related to the silver catalysts. In a subsequent communication the oxidation and influence of aldehydes upon the oxidation of ethylene over silver catalysts will be examined to better understand the possible role of aldehydes in this silver-catalyzed reaction (14).

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ISRAEL E. WACHS
CLAUDIO C. CHERSICH

Corporate Research-Science Laboratories
Exxon Research and Engineering Company
Linden, New Jersey 07036