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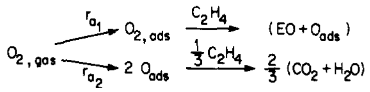
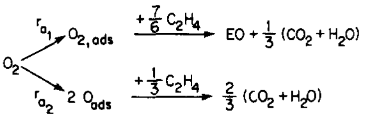
The Role of CH Bond Breaking in the Epoxidation of Ethylene

Recently Cant and Hall (*1*) reported that the rate of epoxidation of ethylene by O_2 catalyzed by Ag is significantly higher for C_2D_4 than for C_2H_4. This is a surprising result vis-à-vis Worbs' widely accepted epoxidation mechanism (*2*), which assumes that oxygen is adsorbed onto Ag both nondissociatively and dissociatively and that the diatomic adsorbed oxygen reacts with ethylene to give the epoxide (EO), whereas the monoatomic oxygen leads to total combustion of ethylene:



(1)

Since the oxygen atom formed in the first of these reactions will subsequently react with ethylene to form CO_2 and H_2O (unless recombination to $O_{2,ads}$ takes place), the stoichiometry of this scheme is given by



(1a)

Upon defining the selectivity S by k_{EO}, i.e., the rate of C_2H_4 conversion to EO, divided by the total rate of C_2H_4 conversion,

$$S = \frac{k_{EO}}{k_{EO} + \frac{1}{2}k_{CO_2}}, \qquad (2)$$

where k_{CO_2} is the rate of C_2H_4 conversion to CO_2, Scheme (1a) leads to

$$S = \frac{6r_{a_1}}{7r_{a_1} + r_{a_2}}. \qquad (3)$$

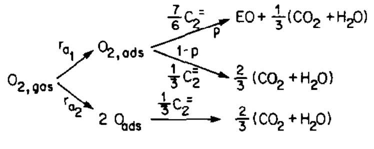
Kilty *et al.* (*3*) supported this model on the basis of infrared evidence, including data obtained with isotopically labeled oxygen, and results on the effect of a chlorine "moderator" on the selectivity. They proposed that chlorine adsorbed on Ag suppresses r_{a_2}, the rate of dissociative adsorption of oxygen.

A different mechanism had been proposed by Twigg (*4*), who assumed that EO is formed by reaction of ethylene with monatomic adsorbed oxygen. In terms of this model Force and Bell (*5*) explained the effect of the moderator by assuming that adsorption of chlorine removes the vacant sites required for chemisorption of ethylene. Only oxygen atoms contiguous to these sites are assumed by these authors to lead to combustion to carbon dioxide and water.

According to both hypotheses the selectivity should increase with increasing coverage of the surface with Cl. It appears, however, that either model requires some further specification in order to account for the isotopic effect found by Cant and Hall.

In the case of the Worbs mechanism the assumption has to be introduced that reactions of ethylene with nondissociatively adsorbed O_2 can lead to either EO ($+CO_2 + H_2O$) or $CO_2 + H_2O$. Formation of EO does not involve CH bond breaking as it proceeds via insertion of an oxygen atom into the double bond of ethylene; the other reaction involves CH bond breaking and leads ultimately to total combustion of ethylene.

The modified reaction mechanism can be schematically represented as follows:



(4)

The competitive reaction mode of ethylene with $O_{2,ads}$ is in agreement with Cant and Hall's finding that the rate of ethylene oxide formation increases but that of CO_2 forma-

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tion decreases when C_2H_4 is replaced by C_2D_4; in other words this is basically an isotope effect of the parameter p.

If chlorine only increases the r_{a_1}/r_{a_2} ratio, as is postulated by Kilty *et al.*, and does not affect the probability p that molecular O_2 gives ethylene oxide, the isotope effect α found upon replacement of C_2H_4 by C_2D_4 should increase with the chlorine coverage of Ag. The isotope effect α is defined as:

$$\alpha = \frac{k^{D}_{EO}}{k^{D}_{CO_2}} \Big/ \frac{k^{H}_{EO}}{k^{H}_{CO_2}}. \tag{5}$$

According to mechanism (4), the expressions for the rate become:

$$k_{EO} = p \cdot r_{a_1},$$
$$\tfrac{1}{2}k_{CO_2} = \tfrac{1}{3}\{(1 - \tfrac{1}{2}p)r_{a_1} + r_{a_2}\}. \tag{6}$$

In order to test the hypothesis that the isotope effect should increase with Cl coverage of Ag we measured the isotope effect as a function of changing moderator concentration at the surface. The experiments were performed in a recirculation apparatus made of Pyrex. Under our conditions ($p_{C_2H_4}$ = 67 mbar, p_{O_2} = 213 mbar, p_{Ar} = 67 mbar, WHSV = 6500 Nl · kg^{-1} · h^{-1}, total volume = 860 ml), no appreciable effects due to a consecutive reaction or to adsorption of reaction products were apparent (Fig. 1). The Ag powder used had been prestabilized by subjecting it to oxidation (O_2) and reduction (H_2) cycles.

The influence of a chlorine-containing moderator was determined by exposing silver precovered with Cl to a reaction mixture containing vinyl chloride at 200°C. Part of the vinyl chloride was burnt to CO_2 and H_2O, while the Cl was adsorbed by the silver. The amount of Cl deposited was calculated from the decrease in vinyl chloride concentration during the decomposition run.

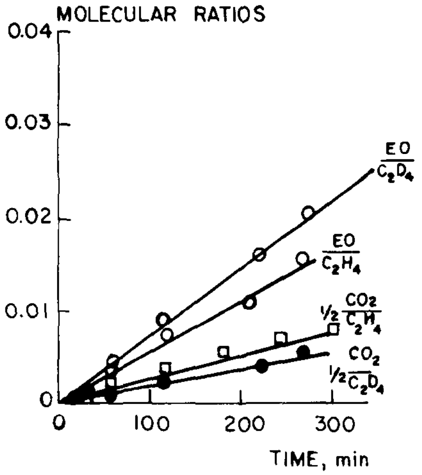

FIG. 1. Comparison of yields for deuterated and nondeuterated ethylene; T = 200°C, $S(C_2H_4)$ = 68%.

Since we observed that at 200°C Cl is only very slowly removed from the silver surface, it is possible to compare the selectivities of C_2H_4 and C_2D_4 epoxidation at that temperature using the same silver catalyst at virtually constant chlorine coverage. After one cycle of two experiments (C_2H_4 and C_2D_4) the selectivity to C_2H_4O proved to be unchanged.

It was found that at 300°C, chlorine can be (partly) stripped from the silver by an $O_2/C_2^=$ mixture. After such treatments the EO selectivity measured at 200°C was found to depend on the amount of chlorine still present. A maximum selectivity of 74% was found for an atomic Cl/Ag surf. ratio of 0.35 ± 0.10. A decrease in coverage of 10% lowered the selectivity to 65% and after extensive stripping of chlorine S decreased to 35%.

In Fig. 2 the isotope effect α is plotted against the selectivity of C_2H_4 to EO measured at a particular Cl coverage and temperature. From these data two conclusions can be drawn:

—the isotope effect strongly decreases with increasing selectivity as a result of precovering the surface with chlorine;

—the isotope effect strongly increases with increasing temperature.

In addition, as is illustrated by Fig. 1, it is found that:

—replacement of C_2H_4 by C_2D_4 increases the rate of EO formation but decreases the rate of CO_2 formation.

The latter observation is in agreement with the results of Cant and Hall (*1*).

Since we also determined the rate of oxygen adsorption on the same Ag powders

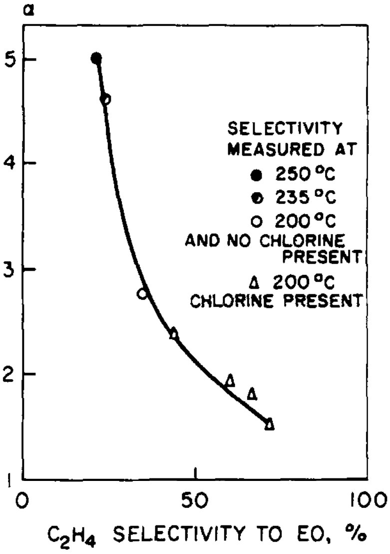

FIG. 2. Isotope effect as a function of selectivity; selectivity measured at: ●, 250°C; ◐, 235°C; ○, 200°C.

as were used in the epoxidation experiment, the rate of oxygen consumption in the epoxidation reaction divided by the number of oxygen collisions with Ag can be compared with the sticking coefficient of O_2 on Ag. These experiments have been done in the absence of chlorine.

At 200°C the sticking coefficient at $\theta_0 = \frac{1}{2}$ $\theta_{\max}$ equals 5×10^{-5}. $\theta_{\max}$ is the surface coverage of O_2 after 30 min of oxygen exposure ($p_{O_2} = 5$ Torr). $\theta_{\max}$ corresponds with O/Ag = 1. At $\theta_{\max}$ the sticking coefficient has dropped to 10^{-6}.

The sticking coefficient at $\theta = \frac{1}{2}\ \theta_{\max}$ measured is of the same order of magnitude as that published by Engelhardt and Menzel (*6*) for the Ag(110) face and that reported by Albers *et al.* (*7*) for Ag(111). From the turnover number of oxygen in the epoxidation reaction we calculated a reaction probability of 10^{-4} per oxygen collision. So we find agreement with the sticking coefficient within a factor of 2.

These findings support the kinetics in which the rate of oxygen adsorption is assumed to be rate limiting.

Our results do not allow us to discriminate between Worbs' and Twigg's mechanisms. They can be reconciled with Worbs' mechanism if this mechanism is modified to include the possibility that molecular oxygen can also react with ethylene to give total combustion (Scheme 4). The chlorine moderator not only changes the relative concentrations of atomic and molecular oxygen, but also increases *p*, the probability that molecular oxygen reacts with ethylene to ethylene oxide.

The assumption that the reaction of ethylene with atomic oxygen leading to total combustion of ethylene does not involve CH bond breaking as the rate-limiting step is in agreement with the observation by Yao (*8*) that replacement of C_2H_4 by C_2D_4 does not change the rate of total combustion on catalysts not selective in ethylene oxide formation. Reaction with ethylene probably occurs with dissociated oxygen.

Our results indicate that the surface oxygen species responsible for epoxide formation can also lead to an ethylene species intermediate giving total combustion of ethylene. The relative probability of both routes shows an isotope effect and is influenced by preadsorption of chlorine.

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R. A. VAN SANTEN
J. MOOLHUYSEN
W. M. H. SACHTLER

Koninklijke/Shell-Laboratorium
(Shell Research B.V.)
Amsterdam, The Netherlands

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