JOURNAL OF CATALYSIS 76, 333–344 (1982)

Kinetic and Adsorption Studies on Vapor-Phase Catalytic Oxidation of Olefins over Silver

MASAMICHI AKIMOTO, KAZUYOSHI ICHIKAWA, AND ETSURO ECHIGOYA[1]

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan

Received August 20, 1981; revised March 5, 1982

The mechanism of the catalytic oxidation of ethylene, propylene, butenes, and pentenes over silver has been investigated. For ethylene, the partial and complete oxidations at 230°C had nearly the same kinetic dependence on olefin and oxygen concentrations. For the complete oxidation of propylene, the reaction order in olefin was smaller than that observed with ethylene whereas the reaction order in oxygen was greater. This change in these two kinds of reaction orders in reverse direction was also observed with butenes and pentenes, and the rate of complete oxidation of olefins (butenes and pentenes) normalized to one allylic hydrogen followed the relation in terms of the type of allylic hydrogens involved, primary < secondary < tertiary, irrespective of the kind of olefin oxidized. Relative rate measurement showed that the small but not negligible normal kinetic isotope effect of hydrogen existed in the complete oxidation of propylene and 2-methyl-1-propene. It is also shown that while ethylene is adsorbed only on the $Ag^{\delta+}$ ($0 < \delta < 1$) formed at the partially oxygenated silver surface, the olefins other than ethylene can be adsorbed on both the $Ag^{\delta+}$ and the completely reduced silver surface. Pentenes inhibited ethylene oxidation over silver at 245°C; the results obtained are readily understood on the basis of the mechanism for epoxide formation involving the reaction of the adsorbed diatomic oxygen with the adsorbed ethylene, not with gas-phase ethylene. These findings are discussed in relation to previous suggestions regarding surface intermediates and the mechanism of these oxidations.

INTRODUCTION

Silver is the only good catalyst for the heterogeneous oxidation of ethylene to ethylene oxide. Even with silver, however, the epoxide yield is quite small for all olefins other than ethylene. It has been suggested that the uniqueness of silver is associated with its ability to adsorb oxygen as the superoxide (*1*). The results of the catalytic (*2*), ir (*3, 4*), and ESR (*5–7*) studies and the reaction of ethylene with silver oxides (*8*) have supported this view. It has also been shown that chlorine compounds inhibit the dissociative adsorption of oxygen over silver to increase the selectivity to ethylene oxide markedly (*4*).

Recently, the catalytic oxidation of ethylene to ethylene oxide over silver has been studied mechanistically by ir spectroscopy (*9, 10*), the stereochemistry of the epoxidation (*11–13*), and the oxidation of deuterated ethylene (*14*). Based on the observation of ir bands during the catalytic oxidation of ethylene, Force and Bell (*9, 10*) have proposed that $Ag–O–CH_2CH_2\cdot$ formed by the reaction between ethylene and an adsorbed monoatomic oxygen is an intermediate which is common to both the epoxide formation and the complete oxidation. That is, they believed that $Ag–O–CH_2CH_2\cdot$ is desorbed as ethylene oxide while $Ag–O–\dot{C}HCH_3$ formed by the intramolecular isomerization of $Ag–O–CH_2CH_2\cdot$ is the intermediate in the complete oxidation route. Force and Bell (*9, 10*) also indicated that while ethylene and oxygen are competitively adsorbed on the positively charged silver atom ($Ag^{\delta+}$), gas-phase ethylene is more selective for epoxide formation than the adsorbed ethylene. On the other hand, Cant and Hall (*14*) could have succeeded in explaining the observed kinetic isotope effects of hydrogen

---

[1] To whom correspondence should be addressed.

0021-9517/82/080333-12$02.00/0

for the formation of epoxide and CO_2 assuming the preliminary formation of an intermediate which is common to both the epoxide formation and the complete oxidation. In contrast to Force and Bell (*10*), however, Cant and Hall (*14*) indicated that the adsorbed species containing peroxide linkage is the common intermediate involved in the epoxide formation and the complete oxidation route. Cant and Hall (*14*) have also proposed for the oxidation of propylene a reaction mechanism similar to that of ethylene and attributed the very low yields of epoxide from propylene to the intramolecular isomerization of the peroxide intermediate involving the breakage of the C–H bond in the methyl group. Thus, it appears that the silver-catalyzed oxidation of olefins (ethylene and propylene) to epoxide and CO_2 takes place via the preliminary formation of an intermediate which is common to these product formations. However, it is difficult to explain the much lower selectivity of epoxidation for propylene as compared with ethylene based on the above reaction mechanism since the C–H bond in the methyl group of the intermediate involved in the oxidation of propylene seems to be stronger than that in the methylene group of the intermediate involved in the oxidation of ethylene as judged from the bond dissociation energies for hydrocarbons reported (*15*). Additionally, the reason for the negligible epoxide yield from butenes and pentenes in relation to the mechanism of the complete oxidation still remains unknown. In this work, we have mechanistically investigated the catalytic oxidation of ethylene, propylene, butenes, and pentenes over silver using kinetic measurement, adsorption study, and inhibition of ethylene oxidation by pentenes.

METHODS

Catalytic oxidation of olefins was carried out using a conventional flow fixed-bed reactor at atmospheric pressure. The reactor system comprised a 13-mm-i.d. Pyrex glass tube, 280 mm long, and a concentric thermowell. The reactor was heated with a cylindrical fluidized thermal bath. The catalyst was mixed with quartz sand (30–50 mesh) and Raschig rings (2 × 2 mm) were added above and below the catalyst bed. Both the quartz sand and Raschig rings were treated with an aqueous solution of nitric acid and were then calcined at 1100°C.

Research grade ethylene, propylene, butenes, and pentenes were used. Pentenes were fed into the reactor by bubbling air through the saturator held at 0°C. Air was purified as shown previously (*16*). The total feed rate was held constant at 400 NTPml/min; the feed composition was olefin 2.0–9.0 vol%, O_2 10–20 vol%, and N_2 71–88 vol%. Nitrogen, hydrogen, and helium were supplied by commercial cylinders. Nitrous oxide of greater than 99.8% purity was used without further purification (impurities were N_2 and H_2O). The hexadeuterated propylene of 99 atom% was purchased from Merk, Sharp and Dohme of Canada. The octadeuterated 2-methyl-1-propene was prepared by dehydration of anhydrous tertiary butyl-d_9-alcohol(99 atom%) over Neobead D-5 alumina at 325°C and was purified by the freeze-pumping method. The result of mass spectroscopic analysis indicated that 2-methyl-1-propene thus prepared was composed of 47.0 mol% C_4D_8, 41.8 mol% C_4HD_7, and 11.2 mol% $C_4H_2D_6$, the average H/D atom ratio being 0.64/7.36.

An unsupported silver catalyst (powder) was prepared by reacting silver nitrate with sodium hydroxide in an aqueous medium, followed by reducing the formed silver oxide with 35 wt% Formalin at pH 11.0 ± 0.5 (*17*). The silver catalyst was further reduced with flowing hydrogen (100 NTPml/min) at 300°C for 1 hr before initial usage. Prestabilization also consisted of the passage of a reactant mixture (C_2H_4 2.5 vol% in air) over the reduced catalyst at 300°C for 2 hr prior to the catalytic reaction. The gaseous effluent from the reactor was analyzed by gas chromatography. Porapak Q (4 mm i.d., 6.0 m) and hydrogen as the carrier gas were used at 110°C.

In an adsorption study using a gas chromatograph, helium was used as the carrier gas. A trace amount of oxygen in the helium was previously removed by passing through a molecular sieve 13X column (4 mm i.d., 1.0 m) cooled with a liquefied nitrogen bath. Silver nitrate supported on C-22 (60–80 mesh firebrick, 3.5 wt%) was prepared by the conventional impregnation method.

RESULTS

Catalytic Results in the Oxidation of Ethylene and Propylene

The effect of contact time on the catalytic oxidation of ethylene over silver at 245°C was studied in order to ascertain the appropriate reaction conditions for the proposed kinetic experiments (Fig. 1). The conversion of ethylene increased from 9.0 to 28.5% with increasing contact time of the reaction from 0.234 to 0.847 g-catalyst · hr/g-mole. However, the value of the selectivity to epoxide remained nearly constant at 45.0%, indicating the negligible degree of the consecutive oxidation of epoxide formed in these reaction conditions employed.

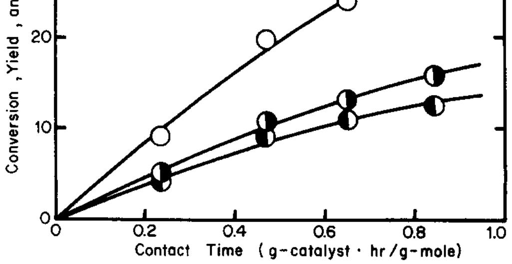


FIG. 1. Effect of contact time on the catalytic oxidation of ethylene over silver. Reaction temperature, 245°C, feed composition, C_2H_4 2.5 vol% in air; ○, conversion of ethylene; ◑, yield of CO_2; ◐, yield of ethylene oxide; ●, selectivity to ethylene oxide.

The apparent activation energies and dependences of reaction rate on olefin and oxygen concentrations determined at 230°C are summarized in Table 1. For ethylene, the partial and complete oxidations had nearly the same kinetic dependence on olefin (reaction order = 0.5) and oxygen (0.3 and 0.2) concentrations. The selectivity to epoxide was much lower for propylene (1–2%) than ethylene (near 45%). For the complete oxidation of propylene, the reaction order in oxygen (0.3) was somewhat greater than that observed with ethylene (0.2) whereas the reaction order in olefin was smaller (0.2 ↔ 0.5). This indicates that propylene is adsorbed on the catalyst surface more strongly than ethylene during the catalytic oxidation over silver. The apparent activation energies found in the present work are not unusual for conventional supported and unsupported silver catalysts.

Catalytic Results in the Oxidation of Butenes and Pentenes

In contrast to ethylene and propylene, the epoxide yield in the oxidation of butenes and pentenes at 230–245°C was quite negligible. No formation of epoxide from *trans*-2-butene found in the present work does not agree with the previously reported result (*11*) in which 25% of the *trans*-2-butene reacted was converted to epoxide at 165–170°C. This disagreement is probably caused by the difference in reaction temperature. The dependences of the rate of complete oxidation of olefins on olefin and oxygen concentrations were similarly determined at 230°C (Table 2). The number and type of allylic hydrogens involved in olefins, the rate of complete oxidation of olefins observed at olefin 2.0 vol% in air, and the rate of complete oxidation of olefins normalized to one allylic hydrogen at this feed concentration are also presented in Table 2. For butenes, the reaction orders in olefin and oxygen change in reverse direc-

TABLE 1

Kinetic Parameters for the Catalytic Oxidation of Ethylene and Propylene over Silver[a]

Olefin	Product	Reaction order in		Apparent activation energy (kcal/g-mole)	Rate of oxidation[b] × 10^4
		Olefin	O_2		
Ethylene	Epoxide	0.5	0.3	14.0	34.4
	$CO_2 + H_2O$	0.5	0.2	17.2	36.5
Propylene	$CO_2 + H_2O$	0.2	0.3	22.0	39.2 (13.1)[c]

[a] Reaction temperature, 230°C; feed composition, olefin 2.0–5.0 vol%, O_2 10–20 vol%.
[b] g-mole olefins/g-catalyst · hr at olefin 2.0 vol% in air.
[c] Rate of oxidation normalized to one allylic hydrogen.

tion. That is, the value of the reaction order in olefin follows the relation: 2-methyl-1-propene < 1-butene < *cis*-2-butene < *trans*-2-butene, whereas the value of the reaction order in oxygen follows the reverse relation: *trans*-2-butene < *cis*-2-butene ≤ 1-butene < 2-methyl-1-propene. Similar results were observed in the case of pentenes (Table 2). Thus, the adsorption of olefins on the silver surface during the catalytic oxidation in one case took place in the relation: *trans*-2-butene < *cis*-2-butene < 1-butene < 2-methyl-1-propene, and in another it took place in the relation: 2-methyl-2-butene < 2-methyl-1-butene < *cis*-2-pentene ≤ 3-methyl-1-butene < 1-pentene.

On the other hand, no special regularity in the rate of complete oxidation of olefins was seen as shown in the fifth column of Table 2. Nevertheless, based on the type of allylic hydrogens involved, the rate of complete oxidation of olefins normalized to one allylic hydrogen could roughly be divided into the following three groups, $2.5 \times 10^{-4} \sim 4.8 \times 10^{-4}$, $7.2 \times 10^{-4} \sim 13.0 \times 10^{-4}$, and 14.4×10^{-4} g-mole olefins/g-catalyst · hr, for olefins having primary, secondary, and tertiary allylic hydrogens, respectively, ir-

TABLE 2

Kinetic Results of the Catalytic Complete Oxidation of Butenes and Pentenes over Silver[a]

Olefin	Number and type of allylic hydrogens	Reaction order in		Rate of oxidation[b] × 10^4	Rate of oxidation[c] × 10^4
		Olefin	O_2		
trans-2-Butene	6p	−0.2	0.7	28.5	4.8
cis-2-Butene	6p	−0.3	0.9	22.8	3.8
1-Butene	2s	−0.5	0.9	26.0	13.0
2-Methyl-1-propene	6p	−0.6	1.1	15.0	2.5
2-Methyl-2-butene	9p	−0.3	0.7	35.0	3.9
2-Methyl-1-butene	2s[d]	−0.4	0.9	14.4	7.2
cis-2-Pentene	2s[d]	−0.5	0.9	23.9	12.0
3-Methyl-1-butene	1t	−0.5	0.9	14.4	14.4
1-Pentene	2s	−0.6	1.0	25.4	12.7

[a] Reaction temperature, 230°C; feed composition, olefin 2.0–5.0 vol%, O_2 10–20 vol%.
[b] g-mole olefins/g-catalyst · hr at olefin 2.0 vol% in air.
[c] Normalized to one allylic hydrogen.
[d] Most reactive allylic hydrogens.

respective of the kind of olefin oxidized. The rate of catalytic oxidation of olefins is decisively affected by their intrinsic reactivities. However, it is additionally modified by steric effects and surface concentrations of olefin and oxygen. The observed rate of complete oxidation of 2-methyl-1-butene is lower than that of *cis*-2-pentene by a factor of nearly two although the surface concentrations of olefin and oxygen are nearly the same in the oxidation of these olefins (see reaction orders in Table 2). Accordingly, the relatively low rate of complete oxidation of 2-methyl-1-butene compared with the other olefins having secondary allylic hydrogens is caused mostly by steric effects. This is probable with 2-methyl-1-propene. Therefore, it could be concluded that the rate of complete oxidation of olefins (butenes and pentenes) over silver normalized to one allylic hydrogen follows the relation in terms of the type of allylic hydrogens involved: primary < secondary < tertiary. This relation paralleled the reactivity of allylic hydrogens in the oxidation of olefins over bismuth molybdate catalysts (*18*), suggesting the role of allylic hydrogens in the complete oxidation of these olefins over silver. The relatively great rate of complete oxidation of propylene normalized to one allylic hydrogen (Table 1) is caused by the large concentration of oxygen on the surface as indicated by the value of the reaction order in oxygen.

Kinetic Isotope Effects in the Oxidation of Propylene and 2-Methyl-1-propene

The catalytic oxidation of both deuterated and undeuterated olefins was carried out at 220°C using a pulse reactor. The silver catalyst (80 mg), which had previously been used in the oxidation of ethylene at 245°C (Fig. 1), was mixed with 0.5 ml of quartz sand (30–50 mesh) and was placed into a 4-mm-i.d. U-shaped Pyrex glass tube. At first, the reactant mixture containing undeuterated olefin and oxygen was injected several times using a syringe until the yield of CO_2 became unchanged. The yield of CO_2 from deuterated and undeuterated olefins was then determined by injecting alternatively the respective reactant mixture into the reactor (Table 3). There were small but not negligible normal kinetic isotope effects of hydrogen, r_D/r_H = 0.84–0.90 and 0.85–0.91, for CO_2 formations from propylene and 2-methyl-1-propene, respectively. These values are not unusual as the primary kinetic isotope effect of hydrogen since the value of 1.1 as the kinetic isotope effect of hydrogen (k_H/k_D, k = rate constant) has been obtained in the oxidative dehydrogenation of *n*-butene over ferrite catalysts (*19*, *20*).

TABLE 3

Kinetic Isotope Effects of Hydrogen for the Catalytic Oxidation of Propylene and 2-Methyl-1-propene over Silver (Pulse Method)[a]

Pulse No.	Olefin	Yield of CO_2 (%)	Kinetic isotope effect(−)[b]
1	C_3H_6	9.8	0.84–0.90
2	C_3D_6	8.7	
3	C_3H_6	9.6	
4	C_3D_6	8.2	
1	C_4H_8	5.7	0.86–0.92 (0.85–0.91)[c]
2	C_4D_8	5.1	
3	C_4H_8	6.0	
4	C_4D_8	5.2	

[a] Reaction temperature, 220°C; catalyst, 80 mg; pulse, 4.0 ml (at 23°C). Oxidation of propylene: carrier gas, He 50 NTPml/min; reactant mixture, olefin 2.6 vol% in air. Oxidation of 2-methyl-1-propene: carrier gas, He 40 NTPml/min; reactant mixture, olefin 2.8 vol% in air.

[b] Yield of CO_2 for deuterated olefin relative to undeuterated olefin.

[c] Recalculated values basing on the (H/D) atom ratio of 0.64/7.36.

Adsorption of Ethylene on Silver

It has well been established (*21*, *22*) that while ethylene does not adsorb on the completely reduced silver surface, it can be adsorbed on the partially oxygenated silver surface. The role of the positively charged silver atom ($Ag^{\delta+}$) formed on the oxygenated silver surface as the proper adsorption site for ethylene has been reported (*9, 10*). Then, the effect of the oxygenation of silver on its ability to adsorb ethylene was investigated by gas chromatography. A column packed with the completely reduced silver was prepared as follows. The silver catalyst (4.0 g) mixed with 4.0 g of quartz sand (50–60 mesh) was placed into a 4-mm-i.d. U-shaped Pyrex glass tube and was reduced with flowing hydrogen (50 NTPml/min) at 300°C for 1 hr. The reduced silver catalyst was then flashed with flowing helium (30 NTP ml/min) at 300°C for 30 min. Following Ref. (*23*), the completely reduced silver catalyst was oxygenated in flowing helium by stepwise injection of nitrous oxide at 270°C. Retention time of ethylene was measured by injecting the mixture of ethylene and nitrogen into the column using a U-shaped bypass injector. The strength and heat of adsorption were evaluated by the following equations (*24*).

$$\mu = (t_2 - t_1)/t_1 \qquad (1)$$

$$\mu/T = (R/V_g)n_m B e^{Q/RT} = (R/V_g)n_m K \qquad (2)$$

where μ = relative retention time of olefin, t_1 = retention time of N_2, t_2 = retention time of olefin, T = column temperature (°K), R = gas constant, V_g = void volume in column, n_m = amount of olefin for making monolayer coverage, $B = e^{\Delta S/R}$ (ΔS = entropy change of adsorption), Q = heat of adsorption, and K = equilibrium adsorption constant.

As shown in Fig. 2, the relative retention time of ethylene over the completely reduced silver catalyst at 0°C was as small as 0.17, but it increased to 0.35 when the silver catalyst had previously been oxygenated by injecting 1.0 NTPml of nitrous oxide. This is the result expected by the previous reports (*9, 10, 21, 22*). However, the relative retention time of ethylene increased markedly with further increase in the total amount of nitrous oxide injected and the maximum relative retention time of ethylene (μ = 2.01 at 7°C) was realized when the total amount of nitrous oxide was 4.0 NTPml; then the relative retention time of ethylene decreased with further increase in the total amount of nitrous oxide and reached a negligible value ($\mu \leq 0.01$ at 0°C) when the total amount of nitrous oxide was 10.0 NTPml (Fig. 2). At this point, it appeared that the silver surface was completely oxygenated. No change in the relative retention time of ethylene with further injection of nitrous oxide supported this view. Similar behavior of the relative retention time of ethylene was obtained when air was employed as an oxidant at 180°C. In this case, the maximum relative retention time of ethylene (μ = 1.00 at 80°C) was seen when the total amount of air injected was 6.0 NTPml, and the negligible relative retention time of ethylene was realized when the total amount of air was 17.0 NTPml. The heat of adsorption of ethylene increased from 8.4 to 13.2 kcal/g-mole with an increase in the total amount of air in-

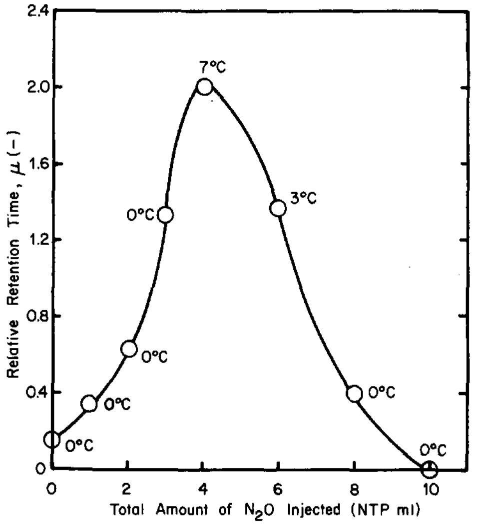


FIG. 2. Variation in the relative retention time of ethylene with increasing oxygenation of silver. Column, silver catalyst (4.0 g) previously reduced with hydrogen at 300°C for 1 hr and then flashed with helium at 300°C for 30 min. Carrier gas, He 30 NTPml/min; ethylene pulse, 0.56 NTPml (C_2H_4 10 vol%, N_2 90 vol%); oxygenation, at 270°C by N_2O. The temperatures shown in the figure are those at which the retention time of ethylene was determined.

jected from 0.8 to 4.0 NTPml. Propylene gave similar results although it could fairly be adsorbed on the completely reduced silver catalyst (μ = 1.05 at 0°C).

Adsorption of Olefins on Completely Reduced Silver Catalyst and Silver Nitrate

Adsorption of olefins on the completely reduced silver catalyst as well as on silver nitrate was investigated by gas chromatography. A column packed with the completely reduced silver catalyst was similarly prepared as described in the previous part of this paper. The silver nitrate supported on C-22 (3.5 wt%) was packed into a 4-mm-i.d. Tefron tube and was dried at 90°C with flowing helium. Relative retention time of olefins was similarly determined using the U-shaped bypass injector mentioned before. The ability of these columns was fully recovered by thermal treatment at 90°C for 10 min with flowing helium after each pulse of olefins. No observation of a difference in retention time between nitrogen and saturated hydrocarbons (ethane, propane, and butane) indicated that the adsorption of olefins is caused by the interaction of their π bond with silver atom. Results are summarized in Table 4. In contrast to ethylene, propylene, butenes, and pentenes could be adsorbed on the completely reduced silver catalyst. The relation of the value of μ/T of olefins is ethylene < propylene, and for butenes it is *trans*-2-butene < *cis*-2-butene < 1-butene < 2-methyl-1-propene. For pentenes, it is 2-methyl-2-butene < 2-methyl-1-butene < *cis*-2-pentene < 3-methyl-1-butene < 1-pentene. Although the values of V_g and n_m are not known, V_g could be constant for the same column and n_m is nearly constant for the respective olefin isomers. For ethylene and propylene, n_m is either at least equal to each other or it increases with a decrease in the size of the olefin molecule. Accordingly, all of the three relations shown above follow the increasing orders of the equilbrium adsorption constant of olefins. It is to be noted that these three relations agree with those of the strength of adsorption of these olefins on the silver surface during catalytic oxidation (Tables 1 and 2).

The olefins were also adsorbed on silver

TABLE 4

Adsorption of Olefins on Completely Reduced Silver Catalyst and Silver Nitrate[a]

Olefin	$\mu/T \times 10^3$(°K^{-1})		Olefin	$\mu/T \times 10^3$(°K^{-1})	
	Reduced silver[b]	Silver nitrate[c]		Reduced silver[d]	Silver nitrate[e]
Ethylene	0.00	1.77	2-Methyl-2-butene	0.89	0.59
Propylene	1.04	4.48	2-Methyl-1-butene	1.09	1.09
trans-2-Butene	1.46	2.45	*cis*-2-Pentene	1.18	1.39
cis-2-Butene	2.46	6.15	3-Methyl-1-butene	1.74	1.70
1-Butene	3.52	7.75	1-Pentene	1.91	1.55
2-Methyl-1-propene	4.82	6.66	—	—	—

[a] Completely reduced silver catalyst column: silver catalyst (4.0 g) previously reduced with hydrogen at 300°C for 1 hr and then flashed with helium at 300°C for 30 min. Silver nitrate column: $AgNO_3$ 3.5 wt% on C-22, 1.0 m (ethylene and propylene), 0.5 m (butenes and pentenes). Carrier gas, He 30 NTPml/min; olefin pulse, 0.56 NTPml (olefin 10 vol%, N_2 90 vol%).

[b] Completely reduced silver catalyst column, at 30°C.

[c] At 60°C.

[d] Completely reduced silver catalyst column, at 50°C.

[e] At 90°C.

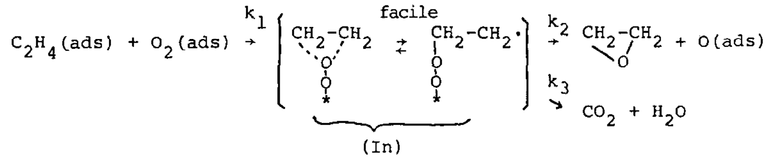
nitrate, i.e., on Ag^+ (Table 4). Ethylene was really adsorbed on it even at 60°C. However, the order of the value of μ/T of olefins, i.e., the order of the equilibrium adsorption constant of olefins, is reversed between 1-butene and 2-methyl-1-propene as well as between 1-pentene and 3-methyl-1-butene when it is compared with the results obtained on the completely reduced silver catalyst.

Inhibition of Ethylene Oxidation by Pentenes

This experiment was carried out in relation to the mechanism of ethylene oxide formation. Here, we assume the following reaction mechanism for epoxide and CO_2 formations in the oxidation of ethylene over silver.

$$C_2H_4(\text{gas}) + * \overset{K_2}{\rightleftarrows} C_2H_4(\text{ads}) \qquad (3)$$

$$O_2(\text{gas}) + * \overset{K_{O_2}}{\rightleftarrows} O_2(\text{ads}) \qquad (4)$$



(5)

Where * is an adsorption site, and K and k are equilibrium adsorption constant and rate constant, respectively. The adsorbed forms of ethylene and diatomic oxygen react together with rate constant k_1 to produce the intermediate (In), which is decomposed to ethylene oxide with rate constant k_2 or is oxidized further to CO_2 and H_2O with rate constant k_3. This mechanism is similar to the one (*14*) already discussed by Cant and Hall. However, we do propose the competitive adsorption of ethylene and oxygen on the $Ag^{\delta+}$ formed on the partially oxygenated silver surface. This point will be discussed later. Application of the steady-state treatment yields (*14*):

Concentration of In

$$= \frac{k_1[C_2H_4(\text{ads})][O_2(\text{ads})]}{k_2 + k_3}. \qquad (6)$$

Hence, the initial rate of epoxide formation in the absence of pentenes is

$$r_0 = \frac{k_1k_2}{k_2 + k_3}[C_2H_4(\text{ads})]_0[O_2(\text{ads})]_0. \qquad (7)$$

Similarly, the initial rate of epoxide formation in the presence of pentenes is

$$r = \frac{k_1k_2}{k_2 + k_3}[C_2H_4(\text{ads})][O_2(\text{ads})]. \qquad (8)$$

Thus,

$$\frac{r_0}{r} = \frac{[C_2H_4(\text{ads})]_0[O_2(\text{ads})]_0}{[C_2H_4(\text{ads})][O_2(\text{ads})]}. \qquad (9)$$

When the Langmuir type adsorption is operative,

$$[C_2H_4(\text{ads})]_0[O_2(\text{ads})]_0$$
$$= \left(\frac{N_sL}{2}\right)\frac{K_2K_{O_2}P_2P_{O_2}}{(1 + K_2P_2 + K_{O_2\kappa O_2})^2}. \qquad (10)$$

N_s and L are the number of the adsorption site ($Ag^{\delta+}$) per 1 g of the silver catalyst and the coordination number of the adsorption site, respectively. Assuming that there is no effect of the adsorption of pentenes on the equilibrium adsorption constants of ethylene and oxygen, it follows that

$$\left(\frac{r_0}{r}\right)^{1/2} = 1 + \frac{K_5P_5}{1 + K_2P_2 + K_{O_2}P_{O_2}} \qquad (11)$$

where K_5 and P_5 are the equilibrium adsorption constant of pentenes on the $Ag^{\delta+}$ and the partial pressure of pentenes in the reactant mixture, respectively. Here, the adsorption term for O(ads) is neglected for the sake of simplicity. This may be justified since a differential reactor was used. Since the concentrations of ethylene and oxygen in the reactant mixture are constant, i.e., $1 + K_2P_2 + K_{O_2}P_{O_2}$ = constant, Eq. (11) becomes:

$$\left(\frac{r_0}{r}\right)^{1/2} = 1 + K_5'P_5$$

$$K_5' = \frac{K_5}{1 + K_2P_2 + K_{O_2}P_{O_2}}. \qquad (12)$$

Therefore, a linear relationship between the value of $(r_0/r)^{1/2}$ and that of P_5 is obtained when the epoxide is produced by the reaction of the competitively adsorbed forms of ethylene and diatomic oxygen. Similarly, the following relation is obtainable when the epoxide is produced by the reaction of gas-phase ethylene with the adsorbed diatomic oxygen although ethylene and oxygen compete the adsorption site.

$$\frac{r_0}{r} = 1 + K_5'P_5. \qquad (13)$$

Figure 3 shows the linear relationships obtained basing on Eq. (12). In contrast, such good linear relationships as shown in Fig. 3 were hardly obtained when the results of inhibition experiments were plotted according to Eq. (13). The results of Fig. 3 indicate that the inhibition effect of pentenes follows the relation: 2-methyl-2-butene < 2-methyl-1-butene < *cis*-2-pentene < 1-pentene < 3-methyl-1-butene. Obviously, this order does not agree with that of the reactivity of pentenes summarized in the fifth column of Table 2. On the other hand, the relation of the apparent equilibrium adsorption constant of pentenes (K_5') at 245°C, which was calculated by the slope of the respective line in Fig. 3, is 2-methyl-2-butene ($K_5'(\mathrm{Torr}^{-1})$ = 0.54) < 2-methyl-1-butene (0.76) < *cis*-2-pentene (0.84) < 1-pentene (0.94) < 3-methyl-1-butene (1.00). This relation agrees with that of the value of μ/T of pentenes obtained in the adsorption on silver nitrate (Table 4).

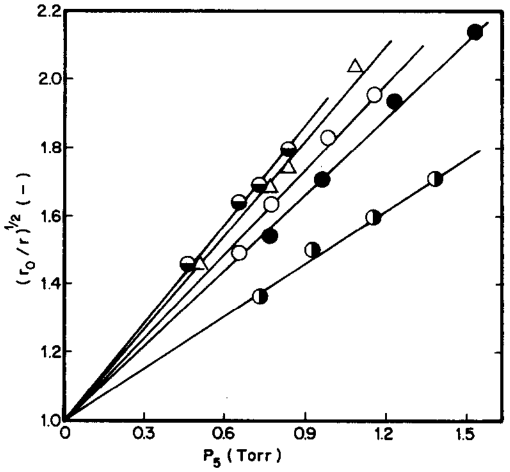


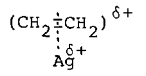
FIG. 3. Inhibition of ethylene oxidation over silver by pentenes. Reaction temperature, 245°C; feed composition, C_2H_4 8.5 vol% in air; contact time, 0.477 g-catalyst · hr/g-mole; ◑, 2-methyl-2-butene; ●, 2-methyl-1-butene; ○, *cis*-2-pentene; △, 1-pentene; ◓, 3-methyl-1-butene.

DISCUSSION

Mechanism of Ethylene Oxidation

The negligible adsorption of ethylene on the completely reduced silver catalyst and the remarkable increase in the relative retention time of ethylene caused by the oxygenation of silver surface (Fig. 2) are evidence supporting the role of the positively charged silver atom ($Ag^{\delta+}$) as the proper adsorption site for ethylene, as already reported (*9, 10, 22*). In contrast, the observed decrease in the relative retention time of ethylene with increasing oxygenation of the silver surface (Fig. 2) indicates that oxygen can be adsorbed on the $Ag^{\delta+}$. That is, in accordance with the previous suggestion (*10*), the competitive adsorption of ethylene and oxygen on the silver atom takes place during the oxidation of ethylene over silver although oxygen can also be adsorbed on the completely reduced silver surface. The formation of epoxide by the reaction of the competitively adsorbed forms of ethylene and diatomic oxygen via formation of an intermediate which is common to both the epoxide formation and the complete oxidation is supported by the results of inhibition experiments, i.e., by the observation of the linear relationship basing on Eq. (12), not on Eq. (13) (Fig. 3). The finding that the partial and complete oxidations of ethylene had nearly the same kinetic dependences on olefin and oxygen concentrations (Table 1) further supports this view. On the other hand, the apparent equilibrium adsorption constant of pentenes (K_5') paralleled the value of μ/T of pentenes on silver nitrate (Fig. 3 and Table 4). This indicates that the silver catalyst is partially oxygenated during the oxidation of ethylene and that the $Ag^{\delta+}$ formed on the surface plays the role of the adsorption site for ethylene and oxygen. Gerei *et al.* (*3*), Kilty *et al.* (*4*), and Force and Bell (*10*) have emphasized the reaction of gas-phase ethylene with the adsorbed oxygens for epoxide formation. Based on the above finding made in the present work, however, it appears that ethylene oxide is produced by the reaction of the competitively adsorbed forms of ethylene and diatomic oxygen as shown by a series of reaction steps, (3), (4), and (5).

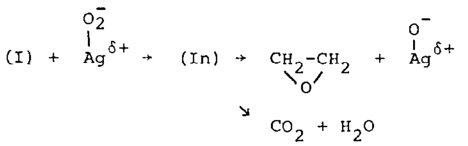
It has been reported (*9, 10*) that the ethylene molecule adsorbed on the silver surface during the catalytic oxidation acquires a positive charge as shown below.



$$\underset{Ag^{\delta+}}{(CH_2 \overset{\cdot}{\vdots} CH_2)^{\delta+}}$$

(I)

On the other hand, based on the formation of O_2^- on oxygen adsorption on the reduced silver surface (*5, 6*), the fairly high thermal stability of the adsorbed O_2^- (*5*), and the ESR studies on the reaction of AgO with ethylene (*7*), the role of the adsorbed O_2^- in ethylene oxide formation has been emphasized (*3, 4, 7, 8*). Therefore, we would like to propose the following mechanism of the oxidation of ethylene in which the positively charged adsorbed ethylene reacts with the negatively charged adsorbed diatomic oxygen O_2^- to produce ethylene oxide or CO_2 and H_2O.



(14)

The reaction of the adsorbed O_2^- with gas-phase ethylene is less attractive since the adsorbed O_2^- could be at least nucleophillic rather than electrophillic as suggested by the strong nucleophillic nature of the homogeneously produced O_2^- reported (*25*). It has been found (*26*) that the addition of the adsorbed O_2^- to the positively charged adsorbed furan took place during the oxidation of furan to maleic anhydride over a phosphorous-promoted titania catalyst. This finding supports the mechanism of the oxidation of ethylene shown by (14). Force and Bell (*10*) believed that Ag–O–$CH_2CH_2\cdot$ is desorbed as ethylene oxide while Ag–O–$\dot{C}HCH_3$ is the intermediate in the complete oxidation route. These two surface species are probably produced via the passway through the peroxide intermediate (In). The oxygen atoms freed from the peroxide intermediate on epoxide formation must be consumed in the complete oxidation process, as pointed out by Sachtler (*27*).

Mechanism for Oxidation of Propylene, Butenes, and Pentenes

The observed behavior of the reaction orders in olefin and oxygen for the complete oxidation of olefins (butenes and pentenes) (Table 2) has a bearing on the mechanism of the surface reaction. That is, the observed change in these two kinds of reaction orders in reverse direction (Table 2) is evidence supporting the reaction which takes place between the competitively adsorbed forms of olefin and oxygen over silver. The observation of the parallelism between the reactivity of allylic hydrogens and the rate of complete oxidation of olefins (butenes and pentenes) normalized to one allylic hydrogen (Table 2) indicates that the reaction is initiated by the abstraction of allylic hydrogen by the adsorbed oxygen and that this initiation step is rate-controlling. The normal kinetic isotope effect of hydrogen obtained in the oxidation of 2-methyl-1-propene (Table 3) supports this reaction mechanism although the value of the kinetic isotope effect of hydrogen obtained is relatively small. On the other hand, the relations of the equilibrium adsorption constant of olefins (butenes and pentenes) at 230°C, which was evaluated by the value of the reaction order in olefin, agreed with those of the μ/T of these olefins on the completely reduced silver catalyst (Tables 2 and 4). This implies that the silver catalyst is nearly completely reduced during the oxidation of butenes and pentenes: the adsorbed olefin molecules probably acquire no positive charge. This is in contrast to the oxidation of ethylene.

Cant and Hall (*14*) proposed a reaction mechanism similar to that of ethylene for the catalytic oxidation of propylene over silver, and they considered the intramolecular isomerization of a peroxide intermediate to allylhydroperoxide involving the breakage of the C–H bond in the methyl group to be a preliminary step for the complete oxidation of propylene. However, the observed much lower selectivity to epoxide for propylene than for ethylene (Table 1) is not understandable based on the reaction mechanism as already discussed (see Introduction). Accordingly, there must be another route for the complete oxidation of propylene over silver. We believe that this route plays a significant role in the complete oxidation of propylene and that this complete oxidation route is initiated by the abstraction of allylic hydrogen in the adsorbed propylene by the adsorbed oxygen as in the case of butenes and pentenes. The observed change in reaction orders in olefin and oxygen in reverse direction (Table 1), the normal kinetic isotope effect of hydrogen obtained in the catalytic oxidation of propylene to CO_2 and H_2O (Table 3), and the formation of the intermediate adsorbed acrolein during the catalytic oxidation of propylene to CO_2 and H_2O over silver (*28*) support this view.

Selectivity for Epoxide Formation

The above discussion revealed that the catalytic oxidation of olefins over silver at 230°C is different in mechanism between ethylene and the other olefins (butenes and pentenes). It appears that both the differences in the structure of the olefin molecules and in the nature of the adsorbed olefin molecules decisively affect the reaction taking place between the adsorbed forms of olefin and oxygen. That is, ethylene has no allylic hydrogen to be abstracted whereas the other olefins have it. Additionally, as discussed previously, the adsorbed ethylene molecule during the catalytic oxidation acquires a positive charge whereas the adsorbed butene and pentene molecules probably acquire no positive charge. Therefore, it is evident that the addition of the adsorbed O_2^- to the adsorbed olefin molecules (butenes and pentenes) hardly takes place. On the other hand, the dehydrogenation of 9,10-dihydroanthracene to anthracene by the homogeneously produced O_2^- has been reported (*29*, *30*). Hence, it is not unreasonable to consider that the adsorbed O_2^- abstracts the allylic hydrogens during the catalytic oxidation of butenes and pentenes over silver. The observed values (0.7–1.1) of reaction order in oxygen (Table 2) suggest that an adsorbed diatomic oxygen reacts with the adsorbed olefins (butenes and pentenes).

On the other hand, the production of propylene oxide with a selectivity of 1–2% (see results) indicates that a small amount of the positively charged propylene molecule adsorbed on the $Ag^{\delta+}$ in addition to the propylene molecules adsorbed on the reduced silver surface is formed during the catalytic oxidation. The first of the above two kinds of adsorbed propylene molecules leads to a peroxide intermediate while the second to CO_2 and H_2O by the abstraction of the hydrogen in the methyl group. It seems that the silver catalyst during the oxidation of propylene is not as completely reduced as in the case of butenes and pentenes and is not as intensively oxygenated as in the case of ethylene.

In conclusion, we feel that while the model presented herein is somewhat speculative, it explains rather well our findings in respect to the reaction orders and the reactivity of butenes and pentenes in the catalytic oxidation and has the virtue of offering a reasonable explanation for the much lower selectivity of epoxidation for propylene, butenes, and pentenes as compared with ethylene when using silver catalysts.

REFERENCES

1. Voge, H. H., and Adams, C. R., *Advan. Catal.* **17,** 151 (1967).
2. Herzog, W., *Ber. Bunsenges. Phys. Chem.* **74,** 216 (1970).
3. Gerei, S. V., Kholyavenko, K. M., and Rubanik, M. Ya., *Ukrain. Khim. Zhur.* **31,** 449 (1965).
4. Kilty, P. A., Rol, N. C., and Sachtler, W. M. H., "Proc. Vth Intern. Congr. Catal., Miami Beach, Fla.," Paper 64, p. 929. American Elsevier, New York, 1972.
5. Clarkson, R. B., and Cirillo, A. C., *J. Vac. Sci. Technol.* **9,** 1073 (1972); *J. Catal.* **33,** 392 (1974).
6. Shimizu, N., Shimokoshi, K., and Yasumori, Y., *Bull. Chem. Soc. Japan* **46,** 2929 (1973).
7. Tanaka, S., and Yamashina, T., *J. Catal.* **40,** 140 (1975).
8. Kagawa, S., Kōno, K., Nida, H., and Seiyama, T., *Kōgyō Kagaku Zasshi* **74,** 819 (1971).
9. Force, E. L., and Bell, A. T., *J. Catal.* **38,** 440 (1975).
10. Force, E. L., and Bell, A. T., *J. Catal.* **40,** 356 (1975).
11. Richey, W. F., *J. Phys. Chem.* **76,** 213 (1972).
12. Larrabee, A. L., and Kuczkowski, R. L., *J. Catal.* **52,** 72 (1978).
13. Egashira, M., Kuczkowski, R. L., and Cant, N. W., *J. Catal.* **65,** 297 (1980).
14. Cant, N. W., and Hall, W. K., *J. Catal.* **52,** 81 (1978).
15. Noller, C. R., "Chemistry of Organic Compounds," 3rd Ed., p. 993. Saunders, Philadelphia, 1965.
16. Akimoto, M., and Echigoya, E., *J. Catal.* **29,** 191 (1973).
17. Gotō, T., Shimatake, S., Hara, I., and Aono, Y., Japan Patent No. 9259 (1963).
18. Adams, C. R., "Proc. 3rd Intern. Congr. Catal., Amsterdam, Netherland," Vol. 1, p. 240. North-Holland, Amsterdam, 1965.
19. Cares, W. R., and Hightower, J. W., *J. Catal.* **23,** 193 (1971).
20. Gibson, M. A., and Hightower, J. W., *J. Catal.* **41,** 420 (1976).
21. Trapnell, B. M. W., *Proc R. Soc. A* **218,** 566 (1953).
22. Marcinkowsky, A. E., and Berty, J. M., *J. Catal.* **29,** 494 (1973).
23. Scholten, J. J. F., Konvalinka, J. A., and Beekman, F. W., *J. Catal.* **28,** 209 (1973).
24. Hara, N., "Jikken Kagaku Kōza," Vol. 9, Gas Chromatography, p. 520. Maruzen Press, Tokyo, 1965.
25. LeBerre, A., and Berguer, Y., *Bull. Soc. Chim. France* 2368 (1966); Dietz, R., Forno, A. E. J., Larcombe, B. E., and Peover, M. E., *J. Chem. Soc.* (*B*) 816 (1970).
26. Akimoto, M., and Echigoya, E., *J. Chem. Soc. Faraday Trans. I* **73,** 193 (1977).
27. Sachtler, W. M. H., *Catal. Rev.* **4,** 27 (1970).
28. Freriks, Ivo L. C., Bouwman, R., and Geenen, P. V., *J. Catal.* **65,** 311 (1980).
29. Tezuka, M., Ohkatsu, Y., and Osa, T., *Bull. Chem. Soc. Japan* **48,** 1471 (1975).
30. Moro-oka, Y., Chung, P. J., Arakawa, H., and Ikawa, T., *Chem. Lett.* (*Tokyo*) **1976,** 1293.