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The Catalytic Oxidation of Propylene

I. Evidence for Surface Initiated Homogeneous Reactions

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The catalytic oxidation of propylene over bismuth molybdate was studied in a flow reactor at atmospheric pressure and at 425°C. Several reactor designs were utilized in an effort to define more clearly the nature and the importance of homogeneous reactions which may be occurring in the postcatalytic volume. Evidence is presented for a surface initiated homogeneous reaction which results in an enhanced conversion of propylene and the formation of propylene oxide. Allyl peroxide or allyl hydroperoxide species, formed on the surface, are suggested as possible initiators for this homogeneous reaction. A modified reaction mechanism is proposed which incorporates the surface initiated homogeneous reaction, as well as a surface reaction of the allyl peroxide or allyl hydroperoxide species. Four additional oxide catalysts, copper–molybdenum, iron–molybdenum, manganese–molybdenum, and zinc, are offered as other examples on which the surface initiated homogeneous reaction occurs.

INTRODUCTION

A number of results have now appeared in the literature concerning the oxidative dehydrogenation of olefins. Many of these results have been extensively discussed in reviews by Margolis (*1*), Sampson and Shooter (*2*), Voge and Adams (*3*), and Sachtler (*4*). The one conclusion which has been firmly established by these studies is that the rate determining step in the oxidative dehydrogenation reaction involves the abstraction of an allylic hydrogen atom.

Even though it is generally accepted that allylic intermediates are important, there is still not a clear explanation of the subsequent reaction sequence of this intermediate. The work of Adams and Jennings (*5*, *6*) strongly suggests that, for the oxidation of propylene over bismuth molybdate and Cu_2O catalysts, a second hydrogen atom is abstracted from the allylic intermediate before the incorporation of oxygen. However, more recent results by Cant and Hall (*7*, *8*), utilizing metal catalysts, suggest that another mechanism in which oxygen is added before the abstraction of a second hydrogen atom may also be operative. A similar mechanism was also proproposed earlier by Margolis (*1*). Thus, depending on the catalyst, several mechanistic schemes may be in operation. The product distribution, therefore, is a function of the importance of one scheme compared to that of others.

In addition to the possibility of several mechanistic schemes operating simultaneously, it is becoming increasingly evident that homogeneous gas phase reactions may further complicate the reaction. Moreover, the product distribution will also reflect the importance of these homogeneous reactions. McCain and Godin (*9*) observed that propylene oxide was formed via a homogeneous pathway in the postcatalytic volume during the catalytic oxidation of

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propylene. A number of Russian workers [see for example (*10*)] have suggested heterogeneous–homogeneous mechanisms for the catalytic oxidation of hydrocarbons over various oxides and metals. In an earlier publication (*11*), we reported that, during the partial oxidation of propylene to acrolein over bismuth molybdate, acrolein subsequently underwent a number of homogeneous reactions in the postcatalytic volume. These reactions were dependent upon the oxygen partial pressure and the postcatalytic volume. In addition, it appeared that the majority of the side products observed in the reaction could be explained by this further reaction of acrolein. In an effort to determine species, which desorb from catalyst surface and initiate homogeneous reactions, Friedli *et al.* (*12*) studied the oxidative dehydrodimerization of propylene and isobutylene. This reaction is similar to the oxidative dehydrogenation of olefins. Consequently, the slow step is believed to be the abstraction of an allylic hydrogen to form an allylic intermediate. They detected allyl radicals in the gas phase when propylene or propylene and oxygen mixtures were reacted with manganese oxide at pressures of 10^{-6}–10^{-7} Torr. Their data did not allow them to predict if allyl radical desorption still occurred at higher pressures. However, Margolis (*13*) has suggested such a pathway for propylene oxidation over oxide catalysts.

Because of the uncertainty surrounding the fate of allyl intermediates, the present investigation aimed for further insight into the oxidation of propylene over various oxide catalysts. Our primary goals were to determine the importance and nature of reactions occurring in the postcatalytic volume and to develop a detailed mechanistic model for the subsequent reactions of the allyl intermediate.

Experimental Methods

Catalysts. The bismuth molybdate (Bi:Mo = 1) catalyst used in the experiments was prepared by coprecipitation from solutions of bismuth nitrate and ammonium molybdate, according to the procedure of Adams and Jennings (*5*). Various other metal oxides were prepared by a thermal decomposition of their respective nitrates, while mixed oxides were prepared by a procedure similar to that used for bismuth molybdate.

Reactor. All oxidation data were obtained using a single-pass, flow reactor, which has been described previously (*11*). The analytical methods, the pretreatment procedures, and the purification of the gases were also the same. However, several different reactor tubes were utilized for the study of the reactions occurring in the postcatalytic volume. Reactor I was constructed of 10 mm Pyrex tubing up to and including the catalyst area. Immediately after the catalyst bed, Reactor I contained 2 mm capillary tubing. In its normal position, the 10 mm tubing was the precatalytic volume and was packed with Pyrex beads. In its inverted position, the 10 mm tubing became the postcatalytic volume (17 ml when empty). Its free volume could be easily varied by packing it with selected amounts of Pyrex wool. This inversion technique was employed whenever it was felt desirable to study the effect of the postcatalytic volume without disturbing the catalyst packing. Reactor II was constructed of 10 mm tubing up to and including the catalyst section and then completed with a section of 20 mm Pyrex tubing. The 10 mm section was packed with Pyrex beads, and the volume of the postcatalytic section could again be varied by packing it with selected amounts of Pyrex wool. When the postcatalytic section was completely empty, it had a volume of 50 ml.

Results

To determine the extent of the purely homogeneous reaction between propylene and O_2 at 425°C and under identical conditions of contact time and C_3H_6:O_2:He ratio as those used in the catalytic experiments, several experiments were conducted with the various reactor tubes without a catalyst. These results are summarized in Table 1. As shown, no reaction was detected in either Reactor I, in either its normal or inverted position, or Reactor II

TABLE 1

PRODUCT DISTRIBUTION OF THE HOMOGENEOUS REACTION BETWEEN PROPYLENE AND OXYGEN

Catalyst, none; temp, 425°C; flow (C_3H_6:O_2:He), 4:3:1; total flow 160 ml (STP) min^{-1}.

Products[a]	Reactor:		
	I[b]	II	II[c]
CO	—	4.72	—
CO_2	Trace	1.11	Trace
C_2H_4	—	0.40	—
Acetaldehyde	—	0.60	—
Acrolein	—	—	—
CH_4	—	0.41	—
Formaldehyde	—	0.41	—
Propylene oxide	—	0.51	—
Propionaldehyde	—	Trace	—
Conversion (%)	—	25	—

[a] Product distribution in terms of the rate of formation (μmoles/min).

[b] Both the normal and inverted positions were used (see Experimental Methods Section).

[c] The postcatalytic volume was packed completely with Pyrex wool.

TABLE 2

PRODUCT DISTRIBUTION OF THE HETEROGENEOUS REACTION BETWEEN PROPYLENE AND OXYGEN[a]

Catalyst, bismuth molybdate, 0.5 ml volume; flow ratio (C_3H_6:O_2:He), 4:3:1; contact time, 0.07 sec.

Product[b]	Temp (°C)			
	400	425	450	460
CO	0.87	0.71	0.90	1.16
CO_2	0.51	0.50	0.52	0.60
C_2H_4	0.02	0.03	0.07	0.10
Acetaldehyde	0.08	0.09	0.13	0.141
Acrolein	0.67	0.73	1.10	1.19
Conversion (%)	14	16	27	32

[a] Reactor I having the postcatalytic volume packed with Pyrex wool was used in all of these experiments.

[b] The product distribution is reported in terms of the rate of formation of the respective products (μmoles/min).

when its postcatalytic volume was packed completely with Pyrex wool. However, when the Pyrex wool was removed from Reactor II, the propylene conversion was observed to be 25%, with Co, Co_2, and H_2O (water is not reported because of inconsistent analytical results), being the major products. The remaining products were acetaldehyde, acrolein, methane, formaldehyde, and propylene oxide. At somewhat higher propylene to oxygen ratios, or at longer contact times, complete conversion of propylene, frequently with explosive force, was observed.

In order to define more exactly the product distribution resulting from solely the heterogeneous reaction, Reactor I was utilized. Furthermore, to minimize the void space between the catalyst particles, we used only 0.5 ml of approximately 100 mesh, unsupported bismuth molybdate powder. Table 2 lists the product distributions obtained when the reaction was studied at various temperatures while maintaining a constant contact time. As expected, the major products observed were acrolein, CO, CO_2 and H_2O. We feel that by packing the postcatalytic volume with Pyrex wool and by minimizing the void fraction in the catalyst bed, the homogeneous reactions have been minimized. In addition, we feel that the amonts of CO, CO_2, ethylene, and acetaldehyde still present under these conditions indicate a parallel pathway directly from propylene for their formation. Unfortunately, our present data does not clearly establish this mechanism. We plan to explore this possibility more thoroughly in future experiments.

After studying the product distributions resulting from both the homogeneous and the heterogeneous reactions of propylene and oxygen, we utilized Reactor I to gain further information regarding the nature and the importance of heterogeneous–homogeneous reactions occurring simultaneously. The results listed in columns 1 and 3 of Table 3 illustrate that the product distribution obtained both with, and without, packing the capillary postcatalytic volume, are essentially the same. The only notable difference is in the increased yield of acrolein when the postcatalytic volume is packed. As indicated above, this is due to the minimizing of the homogeneous, secondary reactions of acrolein. However, when Reactor I was in-

TABLE 3

Product Distribution as a Function of Postcatalytic Volume

Catalyst, bismuth molybdate, 0.5 ml volume; temp, 450°C; flow (C_3H_6:O_2:He), 4:3:1; total flow, 160 ml (STP) min^{-1}.

	Reactor I		
Products[a]	Normal[b]	Inverted[c]	Packed[d]
CO	0.71	3.10	0.52
CO_2	0.50	3.21	0.49
C_2H_4	0.03	0.21	0.03
Acetaldehyde	0.09	0.31	0.06
Acrolein	0.73	0.49	0.94
CH_4	—	1.33	—
Propylene oxide	—	0.13	—
Propionaldehyde	—	Trace	—
Formaldehyde	—	0.11	—
Conversion (%)	16	41	15

[a] Product distribution in terms of the rate of formation (μmoles/min).

[b] This position refers to the catalyst tube in the position in which the 2 mm capillary is the postcatalytic volume.

[c] This position places the 10 mm tubing in the postcatalytic position.

[d] This position has the 10 mm tubing, which is the postcatalytic volume, packed completely with Pyrex wool.

verted, making the empty 10 mm tubing the postcatalytic volume (contact time in the postcatalytic volume = 2.3 sec), the propylene conversion increased from 16 to 41% (column 2, Table 3). Because the amount of catalyst, the flow, and the temperature were identical to the runs listed in columns 1 and 3 of Table 3, it can only be concluded that propylene too, like acrolein (*11*) and acetaldehyde (*9*), can undergo homogeneous, gas phase reactions in the postcatalytic volume. Furthermore, it appears that this homogeneous reaction is initiated by some intermediate, which is formed by the catalytic surface, and then desorbs into the gas phase because no homogeneous reaction was detected under similar conditions without a catalyst (see Table 1).

DISCUSSION

Nature of the chain initiating species. Because of the enhanced conversion of propylene in the presence of bismuth molybdate under conditions that do not cause a homogeneous reaction in the absence of bismuth molybdate, we suggest that the product distribution observed with Reactor I in its inverted position represents a surface initiated homogeneous reaction. The large amount of methane observed in the products lends support to a radical reaction in the gas phase (*14*). We also feel that the propylene oxide formed under conditions which favor homogeneous reactions is a result of the gas phase reaction between propylene and the intermediate, generated on the surface, that initiates this reaction.

The exact nature of the chain initiating species is less tractable because of the high reaction temperatures. Common radical trapping experiments which are effectively utilized at lower temperatures are likely to fail because of the thermal instability of the trapped species. Experiments designed to rapidly quench the gas phase reactions are a possibility, but such experiments could not be conveniently performed with our present apparatus. As an alternative approach, we examined the reactivity of the various products formed in the reaction in an effort to gain additional information regarding the nature of the chain initiating species. As indicated earlier, acrolein and acetaldehyde are frequently observed to undergo homogeneous reactions. When we added either acetaldehyde or acrolein to the propylene and oxygen feed stream, utilizing bismuth molybdate and Reactor I in its inverted position, they were observed to be converted primarily into CO, CO_2, and H_2O. The propylene conversion, however, remained constant; and, in a few experiments, actually decreased slightly. The same results were obtained with propylene oxide.

Another possibility is that the allyl intermediate can desorb into the gas phase as allene. To test this hypothesis, we passed allene and oxygen mixtures through Reactor I in its inverted position both in the presence and absence of bismuth molybdate. At 425°C and in the absence of a catalyst, some 5–7% conversion was observed. The only products observed were CO, CO_2, and H_2O. At 425°C and in the presence of bismuth molybdate, the conversion increased to 10–12%. The major products were still CO, CO_2, and H_2O, but traces of acetaldehyde and ethylene were also detected. When allene was added to a propylene and oxygen mixture, no further enhancement of the conversion of propylene was observed at 425°C with bismuth molybdate and utilizing Reactor I in its inverted position.

From the above results, it appears that the products observed under conditions favoring the surface initiated homogeneous reactions can be eliminated as possible initiators for the chain reaction. It therefore seems reasonable to assume that the initiation step involves the allyl intermediate. A free allyl radical, as suggested by Friedli *et al.* (*12*) and Margolis (*13*), is a possibility. The allyl radical could react further in the gas phase to form an allyl peroxide radical or allyl hydroperoxide. Alternatively, and possibly more likely, the allyl intermediate could react with oxygen on the surface to form a surface allyl peroxide or allyl hydroperoxide species. Subsequent desorption into the gas phase of these species would result in the same intermediates as an allyl radical reacting with O_2 in the gas phase. Distinguishing between these two alternatives is not possible at the present time.

We suggest that gas phase allyl peroxide or allyl hydroperoxide species, or possibly degradation fragments such as $HO_2\cdot$, are the chain initiators for the homogeneous reaction. Propylene oxide is produced as one of the reaction products by direct attack at the π-bond of propylene. In addition, these initiators are produced via a surface reaction involving the allyl intermediate formed from propylene.

Modified mechanism for propylene oxidation. At this point, it is worth reviewing the generally accepted mechanism for propylene oxidation and incorporating additional details into the mechanism which the above hypotheses imply. As postulated by Adams and Jennings (*5*, *6*), the major pathway for propylene oxidation on oxide catalysts has as a rate determining step the formation of an allyl intermediate by the abstraction of an allyl hydrogen atom. Subsequently, the allyl intermediate loses a second hydrogen atom and incorporates oxygen, apparently from the oxide lattice (*15–18*), to form the partially oxygenated compounds before it desorbs. Because the oxygen which becomes incorporated into the products comes from the catalyst, the kinetics are typically first order in propylene pressure and zero order in oxygen pressure.

However, with these same catalysts, surface initiated homogeneous reactions may become important at high propylene to oxygen ratios and in a reactor having a large postcatalytic volume or with a catalyst packing having a large void fraction. This pathway probably involves the desorption of the allyl intermediate as an allyl radical; or, alternatively, the allyl intermediate adds oxygen before losing a second hydrogen atom to form an allyl peroxide or an allyl hydroperoxide intermediate. If this intermediate desorbs into the gas phase, it can react further by a radical mechanism with propylene to produce propylene oxide as one of the reaction products.

This conclusion is in agreement with the recent results of Wragg *et al.* (*16*). They detected an "impurity" of mass 58 during the oxidation of propylene in the absence of oxygen-18. As possibilities, they suggested propylene oxide and acetone which could be formed in the gas phase or on the surface. We did not detect any acetone by our gas chromatographic analysis when the reaction was run under conditions which favor the surface initiated homogeneous reaction. Consequently, we feel that the mass 58 impurity detected by Wragg *et al.* (*16*) is propylene oxide and probably is formed in the gas phase by the surface initiated reaction.

We also suggest that if the allyl intermediate forms a peroxide or hydroperoxide species on the surface, this intermediate may undergo a further surface reaction, as suggested by Cant and Hall (*7*, *8*) and Margolis (*1*). The products of this reaction are the same as those predicted by the mechanism of Adams and Jennings (*5*, *6*).

For catalysts which typically exhibit first order in oxygen pressure and zero order in propylene pressure kinetics, we suggest that the major pathway is the one in which the allyl intermediate prefers to add oxygen before the loss of a second hydrogen atom. Thus, the oxygen does not come from a lattice position, but instead from a chemisorbed layer or directly from the gas phase. Consequently, a kinetic dependence on oxygen pressure is observed. A notable catalyst in this category is Au. The allyl intermediate therefore forms the peroxide or hydroperoxide intermediate, which can decompose on the surface to produce acrolein. In addition, we suggest that this intermediate may desorb into the gas phase to react further with propylene to produce propylene oxide.

To test these ideas further, we have examined four additional catalysts under conditions in which the surface initiated homogeneous reaction pathway should be observed. The results are summarized in Table 4. We felt that the Cu–Mo, Fe–Mo, and Mn–Mo oxide catalysts should be similar to bismuth molybdate, and, thus, form allyl intermediates initially. In each case, propylene oxide, which we feel is indicative of the surface initiated homogeneous pathway, was observed. The fourth catalyst was ZnO. It has been well established by Dent and Kokes (*19*, *20*) that reactive allyl intermediates are formed on ZnO. As indicated in Table 4, this catalyst, too, is capable of producing propylene oxide. In contrast to the other three catalysts, though, which produce acrolein, apparently by the same mechanism as bismuth molybdate, no acrolein was observed. However, it is important to note the in-

TABLE 4

PRODUCT DISTRIBUTION OVER VARIOUS CATALYSTS

Temp, 425°C; flow (C_3H_6:O_2:He), 4:3:1; total flow, 160 ml (STP) min^{-1}.

	Catalysts[a]			
Products[b]	Cu–Mo	Fe–Mo	ZnO	Mn–Mo
CO	3.71	3.04	1.94	2.09
CO_2	0.28	0.99	3.96	2.30
C_2H_4	0.05	0.34	0.24	0.01
Acetaldehyde	0.25	0.39	0.27	0.02
Acrolein	0.04	0.28	0	0.07
CH_4	Trace	Trace	0	Trace
Propylene oxide	0.09	0.20	0.13	0.07
Propionaldehyde	Trace	0	0	0
Formaldehyde	Trace	0.06	0.11	Trace
Conversion (%)	15	19	31	19

[a] See Experimental Methods Section for preparation; ZnO was supported on SiO_2. Catalyst volume, −2 ml in all cases except for ZnO (3 ml).

[b] Reported as rate of formation (μmoles/min).

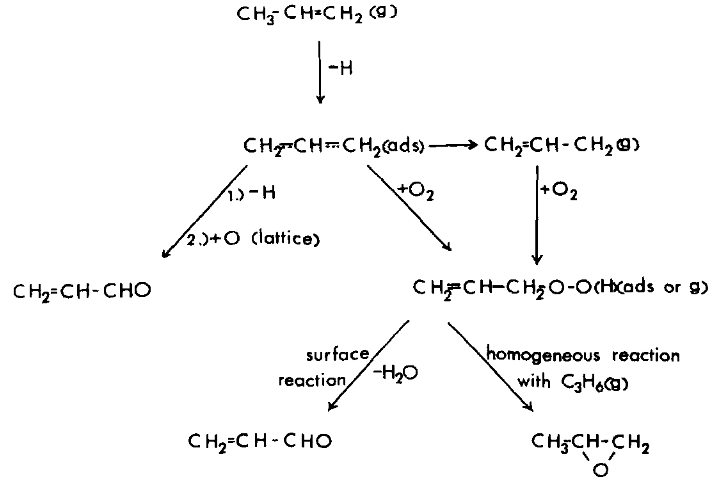

FIG. 1. Reaction mechanism.

creased yield of CO_2 with ZnO. This may indicate that the surface intermediate leading to acrolein is so strongly held that it favors complete combustion rather than desorption as acrolein (*21*).

In conclusion, we feel that our results, along with those published by others, produce a mechanistic model which can explain the oxidation of propylene over metal and metal oxide catalysts. It is also evident that a surface initiated homogeneous reaction pathway leading to propylene oxide is possible at high propylene to oxygen ratios and with reactors having a large postcatalytic volume. Moreover, this reaction is independent of the commonly accepted pathway leading to acrolein and may occur simultaneously. This mechanistic model is schematically illustrated in Fig. 1.

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