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The Catalytic Oxidation of Propylene

III. Additional Evidence for Surface-Initiated, Homogeneous Reactions

CHELLIAH DANIEL,* JOHN R. MONNIER,† AND GEORGE W. KEULKS‡

Department of Chemistry, Laboratory for Surface Studies, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

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The catalytic oxidation of propylene was studied in flow reactors having different postcatalytic volumes. Several different metal oxide catalysts were studied, including bismuth molybdate and cuprous oxide. Additional evidence is presented for a surface-initiated, homogeneous reaction that can occur in the postcatalytic volume. The reaction initiator is apparently an allyl peroxide or allyl hydroperoxide species which is formed on the surface by a mechanism involving the reaction of an adsorbed allyl species with molecular oxygen. Moreover, the results suggest that this allyl peroxide or allyl hydroperoxide species may also undergo a decomposition on the surface to produce acrolein in addition to the initiation of the homogeneous reaction.

INTRODUCTION

In an earlier report, Daniel and Keulks (*1*) presented results which indicated that surface-initiated, homogeneous reactions can occur in the postcatalytic volume when catalysts which are also active for the heterogeneous oxidation of propylene to acrolein are used. Furthermore, the homogeneous reaction did not take place when the reactor with a large postcatalytic zone contained no catalyst, nor did the homogeneous reaction occur when the same catalyst under identical conditions was placed into a reactor with a small postcatalytic volume. The reaction occurring in the postcatalytic volume resulted in the increased conversion of propylene and the formation of propylene oxide and formaldehyde as well as a greatly increased amount of acetaldehyde. This was in agreement with McCain and Godin (*2*), who observed similar reactions under similar conditions.

They also conducted several experiments in an attempt to identify the nature of the homogeneous reaction initiator. The possibility of acrolein and acetaldehyde, which are formed on the surface, being homogeneous reaction initiators was examined by adding acrolein and acetaldehyde to the flow stream. No increase in propylene conversion nor increase in the amount of homogeneous reaction products was observed. It was concluded that neither acrolein nor acetaldehyde was able to initiate the homogeneous gas-phase reaction. In a similar manner, allene was added to the flow stream to check the possibility of initiating the gas-phase reaction by allyl radicals, which may have formed allene. Again, there was no change and the allyl radical was dismissed as a possible initiator.

From the above results, Daniel and Keulks concluded that allyl hydroperoxide (or peroxide) was the initiator of the gas-phase reaction since hydroperoxides are known to be good radical reaction initiators. In addition, it was felt that the decomposi-

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* Present address: Department of Chemistry, Indian Institute of Technology, Madras, India.

† Present address: Eastman Kodak Company, Rochester, NY.

‡ To whom all correspondence should be addressed.

tion or subsequent reaction of allyl hydroperoxide in the gas phase could result in the formation of acrolein and propylene oxide. Kokes (*3*) has suggested a similar scheme for the oxidation of propylene over zinc oxide. Because the allyl hydroperoxide species is so strongly bound to the zinc oxide surface, however, only the products of complete combustion are observed.

The suggestion of the possible operation of a hydroperoxide mechanism for propylene oxidation was in fact proposed by Margolis (*4*) for the oxidation of propylene over cuprous oxide before the mechanism reported by Adams and Jennings (*5*, *6*) for bismuth molybdate and cuprous oxide. The Adams and Jennings mechanism is characterized by the formation of a symmetrical surface allyl species, followed by subsequent hydrogen abstraction and oxygen atom incorporation to form acrolein. A more recent report by Margolis (*7*) modifies her earlier proposal to include the formation of a symmetrical π-allyl surface species as the rate determining step, making her mechanism more consistent with that of Adams and Jennings. The work of Cant and Hall (*8*, *9*) on the oxidation of propylene over the noble metals rhodium and ruthenium supported on low area α-alumina also suggests that surface allyl hydroperoxide species may be formed on these metal catalysts. They suggest that the surface allyl hydroperoxide can decompose on the surface to yield acrolein and water.

It is notable that the mechanisms discussed above, suggesting the existence of allyl hydroperoxide as a reaction intermediate, are in agreement as to how the allyl hydroperoxide (or peroxide) is formed, viz, the reaction of a surface allyl species with molecular oxygen. There is also general agreement in the fate of this intermediate. Unless it is very strongly bound to the surface, it can decompose into acrolein and water.

Because the earlier report of Daniel and Keulks suggested allyl hydroperoxide as a possible initiator for the homogeneous gas-phase reaction, we decided to investigate further the nature of the surface-initiated, homogeneous reaction. Specifically, we have attempted to find conclusive evidence that the homogeneous reaction occurring in the postcatalytic volume is indeed surface initiated, to learn the identity of the gas-phase reaction initiator which is formed on the surface, and to gain further insight as to the mechanism by which the initiator is formed on the surface.

EXPERIMENTAL METHODS

Preparation of catalysts. The bismuth molybdate catalyst used in the experiments was prepared by dissolving Fisher reagent grade bismuth nitrate (29.16 g), $Bi(NO_3)_3 \cdot 5H_2O$, in 200 ml of distilled water containing 10 ml of concentrated nitric acid at 100°C. A second solution was made by dissolving Malinckrodt AR grade ammonium molybdate (10.59 g), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in 200 ml of distilled water at 25°C. After cooling the first solution to room temperature, the second solution was slowly added to the first with constant stirring. A pale, greenish-yellow precipitate formed. The pH of the solution was then increased to pH 6 by adding solid ammonium carbonate. The solution was filtered, and the precipitate washed with 600 ml of distilled water. Finally the precipitate was dried at 120°C for 6 hr and then calcined at 450°C for 4 hr. X-Ray data indicated that this preparation produced a mixture of the α- and γ-forms of bismuth molybdate. The calcined material had a BET surface area of 3.5 m^2/g, and it was ground into 20–30 mesh size before use.

The bismuth hydroxide catalyst used in the experiments was prepared by dissolving Fisher reagent grade bismuth nitrate (40.0 g), $Bi(NO_3)_3 \cdot 5H_2O$, in 300 ml of distilled water containing 10 ml of concentrated nitric acid. Dilute NH_4OH (5 *N*) was slowly added to the bismuth nitrate solution at 25°C with constant stirring until precipitation was complete. The white precipitate was then filtered and washed with 800 ml of distilled water. Finally the precipitate was calcined at 350°C for 3 to 4 hr before use. Thermogravimetric analysis of the calcined material indicated that it began losing weight at 410°C, and that the weight loss was complete before 575°C at a heating rate of 1.5 deg min^{-1}. Under isothermal conditions at 420°C, the weight loss was complete within 2.5 hr. The weight loss curves corresponded to the reaction $2\ \mathrm{Bi(OH)_3} \rightarrow \mathrm{Bi_2O_3} + 3\mathrm{H_2O}$. Therefore, we have assumed that the sample was predominately $\mathrm{Bi(OH)_3}$, but it may have some $\mathrm{Bi_2O_3}$ impurity initially. Under reaction conditions, the hydroxide will ultimately be converted into the oxide.

Fisher's CP grade strontium nitrate, $\mathrm{Sr(NO_3)_2}$, was taken from the bottle and heated at 425°C for 2 hr before use. Heating at 425°C evidently produced a sample which also contained some strontium oxide because in a separate experiment in which a sample of $\mathrm{Sr(NO_3)_2}$ was attached directly to the inlet of a mass spectrometer, $\mathrm{NO_2}$ began to evolve at 270°C. This is in agreement with literature reports on the decomposition of $\mathrm{Sr(NO_3)_2}$ (*10*). However, the decomposition is slow at low temperatures, and we have been able to heat the strontium nitrate to its melting point (~650°C) prior to use without any apparent loss in activity. Consequently, the active component is assumed to be the nitrate and not the oxide because the activity diminishes with time, presumably due to the formation of strontium oxide.

The cuprous oxide catalyst used in the experiments was supported on silica gel and contained 10% (by wt) of copper. It was prepared by adding an appropriate amount of Baker's AR grade cupric nitrate, $\mathrm{Cu(NO_3)_2 \cdot 3H_2O}$, to Cab-O-Sil EH-5 silica gel to form an aqueous slurry. To this slurry a 5% Eastman Chemical's hydrazine solution was obtained. The slurry solution was then evaporated to dryness and calcined at 400°C for 2 hr to form the cuprous oxide catalyst which had a BET surface area of 205.4 $\mathrm{m^2/g}$. The catalyst was pretreated in the reactor by a flow of carbon monoxide at approximately 10 cc/min at 275°C for 1 hr in order to reduce any cupric oxide that may have formed because selective catalysts have been shown to be composed mainly of cuprous oxide or of cuprous oxide and metallic copper (*11*).

Reactor system. The experiments were conducted in single-pass, integral-flow reactors, operating at atmospheric pressure. The desired feed composition was synthesized by controlling the flow rates of oxygen (Airco, 99.6%), propylene (Matheson, 95%), and helium (Matheson, 99.996%) with Hoke microneedle valves. The gas mixture was subsequently homogenized prior to entering the reactor by passage through a spherical mixing volume, packed with short lengths of Pyrex tubing. The total flow rate of the gas mixture was kept at 40 cc (STP) min^{-1} and its composition was determined by gas chromatographic analysis. A switching valve (Carle No. 5521) was used to bypass the reactor in order to analyze the inlet feed.

The gas chromatograph contained an 8 ft long column of 0.25 in. o.d. copper tubing packed with 80/100 mesh Porapak T (Waters Ass.). Quantitative analysis of the effluent gas was accomplished by utilizing an Infotronics 471 digital integrator in conjunction with thermal conductivity response factors for the individual components.

A gas sampling valve (Carle No. 5518), incorporating interchangeable gas sampling loops, was used to sample the effluent gas. Two sample loops of 0.0625 in. o.d. stainless steel tubing having volumes of 0.4 and 0.8 $\mathrm{cm^3}$ were normally used. However, a special cold trap, constructed from a 2 in. piece of stainless steel tubing and packed loosely with Pyrex wool, was used in place of the gas sampling valve to sample the products from the oxidation of propylene over cuprous oxide. Since the activity of the cuprous oxide catalyst was relatively low, collection of the products over a period of 20 sec in the special cold trap immersed in liquid nitrogen provided enough material for consistent gas chromatographic analyses. The collected material was flashed into the gas chromatograph by removing the liquid nitrogen bath and quickly replacing it with a molten tin bath.

Catalytic reactors. The reactors shown in Fig. 1 were used in most of the experiments and were constructed completely of 304

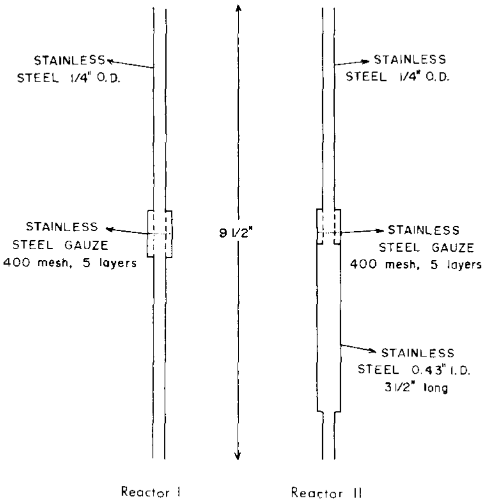

Fig. 1. Catalytic Flow Reactors.

stainless steel. Reactor I had a relatively small postcatalytic volume and was constructed from a 9.5 in. length of 0.25 in o.d. stainless steel tubing. The catalyst was held in position by five layers of 400 mesh stainless steel gauze, located midway between the ends of the reactor. A 1 in. long piece of 0.5 in. o.d., 0.25 in. i.d. stainless steel pipe was fitted around the 0.25 in. tubing to facilitate the welding of the five layers of 400 mesh gauze across the reactor tubing. During use, the postcatalytic volume was packed with Pyrex wool.

Reactor II had a postcatalytic volume of 9 cm^3. The upper portion to the stainless steel gauze was constructed of 0.25 in. o.d. stainless steel tubing. The lower portion was constructed of a 3.5 in. section of 0.5 in. o.d., 0.43 in. i.d. stainless steel tubing. The reactor was terminated with a short piece of 0.25 in. o.d. stainless steel tubing to facilitate linkage with the rest of the system.

A chromel–alumel thermocouple encased in a 0.0625 in. o.d. sheath was inserted into the catalytic bed via a Swagelok thermocouple "tee" mounted at the top of the reactors. In addition, a pressure gauge was attached to the reactors to measure the pressure drop across the reactor, and a two-way switching valve, mounted directly below the reactors, permitted the gas effluent to be vented or diverted into the gas sampling valve.

Results and Discussion

Oxidation of propylene with no catalyst. To determine the extent of the thermal gas-phase reaction between O_2 and C_3H_6 under similar conditions of flow and $O_2{:}C_3H_6{:}He$ ratios as those used in the catalytic experiments, several experiments were conducted using reactors I and II without a catalyst. The results are shown in Table 1. It can be seen that the thermal, gas-phase reaction occurred to only a slight extent at the experimental temperatures (400–475°C) used for the catalytic reactions.

Catalytic activities and product distributions. The catalysts were tested for activity and the product distributions were determined with reactor I (very small postcatalytic volume) and reactor II (9 cc postcatalytic volume). The results are presented in Table 2.

The product distributions obtained with $Bi(OH)_3$ and $Sr(NO_3)_2$ in reactors I and II strongly suggest that these materials are capable of producing an initiator for the homogeneous reactions in the postcatalytic volume. As shown in Table 2, there was essentially no reaction when using reactor I. When using reactor II, the principle products were acetaldehyde, propylene oxide, and CO_2. The reaction was also obviously dependent upon the presence of the catalytic material since there was only a slight thermal, gas-phase reaction in reactor II at these temperatures with propylene and O_2 as shown in Table 1. The fact that the product distributions observed resemble quite closely the product distribution obtained in the thermal oxidation of propylene (*12*) suggests the homogeneous nature of the oxidation reaction.

Consider further the results obtained with $Bi(OH)_3$. In contrast to $Sr(NO_3)_2$ which was active for approximately 1 wk at 400°C, we found that the $Bi(OH)_3$ catalyst lost its activity over a 20 min period at 400°C and over a 2–3 hr period at 365°C. Since the conversion of propylene

TABLE 1

RESULTS OF PROPYLENE OXIDATION AT VARIOUS TEMPERATURES USING NO CATALYST[a]

Reactor	Temp (°C)	Conversion[b] O_2	C_3H_6	Products
II	405	4.0	1.5	CO_2, H_2O
II	430	6.0	4.8	CO_2, H_2O, Tr CH_3CHO
I	450	0.6	$\sim$0.1	—
II	450	6.2	5.0	CO_2, H_2O, Tr CH_3CHO
I	475	1.0	$\sim$0.1	—
II	475	9.3	6.0	CO_2, H_2O, Tr CH_3CHO and propylene oxide

[a] Flow ratio (C_3H_6:O_2:He), 4:3:3; total flow 40 cc (STP) min^{-1}.

[b] Conversion expressed as moles of C_3H_6 or O_2 reacted per 100 moles of total C_3H_6 or O_2.

diminishes to zero with time, this indicates that the initiaton of the reaction is dependent upon the catalytic material. As indicated in the experimental section, the Bi(OH)$_3$ sample decomposes into Bi_2O_3 at 420°C. Presumably, the loss in activity with the Bi(OH)$_3$ sample is associated with its decomposition into Bi_2O_3 since we found that Bi_2O_3 does not initiate the reaction when we ran the experiment with a sample of Bi_2O_3 as the catalyst. We feel that these observations offer strong evidence for the suggestion that the initiator for the homogeneous reaction, which takes place in the postcatalytic volume, is formed on the catalyst surface.

Of course, if the product distributions obtained with Bi(OH)$_3$ and Sr(NO$_3$)$_2$ are indicative of a homogeneous reaction occurring in the postcatalytic volume, then one would expect that this reaction would be critically dependent upon the postcatalytic volume, the C_3H_6/O_2 ratio, the temperature, the pressure, the reactor material, and the amount of inert diluent. We have not made an extensive examination of all of these variables, but we have confirmed that flames or an explosion can occur when the C_3H_6/O_2 ratio is less than 1. We have also observed flames and explosions by increasing the postcatalytic volume to larger volumes, and we have been able to duplicate the results in Table 2 using a Pyrex reactor, indicating that the reactor material is not an important parameter in this reaction. All of these studies were done with

TABLE 2

RESULTS OF C_3H_6 OXIDATION OVER VARIOUS CATALYSTS USING REACTORS I AND II[a]

	Bismuth molybdate T = 430°C		Cu_2O T = 360°C	Bi(OH)$_3$ T = 365°C		Sr(NO$_3$)$_2$ T = 400°C	
Products[b]	I	II	I and II	I	II	I	II
CO	13	48	124	—	131	—	40
CO_2	21	50	116	Tr	43	Tr	30
C_2H_4	—	11	3	—	19	—	16
HCHO	—	2	—	—	1	—	8
Acetaldehyde	6	15	3	—	20	—	43
Acrolein	74	38	19	—	3	—	9
Propylene oxide	—	4	—	—	9	—	27
Conversion (%)	27	37	11	1	17	1	15

[a] Catalyst wt, 0.4 g; flow (C_3H_6:O_2:He), 4:3:3; total flow, 40 cc (STP) min^{-1}.

[b] Expressed as moles formed per 100 moles C_3H_6 reacted.

a residence time in the hot, postcatalytic zone of 4.0 sec or less.

To show that the reaction was definitely surface initiated and homogeneous in nature and not dependent upon the olefin used as the hydrocarbon, the oxidation of 1-butene was carried out using strontium nitrate in reactor II. The results are shown in Table 3. No appreciable activity was observed using reactor II empty until 400°C was reached. However, using strontium nitrate in reactor II, a reaction analogous to that of propylene and O_2 took place at 340°C. Since the reaction with propylene yielded acetaldehyde and propylene oxide, the similar reaction with 1-butene should yield butylene oxide, acrolein, propionaldehyde, and acetaldehyde if the reaction occurring was a surface initiated, homogeneous reaction. This is the case as shown in Table 3.

The strictly heterogeneous oxidation of 1-butene has a high selectivity to butadiene and *cis*- and *trans*-2-butene. The absence of these products at 340°C with reactor II shows that the reaction does not proceed in a purely heterogeneous manner. The product distribution obtained from reactor I at 445°C, however, gives important information to the identity of the reaction initiator. Strontium nitrate appears to be able at elevated temperatures (445°C) to abstract two hydrogen atoms from 1-butene and to form butadiene, which is the usual heterogeneous oxidation product. The fact that strontium nitrate is able to abstract an allylic hydrogen but that no butadiene is observed at 340°C can best be explained by reasoning that after an allylic hydrogen is abstracted from 1-butene on the surface, gas-phase or chemisorbed oxygen is added to the surface species (C_4H_7) forming a butene hydroperoxide (or peroxide) intermediate. This species then desorbs from the surface and initiates the gas-phase reaction. It appears that higher temperatures are needed before strontium nitrate is able to abstract a second hydrogen atom from the C_4 carbon atom and form butadiene via a purely heterogeneous mechanism. In an analogous manner with propylene it seems reasonable to now state that the initiator of the homogeneous gas-phase reaction is indeed allyl hydroperoxide (or peroxide).

Daniel and Keulks (*1*) have shown previously that with sufficiently large quantities of a bismuth molybdate catalyst that as the contact time on the catalyst is decreased by increasing the feed rate, the conversion of propylene decreases, along with a decrease in the rate of formation of the products. This is as expected for a heterogeneous reaction. However, the results shown in Table 4 indicate that as the contact time on the catalyst is decreased by decreasing the amount of catalyst, the rate of formation of acrolein decreases, but the propylene conversion passes through a minimum with a change in the product distribution. Acetaldehyde, ethylene, CO,

TABLE 3

RESULTS OF 1-BUTENE OXIDATION OVER $Sr(NO_3)_2$ USING REACTORS I AND II AND THERMAL REACTION OF 1-BUTENE USING REACTOR II WITH NO CATALYST[a]

Products[b]	I T = 445°C	II T = 340°C	II, no catalyst T = 445°C
CO_2	38	80	127
$C_3H_6 + C_3H_8$	—	6	10
H_2O	127	4	110
CH_3CHO	—	9	4
$CH_2{=}CHCHO + CH_3CH_2CHO$	—	74	75
Butylene oxide	—	18	Tr
Butadiene	72	—	—
1-C_4H_8 conv (%)	9	12	7

[a] Flow ratio (C_4H_8:O_2:He), 5.5:3.2:1.3; total flow, 40 cc (STP) min^{-1}; catalyst wt, 0.47 g.

[b] Expressed as moles formed per 100 moles C_4H_8 reacted.

TABLE 4

Product Distribution as a Function of Contact Time[a]

Products[b]	Vol of catalyst (cc) 2	1	0.75	0.5
CO	349	467	873	955
CO_2	509	297	290	261
C_2H_4	23	51	60	105
Acetaldehyde	29	92	96	111
Acrolein	304	118	107	29
CH_4	—	Tr	Tr	23
Propylene oxide	—	27	30	43
Formaldehyde	—	Tr	Tr	11
Conversion (%)	24	18	25	29

[a] Catalyst, bismuth molybdate; temp, 400°C; flow (C_3H_6:O_2:He), 4:3:2; total flow, 135 cc (STP) min^{-1}. Reactor II described in Ref. (*1*) was used for these experiments.

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

and propylene oxide increase with a decrease in contact time. This type of behavior is rather hard to explain only on the basis of the heterogeneous reaction leading to the formation of acrolein.

Mechanistic suggestions. We suggest that the results obtained in this investigation indicate that there are two parallel reactions occurring on the surface. One reaction pathway is that proposed by Adams and Jennings and leads to the production of acrolein by a heterogeneous mechanism involving lattice oxygen (*13–16*). The other pathway is the surface-initiated, homogeneous reaction initiated by a surface hydroperoxide (or peroxide) formed by the addition of molecular oxygen to the surface allyl intermediate. Short contact times with a small amount of catalyst favor the latter pathway, while long contact times with a larger amount of catalyst favor the heterogeneous pathway.

In addition, these results tend to confirm the earlier suggestion of Daniel and Keulks that the initiator for the homogeneous reaction is not acrolein. For if one assumes that the homogeneous reaction is initiated by acrolein, with a decrease in contact time with the catalyst, as the amount of acrolein decreases, one would expect a decrease, or at least a leveling off, in the products CO, ethylene, acetaldehyde, and propylene oxide. However, as shown in Table 4, these products increase with a decrease in contact time along with an increase in the propylene conversion. Furthermore, the results with cuprous oxide (Table 2) and the larger amount of bismuth molybdate (Table 5) in reactors I and II provide additional evidence that acrolein is not the initiator of the homogeneous reaction. As shown, the product distributions remained essentially constant under these conditions with no increase in propylene oxide. We feel that these results can be explained in the following manner: with a large amount of bismuth molybdate catalyst, any alkyl hydroperoxide (or peroxide) formed on the upper portion of the catalyst would readsorb due to the extended contact time. In effect, the lower portion of the catalyst bed would act as a chain terminator, much like the effect observed by packing the postcatalytic column with Pyrex wool. Upon removing the bismuth molybdate catalyst, used to obtain the results in Table 5, it was noticed that the upper portion was yellow in color (the color normally observed when the catalyst is oxidized), while the lower region was a dark grey, presumably due to a catalyst reaction. Since it has been shown (*17*) that

TABLE 5

Product Distribution with a Large Amount of Catalyst Using Reactors I and II[a]

Product[b]	Reactor I	II
CO_2	40	43
C_2H_4	3	3
Acetaldehyde	6	7
Acrolein	79	73
Conversion (%)	50	53

[a] Catalyst, bismuth molybdate, 1.5 ml volume; temp, 400°C; flow (C_3H_6:O_2:He), 4:3:3; total flow, 40 cc (STP) min^{-1}.

[b] Expressed as moles formed per 100 moles of C_3H_6 reacted.

the reduced form of bismuth molybdate is inactive, it is reasonable to assume that the heterogeneous reaction was occurring on the upper portion, while the lower portion was inactive and served as a surface for product decomposition and radical termination.

We feel that absence of a homogeneous reaction with cuprous oxide is due to a change in the mechanism for acrolein production. As reported by Adams and Jennings, the kinetics of propylene oxidation over cuprous oxide are first order in oxygen and zero order in propylene. This is in contrast to the first order in propylene and zero order in oxygen kinetics observed with bismuth molybdate. It should also be noted that the propylene conversion and product distribution are much different than those obtained with bismuth molybdate. We feel that the low selectivity to acrolein and corresponding high selectivities of CO_2 and H_2O reflect the strength of the surface acrolein precursor bond, similar to that suggested by Kokes for zinc oxide. However, it appears that the bond made with the cuprous oxide surface is somewhat weaker than that made on zinc oxide because some acrolein is produced. Thus, it appears that the reaction mechanism over cuprous oxide involves the formation of a surface allyl hydroperoxide (or peroxide) intermediate which decomposes on the surface to form acrolein and water, as suggested by Kokes (*3*), Margolis (*4*), and Cant and Hall (*8*, *9*).

This explanation is consistent with the recent results reported by Herzog (*18*), who studied the oxidation of propylene over cuprous oxide using nitrous oxide as the oxygen source. It is commonly accepted that nitrous oxide decomposition on surfaces produces an atomic form of oxygen rather than a molecular form (*19*). In contrast to the oxidation of propylene with gas-phase oxygen, Herzog observed only small amounts of acrolein, suggesting that molecular oxygen is necessary for the production of acrolein over cuprous oxide.

At this point it is worth mentioning the possible role of acetaldehyde in the surface initiated homogeneous reaction since Shtern (*20*) felt that acetaldehyde played a dominant role in the thermal, gas-phase oxidation of propylene. In the experiment using a relatively large amount of bismuth molybdate catalyst (Table 5), it was assumed that any allyl hydroperoxide (or peroxide) in the gas phase that was formed on the surface would readsorb and decompose on the surface due to the extended contact time over the catalyst. In addition, the extra amount of catalyst could result in the formation of more acetaldehyde. Therefore, if homogeneous reaction products (propylene oxide and more acetaldehyde) were formed in the absence of allyl hydroperoxide (or peroxide), acetaldehyde would need to be considered as a possible initiator. The results in Table 5 show that no surface initiated reaction took place and the product distribution using reactor II paralleled the product distribution using reactor I. The slight decrease in acrolein when switching from reactor I to reactor II indicated that almost no homogeneous reaction took place in the postcatalytic volume of reactor II. The sizeable amount of acetaldehyde formed using reactor II insured that enough acetaldehyde was present to initiate a homogeneous reaction if, indeed, it was capable of doing so. It therefore seems safe to say that acetaldehyde is not the initiator of the homogeneous gas-phase oxidation of propylene.

In summary, it appears evident that propylene and oxygen are able to undergo a surface initiated, gas-phase reaction over $Bi(OH)_3$ and $Sr(NO_3)_2$ if a large postcatalytic volume is present. The initiator of this reaction appears very likely to be allyl hydroperoxide (or peroxide).

The formation of the allyl hydroperoxide (or peroxide) intermediate occurs via the reaction of a surface allyl species with molecular oxygen. Depending upon the strength of the surface bond, this intermediate may also undergo a surface reaction to produce acrolein and water, e.g., on Cu_2O, or to produce CO_2 and water, e.g., on ZnO.

Finally, with bismuth molybdate, the predominate reaction pathway for acrolein appears to be the heterogeneous mechanism utilizing lattice oxygen. However, some acrolein may also be produced via the hydroperoxide mechanism because a surface-initiated, homogeneous reaction is observed in reactors having a large post-catalytic volume. Since we feel the homogeneous reaction is initiated by the allyl hydroperoxide intermediate, it also is possible that a fraction of this intermediate may decompose into acrolein and water. Recent results obtained in our laboratories utilizing isotopic oxygen are consistent with this assumption.

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