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The Formation of Gas-Phase π-Allyl Radicals from Propylene over Bismuth Oxide and γ-Bismuth Molybdate Catalysts

Wilson Martir and Jack H. Lunsford*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843.

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Abstract: Gas-phase π-allyl radicals were produced when propylene reacted over Bi_2O_3 and γ-bismuth molybdate catalysts at 723 K. The pressure in the catalyst zone was varied between 5×10^{-3} and 1 torr. The radicals were detected by EPR spectroscopy together with a matrix isolation technique in which argon was used as the diluent. The matrix was formed on a sapphire rod at 12 K which was located 33-cm downstream from the catalyst. Bismuth oxide was more effective in the production of gas-phase allyl radicals than γ-bismuth molybdate. By contrast α-bismuth molybdate was ineffective in forming allyl radicals and MoO_3 acted as a sink for radicals which were produced elsewhere in the system. Comparison of the π-allyl radical and the stable product concentrations over Bi_2O_3 revealed that gas-phase radical recombination reactions served as a major pathway for the formation of 1,5-hexadiene. Addition of small amounts of gas-phase oxygen increased the concentration of allyl radicals, and at greater oxygen levels allyl peroxy radicals were detected. Because of the effect of temperature on the equilibrium between allyl and allyl peroxy radicals, the latter product must be formed in the cooler part of the system.

The catalytic oxidation of hydrocarbons over metal oxides has been extensively studied with a view to understanding the mechanisms for these heterogeneous reactions. Recently several investigators have demonstrated the importance of heterogeneous–homogeneous reactions during catalytic processes. In these types of reactions surface intermediates desorb into the gas phase where subsequent homogeneous reactions occur. Studies of the effect of residence time in the postcatalytic volume on the product distribution, during the catalytic oxidation of propylene over a catalyst consisting of bismuth, phosphorus, and molybdenum oxides supported on silica, led McCain and Godin[1] to suggest that the formation of propylene oxide occurred by means of a heterogeneous–homogeneous pathway. Furthermore, Keulks and coworkers[2] have investigated the relationship between the postcatalytic volume in several flow reactors and the product distribution during the heterogeneous and subsequent homogeneous reactions of propylene with oxygen over several metal oxide catalysts. They proposed that the formation of propylene oxide and some acrolein may occur via subsequent reactions or decomposition of the surface-initiated intermediates (allyl hydroperoxides or allyl peroxide) in the gas phase.

Although there is still controversy regarding the overall mechanistic scheme during the heterogeneous catalytic oxidation of propylene to acrolein over bismuth molybdate, it is generally agreed that the rate-determining step of the reaction is the abstraction of a hydrogen atom by lattice oxygen, which results in the formation of an allyl radical.[3] If the radical remains on the surface, it will undergo oxygen addition and a second hydrogen abstraction, though perhaps not in this order, to form acrolein. By contrast over bismuth oxide the radical coupling reaction is favored and 1,5-hexadiene is observed as the principal product.[4]

The formation of surface allyl anions following the reaction of propylene with zinc oxides was observed by Matsuzaki et al.,[5] using spin-trapping techniques. Previously, Dent and Kokes[6] had identified a surface π-allyl species by its infrared spectrum. By means of mass spectrometry direct evidence for the desorption of allyl radicals from oxide surfaces into the gas phase was obtained at pressures of about 10^{-3} torr and at temperatures greater than 800 K. Surprisingly there was no evidence for allyl radical desorption when bismuth molybdate was studied, even though easily measurable amounts of acrolein were reported.[7]

In the present work we have investigated the formation gas-phase radicals, in addition to stable products, during the oxidation of propylene over bismuth molybdates, bismuth oxide, and molybdenum oxide. Both allyl and allyl peroxy radicals have been isolated and identified by employing a flow reactor in tandem with a matrix isolation system. Paramagnetic species in the matrix were detected by EPR spectroscopy. This experimental configuration permits one to trap in a solid environment highly reactive, transient molecules which originated in the reactor zone.

Experimental Section

The system used to carry out these experiments is depicted in Figure 1. The catalyst (1) was first activated under vacuum with the sapphire rod (11) being isolated by means of a gate valve (7). With the sapphire rod at 12 K and the catalyst at 723 K the reacting gases were allowed to flow through the reactor zone for 1 min. Upon closing of valve (8) and opening of valve (7) the matrix began to form. The standard time for matrix formation was 20 min. The total matrix thickness was between 0.5 and 1.0 mm to maintain a high thermal conductivity in the matrix material. At the end of a run valve (7) was closed and the sapphire rod was lowered into the microwave cavity (12). In this configuration the EPR spectrum was recorded.

Upon opening of the variable leak valve (13) fractions of the gas were introduced into a quadrupole mass spectrometer. Alternately, the gases could be diverted through a cold trap by means of valve (5) for collection of the reaction products which were later analyzed by using gas chromatography.

The cryogenic closed-cycle refrigerator (Displex CS 202) was manufactured by Air Products. The temperature of the matrix was monitored by means of a digital temperature indicator connected to a chromel–gold (0.07% Fe) thermocouple which was attached to the holder for the sapphire rod. The sapphire rod (8.89-cm length, 0.2-cm diameter), obtained from Linde Division of Union Carbide, was ground flat along 6.9 cm of its lower length to 0.1-cm thickness. A flat side of the rod was always perpendicular to the direction of molecular flow. The use of flexible metal bellows in the vacuum system permitted smooth motion with a minimum of vibration when the sapphire rod was lowered into the microwave cavity.

The reactor was connected to the system by using "O"-ring joints. The reactor, which was constructed of fused quartz (2.5-cm, i.d., 35.8-cm length), had a thermocouple well centered along its axis. This allowed the measurement of temperature along the reactor length. The heated zone, which was 25 cm in length, contained a preheating region composed of tightly packed fused quartz tubing (0.4-cm o.d., 23-cm length) and the catalyst bed. The postcatalytic region was not heated, and typically the pressure was 2×10^{-5} torr. By inserting a probe (4), we could vary the pressure in the catalytic zone from 5×10^{-3} to 1 torr. The distance between the exit end of the catalyst and the sapphire rod was 24 cm for the low-pressure and 33 cm for the medium-pressure experiments. In one

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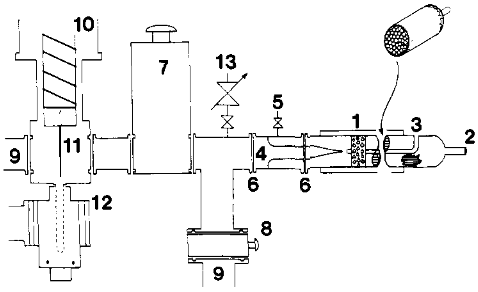

Figure 1. Schematic for the matrix isolation and gas analyzer systems, coupled to the catalytic reactor: (1) catalyst, (2) gas inlet, (3) thermocouple well, (4) pressure probe, (5) metal valve, (6) "O"-ring joints, (7) gate valve, (8) butterfly valve, (9) to vacuum pumps, (10) vacuum shroud, (11) sapphire rod, (12) microwave cavity, (13) quadrupole-MS inlet.

series of experiments this distance was varied by inserting spacers.

The α-bismuth molybdate ($Bi_2Mo_3O_{12}$) and γ-bismuth molybdate (Bi_2MoO_6) samples were supplied by Professor G. W. Keulks of the University of Wisconsin. The Bi_2O_3 and MoO_3 were obtained from Ventron Alfa Division and Mallinkrodt, respectively. The metal oxides in the form of a powder were mixed with sufficient water to form a thick paste which was subsequently dried in air at 633 K for 30 min. The material was broken into chips between 8 and 12 mesh size. A total amount of 1.3 g of catalyst was distributed between thin layers of Pyrex glass wool, and the resulting catalyst bed was placed in the reactor (1). The free volume of the catalyst bed was approximately 1.8 cm^3. Prior to the catalytic reaction all samples were heated in flowing molecular oxygen to 800 K for 3 h. After each reaction they were reoxidized for 0.5 h at 750 K. The catalyst was cooled in oxygen to 523 K and subsequently heated to 723 K under vacuum for 30 min.

The gases were obtained from commercial sources and were of the following purities, as received: 99.99% O_2, 99.0% C_3H_6, and 99.99% Ar. They were further dried by passing them over molecular seives. Flow rates, which were regulated by precision metering valves, were varied from 0.064 to 0.019 cm^3/s for argon and propylene and from 4.8×10^{-3} to approximately 10^{-5} cm^3/s for oxygen. All flow rates are expressed at standard temperature and pressure. The collection periods were varied from 0.17 to 4 h by changing the gas-flow rates; however, for comparison of a series of experiments a deposition period of 0.33 h was used.

The gases exiting from the catalysts were analyzed for stable products by using a Varian Model VGA-100 mass spectrometer and an Antek Model 464 LP gas chromatograph. The latter instrument proved to be more sensitive and thus the results reported here were obtained by gas chromatography. After the products were trapped at 77 K for 20 min in a previously evacuated flask, the temperature of the flask was slowly raised to 226 K and unreacted propylene was pumped out. We demonstrated that no products were lost during the procedure. The sample was then warmed to room temperature, and the gas-phase products were injected over a 15% DC 704-on-chromosorb column (280.3-cm length, 0.3 cm o.d.) operated at 320 K. At 298 K the products were present only in the gas phase.

A Varian Model V4500 spectrometer was used to obtain the EPR spectra. The microwave cavity was operated in the TE_{102} mode. The g values were reported relative to a phosphorous-doped silicon standard with $g = 1.9987$. Spin concentrations were obtained by double integration of the recorded EPR spectrum of the unknown and the standard. Errors for the spin concentration are estimated to be ±25%.

Results

Although π-allyl radicals were observed at 723 K, both with and without the metal oxide catalysts in the reactor, the concentration of the radicals was greatly enhanced by the presence of Bi_2O_3 and γ-bismuth molybdate. Small amounts of gas-phase oxygen resulted in an increased allyl radical concentration; however, larger amounts of O_2 resulted in the formation of the corresponding allyl peroxy radical.

The spectrum of matrix isolated allyl radicals, formed over Bi_2O_3, is depicted in Figure 2a. The spectrum is characterized by $g = 2.0027$ and $a_{iso} = 15.4$ G, which is in good agreement with literature values reported for this radical.[8] The observed spectrum results mainly from the interaction of the unpaired electron with four equivalent protons and a very small hyperfine contribution due to the central β proton. The outer hyperfine lines reveal anisotropy which indicates that the motion of the radical is restricted in the matrix. A detailed analysis of this anisotropy will be presented in a subsequent note. Apart from differences in intensity the same spectrum was observed when the allyl radical was formed over each catalyst.

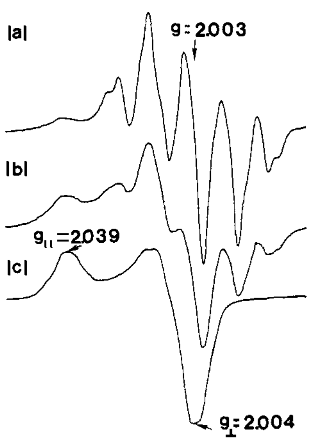

Figure 2. EPR spectra of π-allyl and allyl peroxy radicals formed over Bi_2O_3 as a function of oxygen flow rate: (a) 1.7×10^{-4} cm^3/s; (b) 1.8×10^{-3} cm^3/s; (c) 4.8×10^{-3} cm^3/s; argon flow = 0.064 cm^3/s; C_3H_6 flow = 0.019 cm^3/s; $T = 723$ K, collection time = 20 min. The pressure in the catalytic volume was 1 torr.

Upon increasing of the flow rate of O_2 from 1.7×10^{-4} to 1.8×10^{-3} and then to 4.8×10^{-3} cm^3/s, the spectra of Figure 2b,c were observed. The spectrum of Figure 2c with $g_{\parallel} = 2.039$ and $g_{\perp} = 2.004$ is characteristic of organic peroxy radicals. Although the spectrum of the allyl peroxy radical has not been previously reported, several peroxy radicals have been studied in the solid state. These are characterized either by an axially symmetric spectra with $g_{\parallel} > g_{\perp}$ or by $g_{xx} \neq g_{yy} \neq g_{zz}$ provided the resolution is adequate and molecular rotation around the O–O bond is relatively slow.[9,10] Since the argon to oxygen ratio was only 13:1 at the high flow rates of O_2, the line width of spectrum c is probably dominated by dipolar interactions between the allyl peroxy radicals and molecular oxygen in the matrix.

The experiments were generally carried out in two pressure regimes, depending on whether the probe was used in the system. Without the probe (4) the pressure in the reaction zone was typically 5×10^{-3} torr, which will be referred to as the low-pressure regime. With the probe present the pressure was ca. 1 torr, which will be referred to as the medium-pressure regime. With the system in the intermediate pressure configuration the amounts of allyl and allyl peroxy radicals isolated over a 20-min period are compared in Table I for the several catalysts operating at different O_2-flow rates. These results demonstrate that Bi_2O_3 is the most effective catalyst for the generation of gas-phase π-allyl radicals. It should be noted that allyl radicals are also formed homogeneously and/or on the surface of the Pyrex wool which is designated by homogeneous–Pyrex reactions. To eliminate spurious results from this reaction, we carefully reproduced the amount and configuration of the Pyrex wool. In the table the contribution of the homogeneous–Pyrex reactions has not been subtracted from the other values; thus, the lower radical concentrations observed for MoO_3 means that this catalyst consumed allyl radicals generated by the homogeneous–Pyrex reactions. When MoO_3 was placed immediately downstream from the Bi_2O_3 catalyst, the amount of allyl radicals collected was decreased by a factor of 20.

The concentration of allyl radicals increased significantly over Bi_2O_3 and γ-bismuth molybdate as the oxygen-flow rate was increased to 3.8×10^{-4} cm^3/s and thereafter decreased as more of the allyl radicals were converted to peroxy radicals. The maximum concentration of peroxy radicls, however, was never

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Table I. Radical Species Trapped by Matrix Isolation during the Oxidation of Propylene over Various Catalysts[a]

catalyst[b]	molecular oxygen-flow rate, cm^3/s	radical amount, nmol	
		allyl	allyl peroxy
Bi_2O_3	10^{-5} [c]	4.52	0.00
γ-bismuth molybdate		0.65	0.00
α-bismuth molybdate		0.19	0.00
MoO_3		0.00	0.00
homogeneous–pyrex		0.53[d]	0.00
Bi_2O_3	1.7×10^{-4}	32.05	5.65
γ-bismuth molybdate		4.42	0.78
α-bismuth molybdate		0.97	0.15
MoO_3		0.12	0.022
homogeneous–pyrex		1.03	0.18
Bi_2O_3–MoO_3		1.66	0.40
Bi_2O_3	3.8×10^{-4}	31.72	5.60
γ-bismuth molybdate		3.72	0.65
α-bismuth molybdate		0.82	0.15
MoO_3		0.12	0.022
homogeneous–pyrex		0.84	0.18
Bi_2O_3	1.8×10^{-3}	14.32	17.44
γ-bismuth molybdate		1.15	1.40
α-bismuth molybdate		0.37	0.46
MoO_3		0.18	0.22
Homogeneous–Pyrex		0.45	0.56
Bi_2O_3	4.8×10^{-3}	0.00	7.65

[a] All the reactions were carried out under the following experimental conditions: $T = 723$ K, a collection period = 20 min, argon flow = 0.064 cm^3/s, and C_3H_6 flow = 0.019 cm^3/s. The pressure in the catalytic volume was 1 torr. [b] All metal oxides were pretreated in the same manner (see text) and were obtained from fresh batches. [c] Amount of molecular oxygen in background which corresponds to the indicated flow rate. [d] The observed amount of methyl radicals was approximately 10^{-3} nmol.

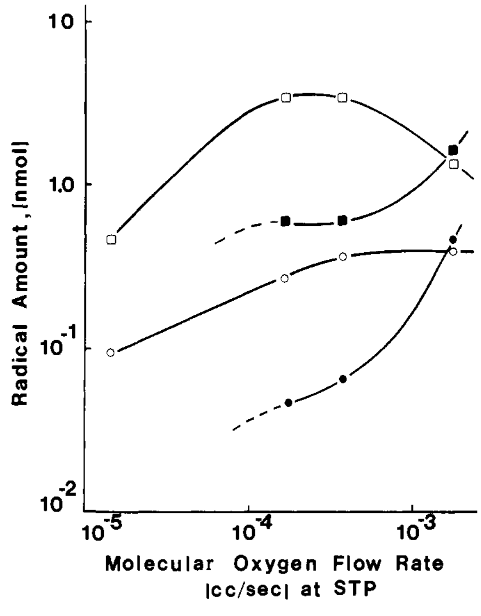

Figure 3. The amount of radicals formed as a function of the molecular oxygen-flow rate during the catalytic oxidation of propylene ($T = 723$ K; collection time = 20 min; the flow rates of argon and propylene were constant at 0.064 and 0.019 cm^3/s, respectively; total pressure in the catalytic volume during the reaction was 5×10^{-3} torr): □, allyl and, ■, allyl peroxy radicals using γ-bismuth molybdate; ○, allyl and, ●, allyl peroxy radicals using α-bismuth molybdate.

as great as the maximum concentration of allyl radicals.

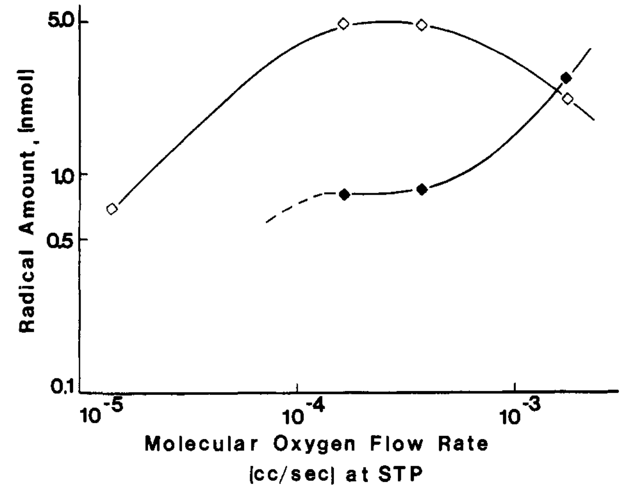

Figure 4. The amount of radicals formed as a function of the molecular oxygen flow rate during the catalytic oxidation of propylene ($T = 723$ K; collection time = 20 min; the flow rates of argon and propylene were constant at 0.064 and 0.019 cm^3/s, respectively; total pressure in the catalytic volume during the reaction was 5×10^{-3} torr): ◇, allyl and, ◆, allyl peroxy radicals using Bi_2O_3.

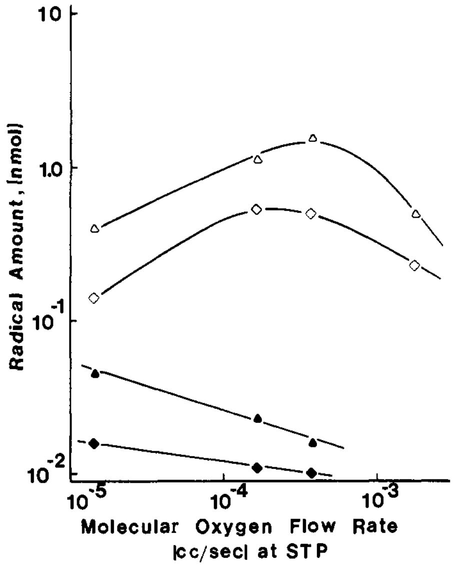

Figure 5. The amount of radicals formed as a function of the molecular oxygen flow rate during the oxidation of propylene ($T = 723$ K; collection time = 20 min; the flow rates of argon and propylene were constant at 0.064 and 0.019 cm^3/s, respectively; total pressure in the catalytic volume during the reaction was 5×10^{-3} torr): △, allyl and, ▲, methyl radicals during homogeneous–pyrex reactions; ◇, allyl and, ◆, methyl radicals using MoO_3.

In the low-pressure configuration similar phenomena were observed as shown in Figures 3 and 4. Although the concentrations of allyl and allyl peroxy radicals were approximately 1 order of magnitude less in these experiments, the trends with respect to oxygen-flow rate were essentially the same. Again, γ-bismuth molybdate was more effective than α-bismuth molybdate in forming gas-phase allyl radicals, but at the lower pressures the differences between γ-bismuth molybdate and Bi_2O_3 were less significant. Moreover, as indicated in Figure 5 the concentration of allyl radicals from the homogeneous–Pyrex reaction was about the same in the low- and medium-pressure configurations. The concentration of allyl radicals was decreased when MoO_3 was present in the reactor.

Methyl radicals were ubiquitous in our system, and their spectrum was quite prominent during the low-pressure oxidation of propylene. The actual amount of methyl radicals, as depicted in Figure 5, was small in the low-pressure studies and even less (ca. 5×10^{-3} nmol) in the medium-pressure experiments. The methyl radicals are believed to result from the pyrolysis of diffusion pump oil and other organic impurities in the system since the concentrations of this radical were essentially the same when propylene was not a reactant.

Table II. The Effect of the Distance between the Probe Inlet and the Catalyst in the Selective Formation of Radicals during the Oxidation of Propylene[a] over Bi_2O_3

dist between probe inlet and catalyst, cm	radical amount, nmol	
	allyl	allyl peroxy
0.50	35.70	6.31
9.00	3.20	3.92
25.26	0.00	5.45

[a] All the reactions were carried under the following experimental conditions: $T = 723$ K, collection period = 20 min, argon flow = 0.064 cm³/s, C_3H_6 flow = 0.019 cm³/s, and O_2 flow = 3.8×10^{-4} cm³/s. The pressure in the catalytic volume was 1 torr.

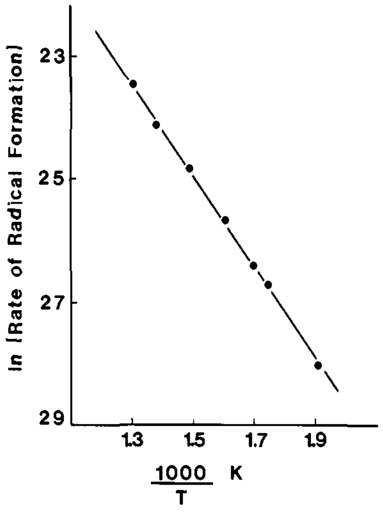

Figure 6. The rate of radical formation during the catalytic oxidation of propylene over Bi_2O_3, as a function of the reciprocal of the absolute temperature: argon flow = 0.064 cm³/s; C_3H_6 flow = 0.019 cm³/s; O_2 flow = 3.8×10^{-4} cm³/s; collection time = 20 min. The pressure in the catalytic volume was 1 torr. Rate is expressed in molecules/s.

In order to evaluate the significance of radical recombination reactions under medium-pressure conditions, we varied the distance between the probe inlet and the Bi_2O_3 catalyst. It is evident from the results of Table II that the allyl radical concentration decreased as the distance was increased, whereas the concentration of allyl peroxy radicals remained almost constant, within experimental error. The latter result probably reflects a steady-state concentration of peroxy radicals. Clearly, the allyl radicals were being removed by subsequent reactions in the postcatalytic volume.

The effect of temperature on allyl radical formation was determined over Bi_2O_3 under medium-pressure conditions. The rate of radical formation was determined, assuming that the rate was constant over the period of collection, and the results are plotted as a function of reciprocal temperature in Figure 6. Over the temperature range from 523 to 723 K the apparent activation energy was 14 kcal mol^{-1}.

The significance of these results in understanding the catalytic oxidation of propylene may be evaluated if one knows the relative concentrations of radicals and stable products. Therefore, under identical conditions of catalyst configuration, flow rate, gas composition, and temperature the products were pumped through a cold trap rather than collected on the sapphire rod. As described in the previous section the stable products were analyzed by gas chromatography, and the data are given in Table III. Qualitatively, the results are about as expected, on the basis of the reported activities and selectivities of these catalysts at somewhat greater pressures; i.e., Bi_2O_3 is an effective catalyst for the formation of 1,5-hexadiene,[4] while bismuth molybdates are catalysts for the formation of acrolein. In agreement with other studies γ-bismuth molybdate is more active than α-bismuth molybdate.[11] Molybdenum oxide was inactive for the formation of 1,5-hexadiene and only slightly active for the formation of acrolein. When this material was placed downstream from Bi_2O_3, no 1,5-hexadiene was formed, and the conversion to acrolein was increased by a small amount. The homogeneous–Pyrex reaction of propylene resulted mainly in the formation of 3-methylpentane.

Table III. Product Distribution during the Oxidation of Propylene[a] over Various Catalysts

catalyst[b]	stable products,[c] nmol		
	1,5-hexadiene	acrolein	3-methylpentane
Bi_2O_3	33.2	7.0	36.1
γ-bismuth molybdate	0.0	2950	31.0
α-bismuth molybdate	0.0	311	24.3
MoO_3	0.0	25.0	38.7
homogeneous-pyrex	0.0	3.5	51.6
Bi_2O_3–MoO_3[d]	0.0	37.0	34.6

[a] All the reactions were carried under the following experimental conditions: $T = 723$ K, a collecting period = 20 min, argon flow = 0.064 cm³/s, C_3H_6 flow = 0.019 cm³/s, and O_2 flow = 3.8×10^{-4} cm³/s. The pressure in the catalytic volume was 1 torr. [b] All the metal oxides were pretreated in the same manner (see text). [c] Similar product distributions within ±25% error were obtained when the oxygen flow rates used were 10^{-5}, 1.7×10^{-4}, and 1.8×10^{-3} cm³/s. [d] The Bi_2O_3 catalyst was upstream from the MoO_3 catalyst.

The most important feature of this experiment is the quantitative agreement between the number of 1,5-hexadiene molecules formed and the number of allyl radicals which were observed by EPR. Under the same experimental conditions 33.2 nmol of 1,5-hexadiene was produced whereas 31.7 nmol of allyl radicals was collected. Of course, two allyl radicals are required to form a molecule of 1,5-hexadiene; however, if one assumes a radical collection efficiency of 50%, the stoichiometric amounts of the radical and the stable product are essentially equivalent. This means that the post catalytic recombination of allyl radicals serves as a *major* pathway for the formation of 1,5-hexadiene. By contrast the amount of acrolein formed over γ-bismuth molybdate is $\sim 10^3$ greater than the amount of gas-phase allyl radicals produced on this material. No propylene oxide or other oxygenated products were detected in these experiments.

Discussion

These results confirm that allyl radicals are formed on the surface of Bi_2O_3 and γ-bismuth molybdate at temperatures corresponding to those which are normally used in the partial oxidation of propylene. Part of the radicals desorb and these are carried downstream from the catalyst. The radicals may either be trapped in an argon matrix or undergo subsequent gas-phase reactions. The smaller rate of formation of gas-phase radicals over γ-bismuth molybdate compared with Bi_2O_3 is consistent with the mechanism outlined previously for the formation of acrolein. That is, over γ-bismuth molybdate an adsorbed allyl radical may rapidly react with an oxygen atom from the lattice and lose another hydrogen atom before it desorbs or at least before it exits from the catalyst bed.

At the other extreme one has MoO_3 which is ineffective in producing gas-phase radicals and scavenges those which are produced on other surfaces. Haber and Grzybowska[12] have suggested that in the formation of acrolein allyl radicals are produced on bismuth oxide centers and these radicals subsequently react to form acrolein on molybdenum oxide centers. The data of Table III, however, suggest that the conversion of allyl radicals to acrolein is not particularly efficient over MoO_3. Thus, it appears that the functions of the two oxides are not additive and that active sites consisting of bismuth, molybdenum, and oxygen are responsible for the oxidation of propylene to acrolein.

The role of gas-phase oxygen in promoting the formation of allyl radicals may be twofold. First, it is known that homogeneous

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abstraction of hydrogen from propylene occurs at high temperatures; however, this reaction is endothermic to the extent of ca. 40 kcal mol^{-1}. The resulting hydroperoxide ($\cdot HO_2$) radical was not detected in these experiments. The second, and more likely role of oxygen with the active catalysts, is to replenish the surface oxygen ions which were removed during the partial oxidation of propylene. This surface oxygen, perhaps in the form of O^- ions, is responsible for the abstraction of hydrogen.[13]

Although there is considerable speculation in the literature that allyl peroxy radicals are surface intermediates in the formation of acrolein over catalysts such as cuprous oxide,[14] zinc oxide,[6] and supported noble metals,[15] it is evident that most of the peroxy radicals in this experiment were formed in the cooler postcatalytic volume. Benson[16] has estimated that the value of K_{eq} for the gas-phase association reaction

$$C_3H_5\cdot + O_2 \rightleftarrows C_3H_5O_2\cdot$$

would be 0.1 atm^{-1} at 700 K, which means that $[C_3H_5O_2\cdot]/[C_3H_5\cdot] = 10^{-6}$ for an oxygen partial pressure at 10^{-5} atm. By contrast, at 300 K, $K_{eq} = 10^5$ atm^{-1}, and at the same oxygen partial pressure $[C_3H_5O_2\cdot]/[C_3H_5\cdot] = 1$, which is comparable to the ratios listed in Table I for oxygen-flow rates of 1.8×10^{-3} cm^3/s.

The activation energy of 14 kcal mol^{-1} is less than the value of 22 kcal mol^{-1} reported by White and Hightower,[17] for the catalytic reaction of propylene and oxygen to form 1,5-hexadiene over Bi_2O_3, and the value of 27.5 kcal mol^{-1} reported by Swift et al.,[4] for the cyclic reduction of Bi_2O_3. White and Hightower interpreted a large primary kinetic isotope effect as evidence for the cleavage of C–H bonds in the rate-limiting step of the catalytic reaction, and they proposed the symmetric π-allyl radical as the surface intermediate which leads to the formation of 1,5-hexadiene. We suggest that the nature of the surface sites will be a factor in the activation energy required for the breaking of the C-H bond, and considering the wide range of conditions employed in the experiments by the three different research groups, it is not surprising that the observed activation energies did not agree.

From the results of Table I we conclude that the ability of the various materials to form gas-phase π-allyl radicals decreases in the order $Bi_2O_3 >$ γ-bismuth molybdate > homogeneous–Pyrex. The rate of formation of gas-phase π-allyl radicals over α-bismuth molybdate was about equivalent to the background rate (homogeneous–Pyrex) whereas MoO_3 effectively consumed radicals that were formed elsewhere. The generation of surface radicals may indeed have been greater on the γ-bismuth molybdate than on Bi_2O_3, judging from the relative amounts of stable products, but in the former case reactions leading to the formation of acrolein were more rapid than the rate of desorption.

Although our results confirm the postulate of Keulks and coworkers[2] surface initiated, gas-phase intermediates such as allyl peroxide (or hydroperoxide) are formed during the reaction of propylene and oxygen over certain catalysts, we have not found evidence for propylene oxide and other oxygenated products which they observed. These inconsistencies may be the result of differences in the postcatalytic configurations of the two systems. In the earlier work the gas-phase radicals remained in a heated region at much greater pressures of oxygen; whereas, in our experiments the gases were rapidly swept into a cooler region at a much lower pressure.

The efficient production and recombination of gas-phase allyl radicals to form 1,5-hexadiene further emphasizes the need to consider postcatalytic reactions in the interpretation of results obtained over heterogeneous catalysts. It is premature to generalize concerning the importance of these surface-initiated, gas-phase radicals; however, one would expect that they may play a role in a variety of oxygen addition and oxidative dehydrogenation reactions.

Conclusions

1. Gas-phase π-allyl radicals are formed over the surface of Bi_2O_3 and γ-bismuth molybdate catalysts during the partial oxidation of propylene.

2. Over Bi_2O_3 gas-phase reactions between these allyl radicals serve as a major pathway for the formation of 1,5-hexadiene, which is the primary reaction product.

3. In the presence of excess oxygen the allyl radicals form allyl peroxy radicals, but the concentration of these radicals is limited by the equilibrium of the reaction.

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