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The Oxidation of Propene over Bismuth Oxide, Molybdenum Oxide, and Bismuth Molybdate Catalysts

IV. The Selective Oxidation of Propene

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A low-pressure static system, with mass spectrometric analysis of the gas phase, has been used to study the reactions of propene with bismuth molybdate, molybdenum oxide, and bismuth oxide in the absence and in the presence of gaseous oxygen at temperatures between 425 and 500°C. Propene reduces bismuth molybdate and the oxygen appearing in the gaseous products can be quantitatively replaced in the lattice; many layers of ions in the catalyst appear to be reduced. Acrolein forms nearly 80% of the products to nearly 50% conversion; the selectivity is higher with oxygen present, and the amount of carbon dioxide found is then greatly reduced relative to acrolein and carbon monoxide. The activation energy of acrolein formation is 31 ± 4 kcal in the absence of gaseous oxygen, and 17 ± 4 in its presence. Over molybdenum oxide the initial selectivity is much lower and more carbon monoxide is formed. The rate of oxidation of gaseous acrolein is rather slower on the molybdenum oxide than on the bismuth molybdate, and the selectivity of the bismuth molybdate is ascribed to alternative reactions of the adsorbed allylic hydrocarbon radicals. In particular, attention is drawn to the possible effects of oxygen gas and bismuth ions on the bonding of these radicals to the catalysts and the subsequent ease of desorption of acrolein.

INTRODUCTION

The ESR results described in Part II of this series show that Mo^{6+} in molybdenum oxide and bismuth molybdate catalysts is reduced to Mo^{5+} by propene, slowly at 225°C and much more rapidly at higher temperatures. Attempts to follow the adsorption of propene, using a sensitive Pirani gauge, were unsuccessful, but direct sampling of a low-volume reaction vessel by a mass spectrometer showed that propene reacts with the catalysts, slowly at 425°C and rapidly and extensively at 500°C (*1*). Comparison of the relative rates and selectivities of production of acrolein from propene, in the absence and presence of gaseous oxygen, suggests that the selective oxidation in the presence of oxygen proceeds by simultaneous reduction of the surface by propene and reoxidation by oxygen, in keeping with the general features of the mechanism proposed for the selective oxidation of butene to butadiene (*2*, *3*). Parallel studies were made of the oxidation of acrolein over the catalysts (*1*). This work, together with the results described in Parts II and III, allow proposals to be made for the best conditions for high selectivity in the oxidation and about the possible role of bismuth in the bismuth molybdate catalysts.

APPARATUS AND EXPERIMENTAL PROCEDURE

The Pyrex reaction vessel had an internal diameter of 1 cm and a volume of 15 ml, and was immersed in a furnace with

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controlled temperature. It was blackened to prevent photopolymerization of acrolein. The temperature of the sample was measured by a thermocouple strapped to the side of the vessel. The sampling probe was constructed by partially collapsing a Pyrex capillary; the "open" end of the capillary was sealed to a high vacuum line, opened to the pumps, and the constriction was heated with a soft gas flame until the vacuum gauge registered about 5 × 10^{-5} torr. This leak, suitably trimmed, was sealed inside a Pyrex tube and mounted about halfway down the vessel. The outlet from the leak was directly connected to a mass spectrometer (A.E.I. MS10).

The direct sampling leak was calibrated for various gas mixtures in the reaction vessel first using the pure gases described in Part I, and then known mixtures. The leak gave very satisfactory sampling with no fractionation for mixtures of C_3H_6, C_3H_4O, CO_2, CO, and O_2 over the range 0–100 torr with a time response of less than 1 sec.

The sample, weighed into the vessel, was activated as usual at 500°C with 150 torr of O_2 for at least 1 hr, followed by evacuation to 10^{-2} torr. The furnace was adjusted to the required temperature and the background spectrum recorded. The gases were admitted, and the required peak heights were measured at selected time intervals. After the end of some of the reduction runs, the amount of oxygen taken up by the catalyst during reoxidation at the reaction temperature was determined, together with any CO or CO_2 produced by this reoxidation.

An estimate of the time taken for the contents of the vessel to become sensibly uniform was made by treating the vessel as a one-dimensional diffusion system with various concentrations of "product" instantaneously formed and maintained at the sample end. The time for the concentration of this product to reach 95% of its "uniform" value at the far end of the tube was shown to be less than 5 sec with typical reaction pressures and compositions. Thus it was considered that reaction sampling closely resembled calibration sampling. Control experiments also showed that the rate of loss of gas through the leak was quite negligible under the experi-

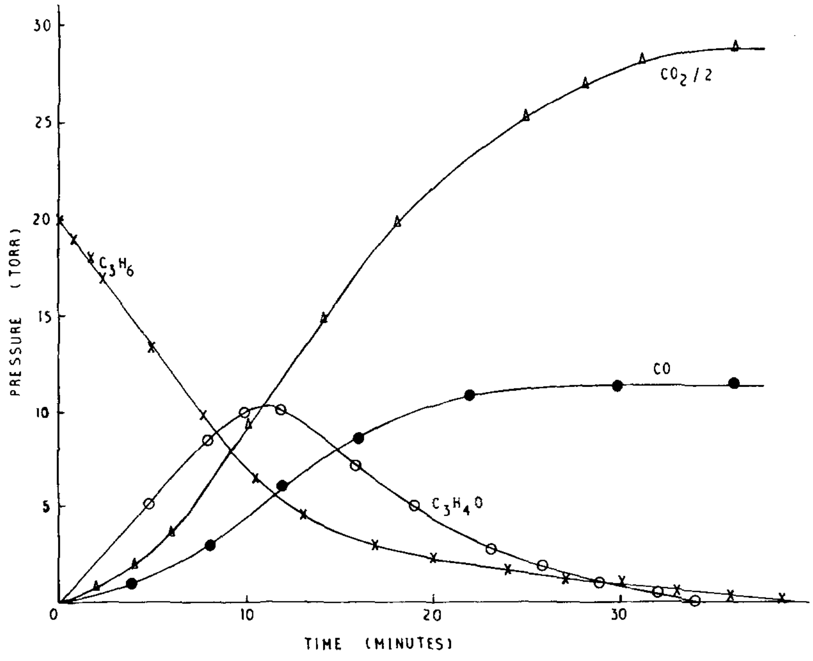

FIG. 1. Composition of gas phase from reaction of 20 torr C_3H_6 at 500°C over SBM-3.

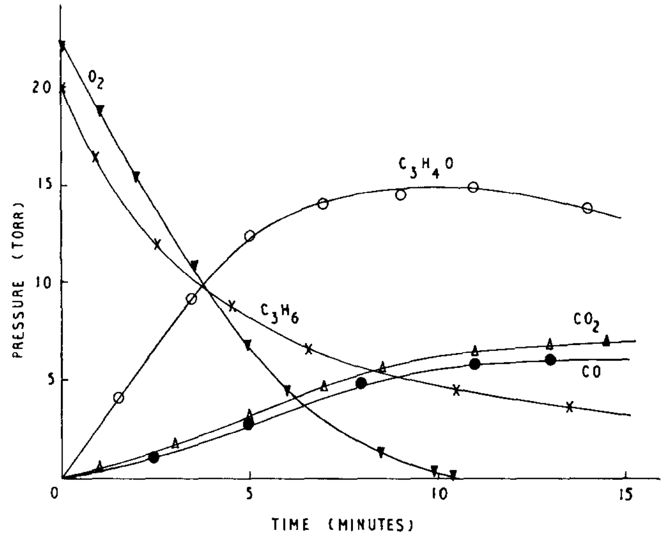

FIG. 2. Composition of gas phase from reaction of 20 torr C_3H_6 plus 22 torr O_2 at 500°C over SBM-3.

mental conditions used in the reactions with the catalyst.

RESULTS

Bismuth molybdate catalysts SBM-3 and UBM-4. Figure 1 shows the composition of the gas products during the reaction of propene over 0.07 g of catalyst SBM-3 at 500°C at an initial pressure of 20 torr in a volume of 15 ml. Particularly notable is the high initial rate of production of acrolein (1.15 torr min^{-1}) which is 81% of the initial rate of removal of propene (1.30 torr min^{-1}). The partial pressure of acrolein rises steadily to a fairly sharp maximum, and the rates of formation of CO and CO_2 increase from low initial values to maxima close to the time of the maximum acrolein pressure. It appears that most of the CO and CO_2 are formed by oxidation of the acrolein over this catalyst. The carbon balance through-

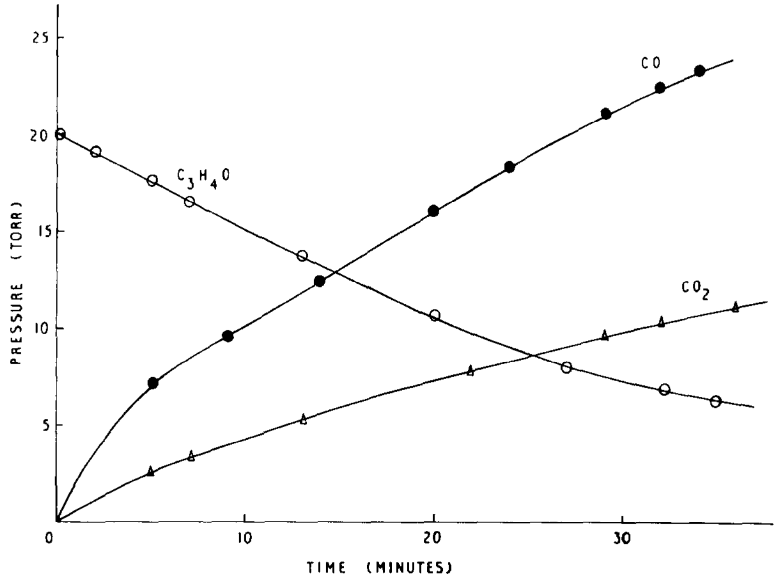

FIG. 3. Composition of gas phase from reaction of 20 torr C_3H_4O at 500°C over SBM-3.

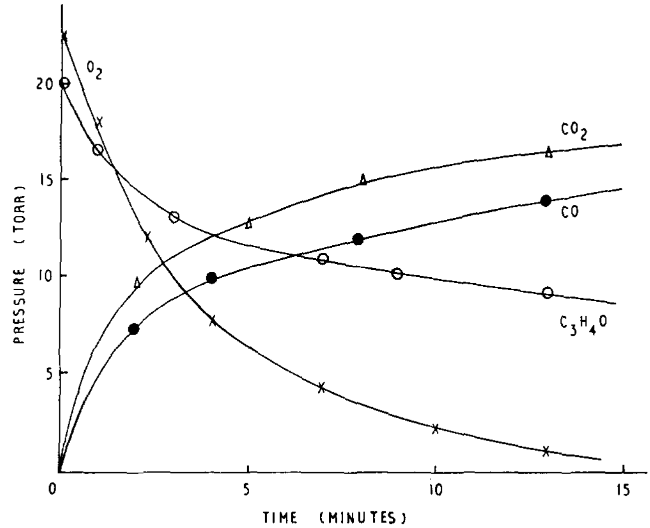

FIG. 4. Composition of gas phase from reaction of 20 torr C_3H_4O plus 22 torr O_2 at 500°C over SBM-3.

out the run suggests there is overestimation of products by 5–10% (as C); some of this may be overestimation of CO, as explained in Part I. However, it seems unlikely that any other compounds are formed in more than trace proportions.

At the end of one of the runs at 500°C, it was calculated that the observed products CO and CO_2, together with the product H_2O formed, it was assumed, by *all* the hydrogen in the original amount of propene, contained 1.80 (±0.06) × 10^{19} atoms of oxygen. On admitting a known amount of oxygen to the reduced catalyst at 500°C, it was found that 1.87 (±0.03) × 10^{19} atoms of oxygen were taken up by the catalyst. Several other checks were made, with similar results, and it appears that the propene is oxidized by the lattice oxygen which is replaced when gaseous oxygen is admitted. It was calculated that the sample (0.07 g

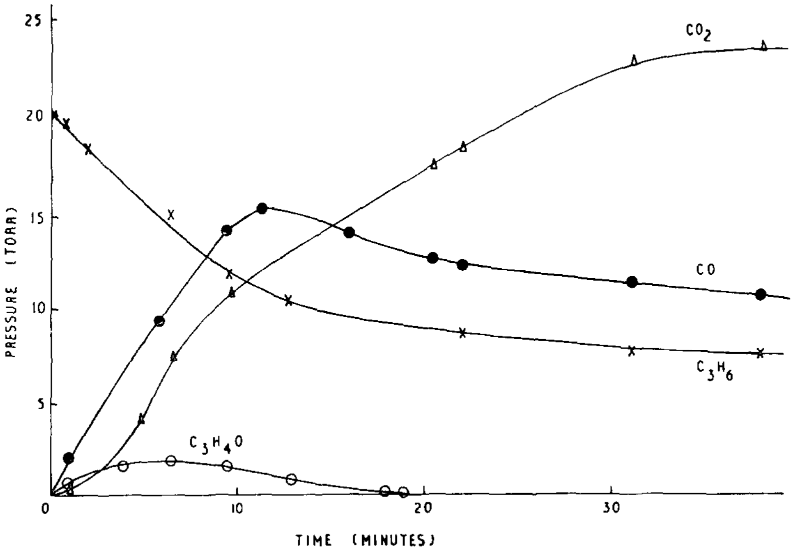

FIG. 5. Composition of gas phase from reaction of 20 torr C_3H_6 at 500°C over SM-2.

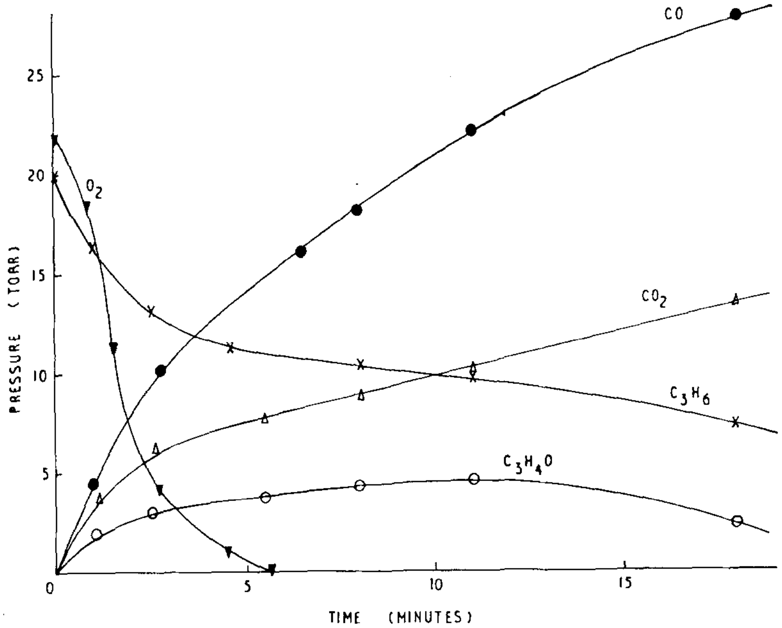

FIG. 6. Composition of gas phase from reaction of 20 torr C_3H_6 plus 22 torr O_2 at 500°C over SM-2.

of SBM-3) contained about 2×10^{20} atoms of O, assuming the bismuth is present as Bi_2O_3 and the molybdenum as MoO_3. Thus there are enough lattice oxygen atoms to produce the products, leaving the catalyst 9–10% reduced at the end of the run.

Very similar kinetic results were found at 475°C, but the acrolein peak is lower (about 5 torr) and the initial rates are about one-third of the values at 500°C. At 425°C the rates have dropped to one-thirteenth of the 500°C values. These changes of rate with temperature correspond to an activation energy of 31 ± 4 kcal.

Figure 2 shows the results of reacting 20 torr of propene and 22 torr of oxygen over the catalyst SBM-3. The early rates of removal of oxygen and propene are nearly the same (3.6 and 3.5 torr min^{-1}) and the

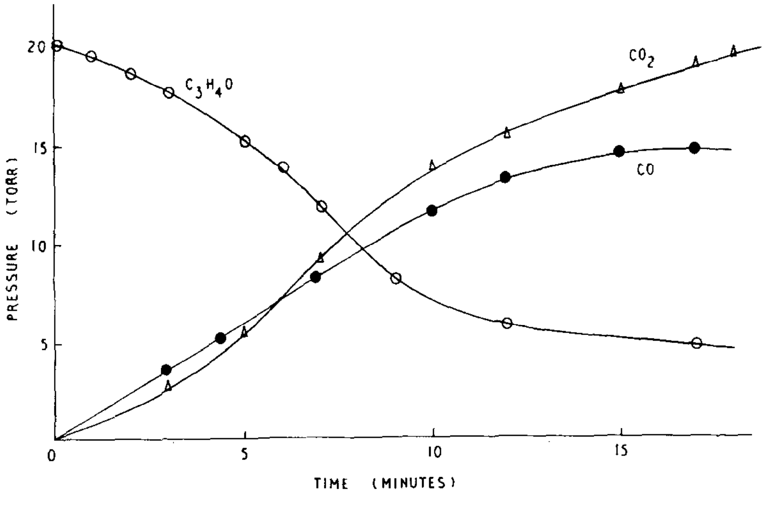

FIG. 7. Composition of gas phase from reaction of 20 torr C_3H_4O at 500°C over SM-2.

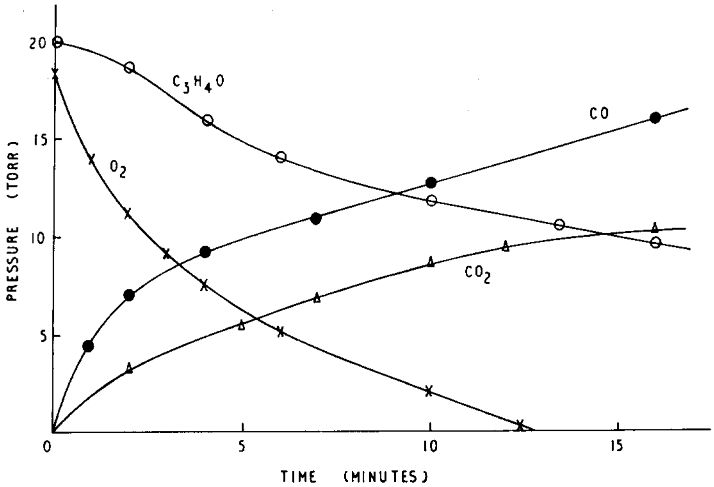

FIG. 8. Composition of gas phase from reaction of 20 torr C_3H_4O plus 18 torr O_2 at 500°C over SM-2.

selectivity for propene → acrolein is about 83%. These results point to the principal reaction being

$$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O.$$

Also, with O_2 present, the selectivity is maintained for longer, and the peak pressure of acrolein is higher and occurs later; considerably less CO and much less CO_2 are produced than in the absence of O_2. The oxygen is fully consumed in 10 min, and is removed at a nearly constant rate until 75–80% is consumed. After 10 min the propene and the acrolein are still being slowly oxidized by the lattice oxygen.

Very similar results were obtained at 475 and 425°C. The oxygen is consumed at a practically constant rate, agreeing with the zero-order rate law found in flow systems for this reactant. The propene is removed in a reaction of higher order, roughly first, and the initial selectivities remained high, in agreement with the catalytic tests described in Part I. The effect of changing the temperature is not as great as in the absence of oxygen, corresponding to an activation energy, for the initial rates of production of acrolein, of 17 ± 1 instead of 31 ± 4 kcal.

Catalyst UBM-4 was found to display the same features as SBM-3, both with and without oxygen present.

The reactions of acrolein, and of acrolein and oxygen, were briefly studied over SBM-3. Figure 3 shows that 20 torr of acrolein were oxidized at a nearly constant rate of about 0.5 torr min^{-1} for a long period at 500°C—thus the rate is about 0.4 of the rate of oxidation of a similar pressure of propene at this temperature. Figure 4 shows that with 22 torr of oxygen present oxygen is removed more rapidly throughout the run; the initial rate of removal of acrolein is high (3.3 torr min^{-1}) and nearly equal to the rate of removal of propene in oxygen (3.6 torr min^{-1}). However, it is most important to note that the rate declines very rapidly, and after 40% of the acrolein has been removed (leaving 12 torr acrolein and 5 torr oxygen) the rate is only 0.33 torr min^{-1}. Thus acrolein oxidation seems to be much more sensitive to the oxygen partial pressure than propene oxidation. It follows that if propene and oxygen are admitted to a catalyst at 500°C, by the time the acrolein concentration has built up to a level equal to that of the remaining gas-phase propene the lower oxygen pressure that is then present in the gas phase leads to only a relatively low rate of acrolein oxidation. This partially explains why the selectivity is maintained in the reaction of propene and oxygen, and is in complete contrast to the results on SM-2 which are described next.

Reactions over SM-2. Reactions of propene or acrolein with and without oxygen present, were carried out over 0.04 g of

SM-2 (Figs. 5–8) at 500°C, for comparison with the results obtained on SBM-3. The mass balances with propene were again good, being accurate to about 5% on a carbon or oxygen basis (assuming that all the hydrogen lost by the propene is converted to water). Those found with acrolein were less satisfactory, being accurate to only 10% later in the reactions. The quantity of oxygen taken up by the reduced catalyst after reaction with propene closely corresponded to the oxygen in the products, so once again the catalyst is quantitatively reduced by the propene. However, the progress of the reactions and the product distributions are very different from those with SBM-3.

The rate of propene removal is slower over the SM-2 sample, and falls off rapidly as the catalyst is reduced (Fig. 5), whereas on SBM-3 the higher initial rate is sustained for nearly 75% conversion of propene (Fig. 1). In the presence of gaseous oxygen, however, the rate of removal of propene is increased by a bigger factor with SM-2 than with SBM-3, so that the rates in the presence of oxygen become nearly equal (3.18 torr min^{-1} over SBM-3, Fig. 2, and 3.33 torr min^{-1} over SM-2, Fig. 6). However, although *oxygen* is initially removed at the same rate as propene (Fig. 6) the rate *increases*, and this appears to be because of oxidation of the intermediate C_3H_4O. Reference to Figs. 7 and 8 show that over SM-2 the oxidation of acrolein *increases* in rate as the reaction proceeds, in contrast to the behaviour with SBM-3 (Figs. 3 and 4), where the rate is constant or *decreases* at higher conversions. These differences partially explain why acrolein does not accumulate when SM-2 is used, whereas it accumulates, giving sustained selectivity, to higher conversions over SBM-3.

It is difficult to determine the *initial* selectivity to acrolein over SM-2, because of the pronounced early curvature of the acrolein-time plots in Figs. 5 and 6. It appears to be about 50–60%; the lower values found in flow systems (e.g., Fig. 3 in Part I), are easily explained by the rapid decline in selectivity caused by the oxidation of acrolein mentioned above. However, the initial distribution of products CO and CO_2, relative to acrolein, is different on SM-2 and SBM-3. Relatively more CO is formed over SM-2 from the start (compare Figs. 6 and 2, and also Figs. 5 and 1). This points to the production of CO and CO_2 by a path, other than through acrolein, which is faster on SM-2 than on SBM-3. The autocatalytic shape of the curves in Figs. 7 and 8 are reminiscent of gas-phase oxidations of hydrocarbons; however, the effects seen here are undoubtedly heterogeneously catalytic as they occur with SM-2 but not with SBM-3, at the same temperature. Without further experimental information their cause remains unknown. In retrospect, it would have been interesting to see if the addition of propene altered the curves shown in Figs. 7 and 8 to test whether it is valid to assume that these curves apply to the oxidation of acrolein in the presence of propene. It is however, known that acrolein does not alter the rate of conversion of propene in flow systems unless present in very high concentrations, suggesting no coupling of the reactions (*4*). The reactions over SM-2 at other temperatures were not investigated.

Reactions over SB-2. These were not investigated in any detail as the system is not interesting catalytically. It was shown that propene reacts only very slowly with SB-2 at 500°, giving mostly CO_2 and some CO but no detectable C_3H_4O. With 20 torr of propene and 20 torr of oxygen, the oxygen is removed rapidly (completely within 7 min) and some propene is oxidized to give CO and CO_2 in a final ratio 1:4, with no sign of other carbon compounds.

DISCUSSION

It is clear from these results that propene can be oxidized rapidly and extensively by the solid catalysts SBM-3 and SM-2. The initial reaction with SBM-3 is very highly selective for the formation of acrolein, that with SM-2 less selective. The reduced SBM-3 can be reoxidized by oxygen, with quantitative replacement of the lattice oxygen removed by reduction.

The activation energy for the reduction of SBM-3 by propene is about 31 ± 4 kcal. It is very interesting to note that this is close to the value found by Batist *et al.* (*2, 3*) for the reduction of bismuth molybdate by 1-butene. It seems likely that on the reduced catalysts the rate of oxidation of propene or butene is limited by diffusion of oxygen to the surface. In the presence of gaseous oxygen, this step would not be necessary, and the oxidation depends on some other step which in the case of propene has an activation energy of 17 ± 3 kcal. This may be the initial activated chemisorption of the propene.

With mixtures of propene and oxygen, the initial rates of removal of propene are nearly the same over both catalysts, and are 2.5–3.5 times the rate in the absence of oxygen. The high initial selectivity over SBM-3 is sustained, whereas the lower initial selectivity over SM-2 falls further; this difference can be attributed to the increase in the rate of removal of acrolein over SM-2 as the reaction proceeds, in contrast to the low rate of acrolein oxidation over SBM-3 when the catalyst is partially reduced.

As was presented in Part III, when propene and oxygen are reacting over SBM-3 and SM-2, both catalysts are in reduced states, but to different extents. Bismuth molybdate is about 10% reduced, while molybdenum oxide is only very slightly reduced. This suggests strongly that in each case the mechanism of oxidation is successive reaction of propene with lattice oxygen, followed by replacement of oxide ions from gaseous oxygen, rather than reaction of propene with oxygen chemisorbed on the surface of a stoichiometric oxide. It is also essential to recall the arguments of Part II, where it was pointed out that the greater reduction of the bismuth molybdate does not necessarily mean that *molybdenum* ions are in a lower oxidation state on these surfaces than on molybdenum oxide; it was suggested that ease of reduction of Bi^{3+} might also account for the disappearance of Mo^{5+} signals by reactions like $Bi^{3+} + Mo^{5+} \rightarrow Mo^{6+} + Bi^{2+}$.

These suggestions can help to account for the improved selectivity shown in bismuth molybdate compared with molybdenum oxide. If the initial step is the same on each catalyst, and is formulated as in Part II,

$$C_3H_6 + Mo^{6+} + O^{2-} \rightarrow [C_3H_5\text{--}Mo]^{6+} + OH^- + e^-, \quad (I)$$

then on molybdenum oxide the electron may be localized on, and reduce, a second Mo^{6+}, or be localized on the chemisorption complex. In the latter case, the allyl species would be more strongly bonded to molybdenum, but the C–C bonds would probably be relatively weakened, as noted in Part II. Hence C–C fission within the allyl species could increase the rate of formation of CO and CO_2 by a route not involving acrolein, in competition with oxidation of the allyl species to acrolein. If the electron reduces a second molybdenum ion to Mo^{5+}, this could provide a site for chemisorption of propene by a reaction similar to Eq. (I), but giving a complex more strongly bonded than in (I), and which would undergo the competitive reactions discussed above. Moreover, molybdenum ions in still lower oxidation states would increase this trend.

On the other hand, if the electron in Eq. (I) can be localized on bismuth ions, the bonding of the allyl species to the molybdenum remains weak; the C–C fission reaction is less likely, and also when the acrolein is formed, its 1–3 conjugation weakens the σ-bond to the molybdenum and allows easy desorption.

Thus the bismuth possibly allows a greater fraction of the molybdenum ions to remain in, or return to, higher oxidation states than for the pure molybdenum oxide, with resulting changes in bonding of the allyl species which favor reactions 1 rather

than 2. Reaction 3 does not assume major importance until later conversions, when it is more important over molybdenum oxide than over bismuth molybdates. The combined effects produce a lower initial selectivity, and a much lower later selectivity, over molybdenum oxide.

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