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

III. Electrical Conductivities of Bismuth Molybdate, MoO_3 and Bi_2O_3

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On exposure to propene, 1-butene or hydrogen, pressed discs of the catalysts bismuth molybdate and molybdenum oxide show rapid and reproducible increases of electrical conductivity at temperatures between 400 and 550°C. The conductivities decrease to their original values on reoxidation by gaseous oxygen. At any selected stage of reduction or reoxidation, the rates of reduction or reoxidation are linear functions of the gas pressures. If the gases are removed at a given extent of reduction, the conductivities then change with temperature as expected for semiconductors, and the energy gaps fall to very low values on moderately-reduced catalysts. In the presence of an excess of a 1:1 mixture of propene and oxygen, bismuth molybdate shows a nearly constant conductivity corresponding to roughly 10% reduction, and this extent of reduction varies only slightly as the proportions of propene and oxygen are changed from 9:1 to 1:9. With 1:1 mixtures of the gases molybdenum oxide appears to be reduced to only a very small extent. Bismuth oxide shows an initial decrease of conductivity followed by an increase when contacted with propene, and the conductivity falls on reoxidation.

The oxides MoO_3 and Bi_2O_3 and the mixed oxides are semiconductors, the conductivities depending markedly upon the preparation and pretreatment. The MoO_3 is an *n*-type semiconductor, with an energy gap between 1.0 and 1.4 eV for a single crystal (*1*) at 400°C, and 0.9 eV for a polycrystalline sample (*2*). The Bi_2O_3 is a *p*-type semiconductor at normal temperatures and pressures, but becomes *n*-type at temperatures above 550°C and oxygen pressures below 10^{-3} torr, because of loss of oxygen (*3*). Bismuth molybdates have been reported (*4*) as *n*-type semiconductors at 290–500° with an energy gap of about 1.0 eV. Margolis (*5*) showed that the conductivity of the bismuth molybdates was at a maximum at Bi/Mo ratios close to the composition giving maximum selectivity for the oxidation of propene, while Gel'bshtein (*6*) stated that the conductivity was inversely proportional to the activity of the catalysts for the oxidation and oxidative ammonolysis of propene. Little detail was given of the experimental conditions for these studies. After our experimental work was completed, conductimetric studies of the reduction by propene, followed by reoxidation, of MoO_3, Bi_2O_3, and bismuth molybdate were reported by Pluta (*7*): his results are compared with ours in the "Discussion."

Our work comprised dc and low frequency ac measurements of the resistance of pressed discs of the catalysts. The aim was to detect and measure the relative rates of reduction and oxidation of the surfaces, as preliminary experiments showed that extensive conductivity changes occurred and varied with the reaction condi-

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tions. No attempt is made to apply boundary layer semiconductor theory in any detail to our results. Their chief importance lies in the information they give about the net states of reduction of the catalyst surfaces during the early stages of the selective and nonselective oxidation of propene.

APPARATUS AND EXPERIMENTAL PROCEDURE

The sample to be examined was compacted into a disc containing two electrodes, each made from a 5-mm square of 30 mesh platinum gauze on to which platinum leads (0.3 mm diam) were spot-welded. The final disc was about 2 mm thick and 10 mm diameter, with the electrodes about 1 mm apart. The discs were pressed at 2×10^4 kg/cm^2 in a circular die. Most of the work was done on an unsupported sample of bismuth molybdate (UBM-4) but comparative runs on SBM-3 established that they behaved in an essentially identical manner. For MoO_3, only the supported catalyst SM-2 could be compacted satisfactorily. For Bi_2O_3, the catalyst UB-3 was used. Measurements on any one disc were reproducible with surprising accuracy in separate runs after quite different intermediate treatments. However, as the exact geometry of the discs could not be specified, it is only possible to compare results on different discs in a semiquantitative manner.

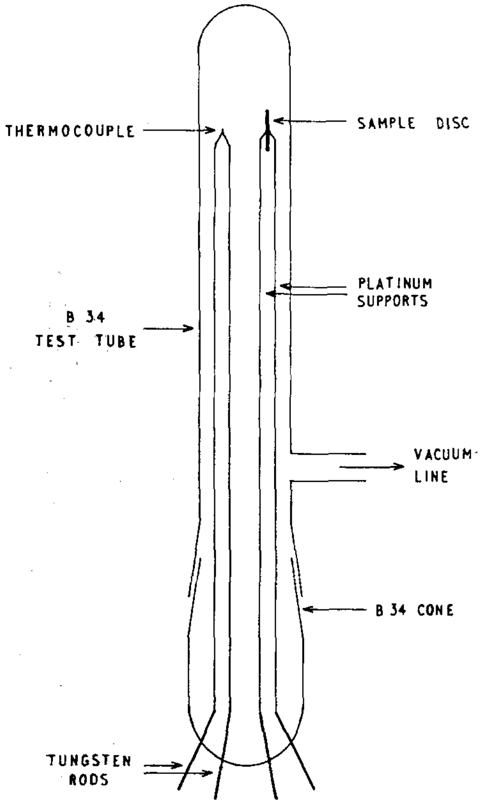

FIG. 1. The conductivity cell.

The conductivity cell (Fig. 1) had a total volume of about 150 ml, so that little loss of the reducing gas occurred in the short times of reduction used. The cell was attached to the vacuum line and immersed in and surrounded by a furnace at a controlled temperature. The disc was on the axis of the cell and the internal thermocouple was placed very close to its center; it was found in practice easy to establish and maintain the disc temperature.

For the dc measurements, a stable emf (E volts) from a high capacity Leclanché dry cell, was connected by single core screened earthed coaxial cable across the disc in series with a variable resistance (R_B ohms), and the potential drop (V volts) across the disc was measured with a high impedance "Vibron" electrometer (model 33B). If R_D is the disc resistance, then

$$R_D = \frac{VR_B}{(E - V)} \text{ ohms.}$$

The potential V was recorded continuously on one channel of a matched dual-channel milliametric recorder, while the temperature was recorded on the second channel via another "Vibron" electrometer.

The results for the UBM-4 sample were checked with an ac Cambridge Instrument Company conductivity bridge at 1000 cycle sec^{-1}. There was excellent agreement of the values obtained over the total range of resistances measured (roughly 10 to 10^7 ohms) (*8*).

All the results are reported as conductances, i.e., as $\sigma = 1/R_D$. The uncertain geometry of the discs made it pointless to

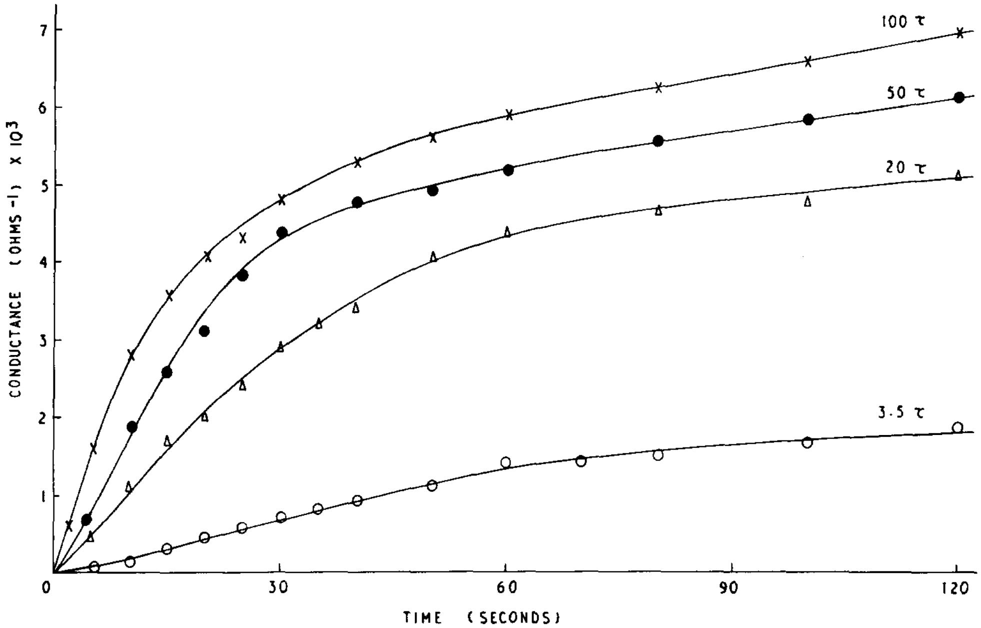

FIG. 2. Change of conductance with time for various pressures of C_3H_6 over UBM-4 at 500°C.

calculate the corresponding specific conductances.

RESULTS

Bismuth Molybdates. Preliminary work showed that the UBM-4 disc had a stable conductance after activation in oxygen at 500° of 2.3×10^{-6} ohm^{-1}, in the absence of tap grease vapor. Some small changes on evacuation were traced to a transient fall of temperature, or to reduction by grease vapor in "unguarded" systems.

The effects of admitting various pressures of C_3H_6 to the activated disc is shown in Fig. 2; changes of conductance occurred over three orders of magnitude. The reoxidation of the disc after reduction to a standard conductance of 2.5×10^{-3} ohm^{-1} is shown in Fig. 3. The conductance of the activated disc was restored only after a longer period of time than that shown in Fig. 3.

If we assume that a given conductance corresponds to a definite state of the surface and underlying layers of the catalyst, it is possible to determine how the rates of oxidation and reduction depend on the pressure of oxygen and propene respectively. Figure 4 shows that the rate of reduction of a partially reduced surface is directly proportional to the ambient propene pressure and also decreases as the catalyst conductance increases. Similarly, Fig. 5 shows that the rate of oxidation of a partially reduced surface depends linearly on the ambient oxygen pressure, and that the rate decreases as the conductance decreases. Furthermore, at equal pressures the rate of reduction of the activated sample is much greater than the rate of oxidation of a highly reduced sample. It follows that there is some partially reduced surface where the rates of reduction and oxidation by an equimolar mixture would be equal. Careful examination of plots like those in Figs. 4 and 5 leads to the conclusion that a steady state should occur with the conductance around 4×10^{-4} ohm^{-1}.

This conclusion was substantiated by experiments in which various mixtures of propene and oxygen were admitted to UBM-4 samples in the conductance cell at 500°C. Figure 6 shows that there is a rapid initial change of conductance, followed by a much slower change, which may be due to slow changes in composition of the ambient gas

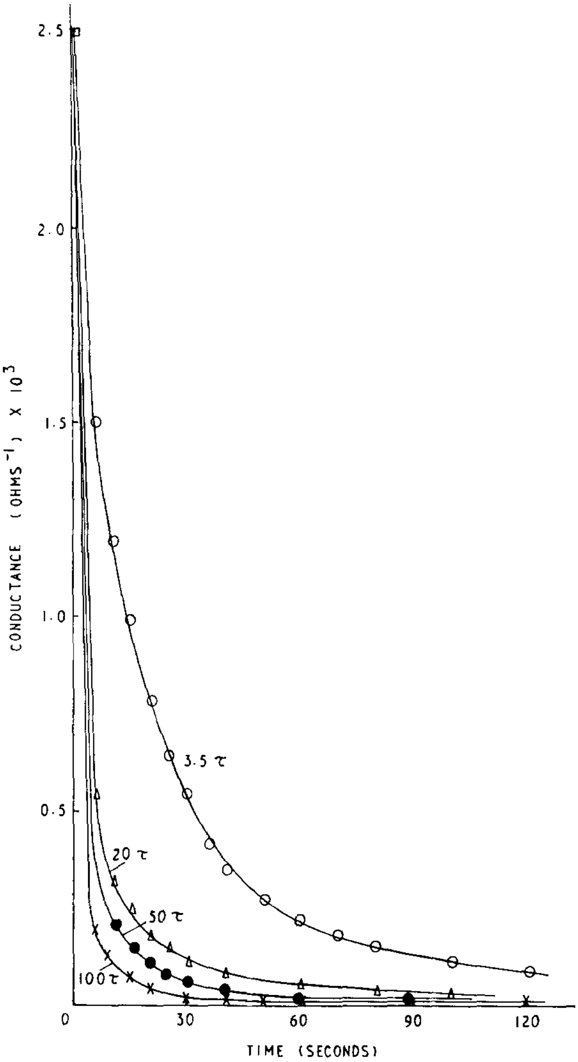

FIG. 3. Change of conductance with time for various pressures of O_2 over reduced UBM-4 at 500°C.

phase mixture in accordance with the investigations reported in Part IV. However, the disc conductivity for mixtures containing between 10 and 70% of propene is close to the predicted value of 4×10^{-4} ohm^{-1}. In total, these results show two factors of importance. Firstly, the conductance changes shown in Fig. 6 suggest that the bismuth molybdate catalysts are about 10% reduced when the catalyst is operating in its normal "steady-state" conditions with mixtures of propene and oxygen. Secondly, the agreement between the experimentally determined steady-state conductance and that predicted above could be taken as evidence that the reactions of propene and oxygen with the catalyst are quite independent, with the latter gas simply serving to replace lattice oxygen ions removed during oxidation of chemisorbed propene.

Experiments at other temperatures showed that the rates of reduction and oxidation are greater at higher temperatures (Fig. 7). As the conductance itself varies with temperature, it is not valid to use the rates at identical conductances in attempts to determine the activation energies of the reduction and oxidation reactions. However, in studying this problem it emerged that the catalyst, if reduced to a given con-

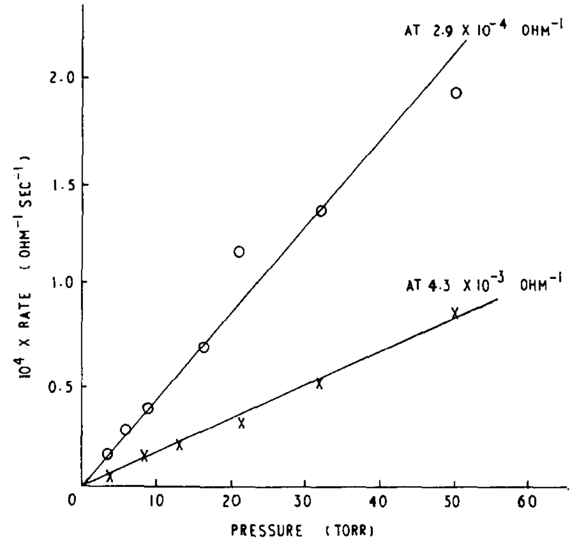

FIG. 4. Rate of change of conductance with C_3H_6 pressure at two different reduction (conductance) levels of UBM-4 at 500°C.

ductance, could be evacuated and then cycled repeatedly through substantial temperature changes. Such cycles led to linear plots of log σ against 1/T, so that the conductances, σ, fit the theoretical equation for a semiconductor

$$\sigma = A \exp(-E/2kT) \qquad (1)$$

where E is the energy gap and A is a constant for each reduction state. Figure 8 shows two such plots, typical of many determined for UBM-4 and for SBM-3 at different states of reduction. Table 1 shows the energy gaps calculated for the fully activated UBM-3 and for different extents of reduction by propene, 1-butene and hydrogen, while Table 2 shows similar results for SBM-3.

An interesting feature of these results is that they indicate a considerable perturbation of the band structure of the catalysts under the reaction conditions. Consequently, one may expect little relationship between predictions of catalyst behavior and performance based on a boundary layer theory and those found in practice. It

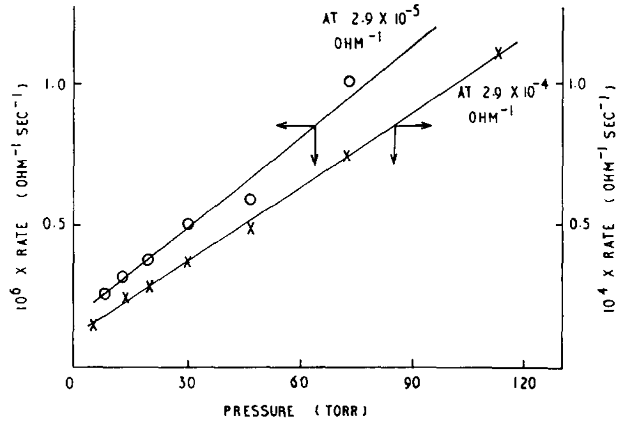

FIG. 5. Rate of change of conductance with O_2 pressure at two different reduction (conductance) levels of UBM-4 at 500°C.

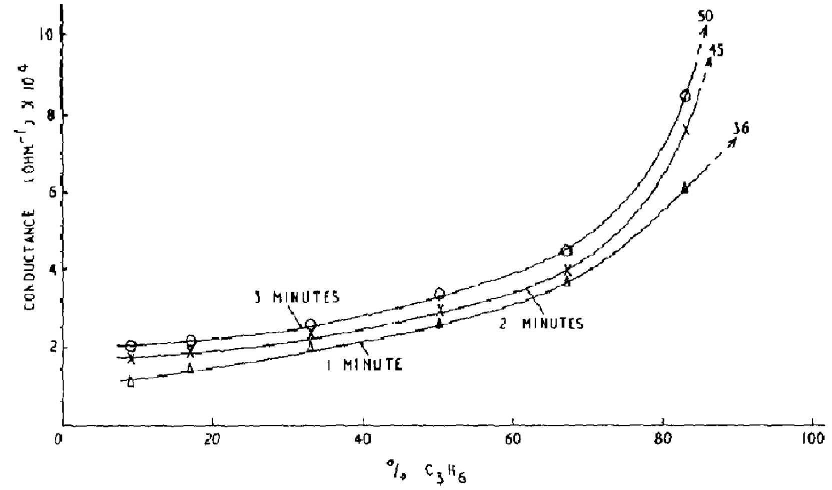

FIG. 6. Variation of conductance at 1-, 2-, and 3-min exposure of UBM-4 to 20 torr of mixture $C_3H_6 + O_2$ at 500°C. (The values at the right show the corresponding ordinates for 100% C_3H_6.)

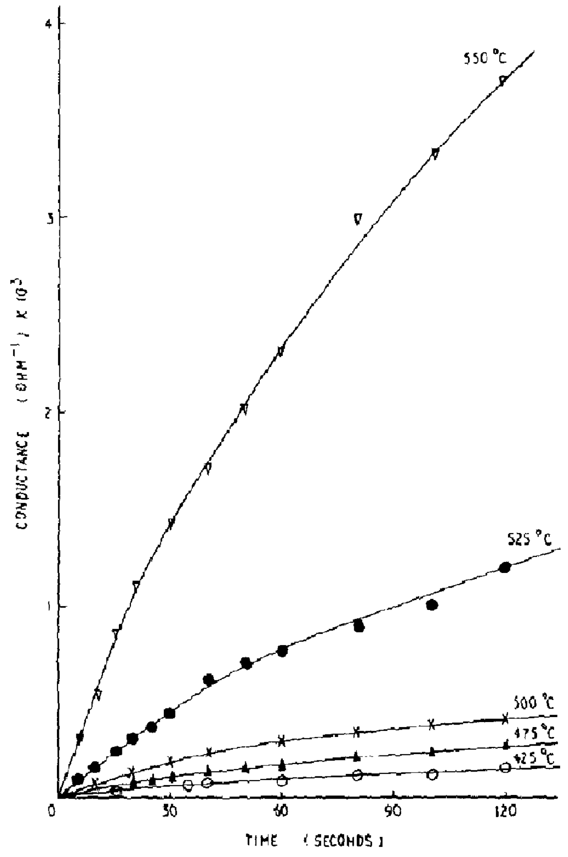

FIG. 7. Change of conductance with time of UBM-4 at 425, 475, 500, 525, and 550°C on exposure to 5 torr of propene.

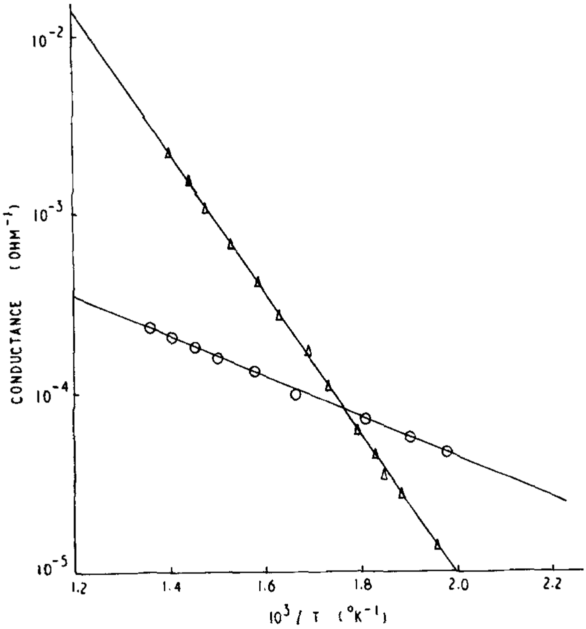

FIG. 8. Plots of conductance versus reciprocal of temperature for: (△), UBM-4 after reduction with 20 torr H_2 at 550°C for 10 min; (○), SBM-3 after reduction with 20 torr C_3H_6 at 450°C for 50 min.

is also noticeable that radiation of "frequencies" greater than $2.5–3.0 \times 10^3$ cm^{-1} would be of sufficient energy to induce electronic transitions into the conduction bands. This explains why the infrared studies of the catalysts under reducing conditions, mentioned in Part I, show 100% adsorption in that region, namely 2800–3300 cm^{-1}, where one would look for bands associated with chemisorbed hydrocarbon species.

Further experiments at 450 and 500°C showed that the rate of increase of conductance of UBM-4 was greater when reducing with 1-butene than with propene, and the rate with hydrogen was about an order of magnitude smaller. These results are in keeping with rates of reduction revealed by the ESR experiments described in Part II.

MoO_3. We have not made full studies of MoO_3 and Bi_2O_3 catalysts and only key experiments for comparison with particular

TABLE 1
ENERGY GAPS FOR UBM-4

State	Reduction time (min)	Temp. (°C)	E(eV)
Activated in O_2	—	500	2.14
Reduced by 20 torr C_3H_6	15	450	0.66
	35		0.56
	80		0.30
	150		0.00
Reduced by 20 torr 1-butene	10	500	1.55
	25		0.06
Reduced by 20 torr H_2	10	550	1.49
	35	500	1.48
	60		0.00

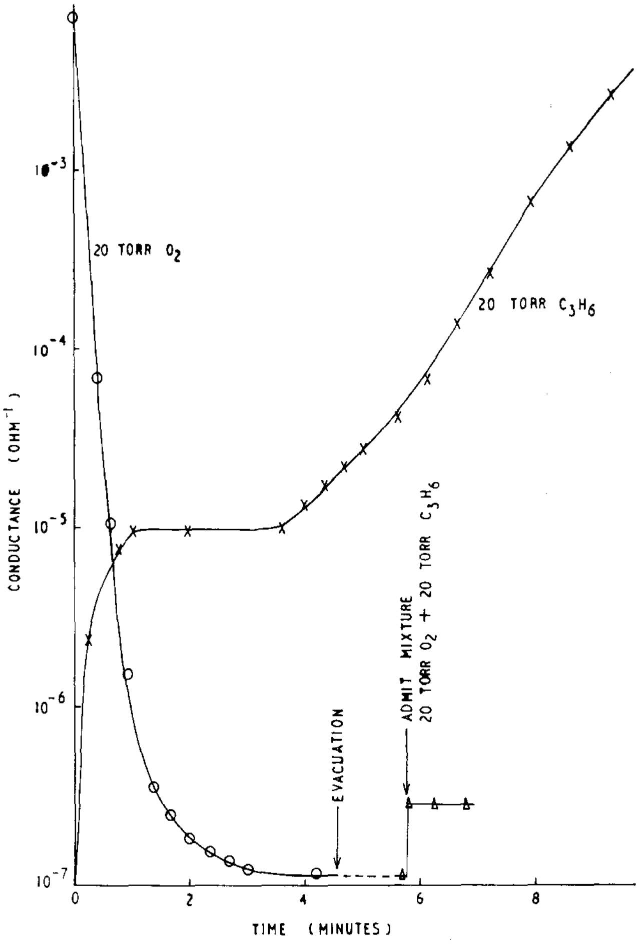

FIG. 9. Change of conductance with time of SM-2 at 500°C on exposure to C_3H_6 or O_2 or a mixture of the gases.

features of the work on bismuth molybdate catalysts were carried out. In particular, the effects of reduction and reoxidation at 500°C were determined for selected pressures of C_3H_6 and O_2 and a mixture of the gases, but the pressure dependence of the rates of change of conductance were not investigated. The energy gaps for activated

TABLE 2

ENERGY GAPS FOR SBM-3

State	Reduction time (min)	Temp. (°C)	E(eV)
Activated in O_2	—	550	2.55
Reduced by 20 torr C_3H_6	10	450	1.61
	35		0.85
	50		0.42
	90		0.00
Reduced by 20 torr H_2	5	450	2.12

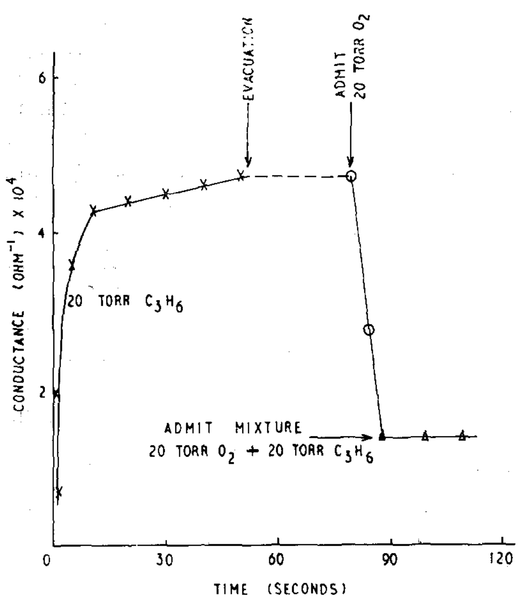

FIG. 10. Change of conductance with time of UB-3 at 500°C on exposure to C_3H_6 or O_2 or a mixture of the gases.

and reduced surfaces were investigated by the technique used for bismuth molybdate.

Figure 9 shows that the conductance of an active sample of SM-2, which when isolated had a steady value around 10^{-7} ohm^{-1}, increases rapidly on admission of 20 torr of C_3H_6 at 500°C. There is a marked arrest at 10^{-5} ohm^{-1}, followed by an increasing rate of conductance rise. No explanation has been found of this strange but reproducible effect, reminiscent of phenomena connected with phase changes in solid–gas systems.

As clearly shown in Fig. 9, the rate of reoxidation is fast, relative to the rate of reduction, at conductances down to 10^{-6} ohm^{-1}. Consequently it would be expected that in the presence of mixtures of C_3H_6 and O_2 the equilibrium state would lie well towards the oxidized state. This is confirmed by the measured conductance of 2.7×10^{-7} found on admitting a mixture of 20 torr of C_3H_6 and 20 torr of O_2. This well-oxidized state is in contrast to the 10% reduced state found under corresponding conditions with bismuth molybdate catalysts.

The variation of conductance with temperature for activated and partially reduced samples, *in vacuo,* was found to give linear plots of log σ against 1/T, from which the energy gaps were calculated. Values for SM-2 are tabulated with those for UB-3 in Table 3.

It was noticed, as with bismuth molybdate, that unless the vapors of tap grease were excluded the conductance of SM-2 *in vacuo* rose slowly. In addition, with prolonged use the disc became whiter and blue MoO_3 was deposited in cooler parts of the cell. This did not appear to affect the conductance measurements, perhaps because the interior of the disc was not altered.

Bi_2O_3. A disc of UB-3 was used for these measurements. When activated, this disc showed a steady fall of conductance *in vacuo,* in complete contrast to the bismuth molybdate and the MoO_3. It was found that a steady pressure of oxygen over UB-3

TABLE 3

ENERGY GAPS FOR MoO_3 AND Bi_2O_3 AT 500°C

Catalyst	State	Reduction time (min)	E(eV)
SM-2	Activated	—	1.82
	Reduced by 20 torr C_3H_6	5	1.62
	Reduced by 20 torr C_3H_6	60	0.00
UB-3	In presence of 150 torr O_2	—	1.18
	Evacuated to 10^{-3} torr O_2	—	1.31
	Reduced by 20 torr C_3H_6	3	1.18
	Reduced by 20 torr C_3H_6	60	0.00

produced a steady value of the conductance, but the conductance depends on the oxygen pressure. On evacuating the disc, the conductance fell as dissociation occurred, but rose rapidly on admitting 20 torr of C_3H_6. On replacing the C_3H_6 by 20 torr of O_2 the conductance fell as expected. An equimolar mixture of C_3H_6 and O_2 left the catalyst in an oxidized state, as shown in Fig. 10.

DISCUSSION

A notable feature of the results is the reproducibility of the conductance measurements. This is shown by concordant values after many cycles of reduction and oxidation and by the stability of the conductances of the partially reduced catalysts when the gases were removed. Not even the changes of temperature from 500 to 225°C and back, used in the determination of the energy gaps, caused variations of the conductances under standard conditions. This stability points to the virtual absence of effects from transient or chemisorbed species, and suggests that major changes in the lattice ions themselves cause the changes in conductance.

The results of Part II show changes in the oxidation states of Mo ions, while those of Part IV show that the lattice oxygen used to oxidize propene to acrolein, CO, CO_2, and H_2O can be replaced by exposure to gaseous oxygen quite rapidly at 500°C; consequently, there seems little doubt that the increases in conductance are brought about by extensive reduction of the surface layers of the catalysts, and the decreases by reoxidation of the reduced surfaces. We are not concerned with comparatively small and condition-sensitive chemisorption effects, at any rate at the temperature used. The direction of these changes are in agreement with the known assignment of MoO_3 and the bismuth molybdates as *n*-type semiconductors. The effects of oxygen removal or addition on the conductance of Bi_2O_3 agree with its assignment as a *p*-type semiconductor; but the reversal on exposure to C_3H_6 suggests that some more substantial change then occurs and the type of conduction becomes *n*-type like that of MoO_3 or bismuth molybdate. It has been reported previously that such a change occurs at 550° as oxygen is lost on evacuation (*3*), which would result in similar but less extensive reduction than with C_3H_6. These effects are important in comparing our results with those recently published by Pluta (*7*).

Pluta reduced the separate oxides and bismuth molybdate with propene, and reoxidized with air, as well as examining the effects of evacuating the sample after reduction. His temperatures were rather lower than ours, and he used atmospheric pressures of the gases. The reduction of bismuth molybdate produced a marked increase in conductance, the change occurring at faster rates at higher temperatures. After 31 min the gases were removed resulting in steady conductances at 410°C. These results are like ours. Evacuation at lower temperatures (380 and 340°C) resulted in a continuation of the rise of conductance, as though a solid state reaction lagged behind the surface changes. The reoxidation was rapid, as we found, at all temperatures. On molybdenum oxide, his results were also similar to ours. On bismuth oxide his results for reduction and for evacuation closely resemble ours, but the reoxidation seems at first sight to be directly contradictory to ours, as he finds a decrease in conductance with propene and an increase on exposure to air. However, the temperatures were lower than in our experiment (380, 420, and 460°C compared with 500°C) and it may be that the reversal of semiconductor type does not occur, or occurs much more slowly, at lower temperatures.

It is clear that these systems, showing large changes of conductance and a marked decrease of energy gap on reduction, would be interesting tests of semiconductor theory. Some further attempts to disentangle the effects of temperature on conductance and on the rates of the gas–solid reactions would also be interesting. We shall merely point out those features that seem to have some bearing on any interpretations of the catalyzed oxidation of the olefins.

The changes of conductance appear to be

systematically linked with the state of reduction of the surface and perhaps a few layers under the surface. Certain differences in the conductances of the samples under the conditions of olefin oxidation therefore point to different states of reduction of the surfaces, and this may be intimately linked with the selectivity of the surfaces once again as the results described in Part IV illustrate.

It seems clear from Fig. 6 that bismuth molybdate is in a considerably reduced state during the oxidation of propene by oxygen over the catalyst, whereas from Fig. 9 the MoO_3 catalyst is in a well oxidized state. (Bi_2O_3 behaves like MoO_3 and is in an oxidized state during the catalyzed reaction of propene and oxygen.) These conclusions were borne out, as mentioned, by examination of the individual rates of reduction and reoxidation of partially reduced surfaces. This finding has been used in discussing the ESR results described in Part II, where it appears that on MoO_3 the reduction proceeds mainly to Mo^{5+}, whereas on bismuth molybdate Mo^{5+} is formed about as rapidly as on MoO_3 but is removed, perhaps by reoxidation by bismuth ions, at rates that become very rapid at temperatures near 500°C. Unfortunately, the conductance measurements give only general information about the reduction of the surface, and do not give any detailed information about the oxidation states of Mo or Bi ions present in the surface or in underlying layers.

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