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Heterogeneous Selective Ammoxidation over Bismuth Molybdate Catalysts

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The ammoxidation of propene and of acrolein has been studied over two catalysts, one (UBM4) with Bi:Mo = 0.73:1 similar to commercial bismuth molybdate catalysts and the other (GS1) consisting of the koechlinite phase $Bi_2O_3 \cdot MoO_3$. The rates, reaction orders, Arrhenius parameters, and selectivities of the ammoxidations and of several selected reactions which appear in routes proposed by other workers were studied in a static vessel at 400°C. The results show that oxides of nitrogen are not realistic intermediates in the ammoxidations, nor is the main route for ammoxidation of propene over UBM4 through gaseous acrolein, even though the dissociative adsorption of propene is probably the rate determining step. The ammoxidations over GS1 show resemblances to the reactions over UBM4 in rate laws, and in the rates per unit area of the catalysts at 400°C. However, the selectivities are much higher, being about 95% for both over GS1 compared with 50% for propene and 70% for acrolein over UBM4. The rate of ammoxidation over GS1 is twice the rate of selective oxidation, suggesting that the adsorbing propene molecule reacts immediately with a surface species containing nitrogen, rather than reacting first with the oxide lattice to form allyl and hydroxyl radicals as it seems to do on UBM4.

INTRODUCTION

The heterogeneous selective oxidation of alkenes to unsaturated 1,3 conjugated products over mixed-oxide catalysts has been widely studied. Certain general conclusions have emerged. For the lower hydrocarbons over most catalysts the rate of oxidation is proportional to the hydrocarbon pressure, and independent of the oxygen pressure. It is thought that the rate-determining step of the oxidation is the abstraction of an allylic hydrogen which leads to a symmetrical chemisorbed allylic intermediate (*1–6*). Bismuth molybdate catalysts are also able to oxidize alkenes selectively in the absence of molecular oxygen (*7, 8*), although the selectivity of the oxidation is maintained at a high level for a much shorter time than when oxygen is present. The decrease in selectivity is associated with the progressive reduction of the catalyst, and it appears that the oxidation level of the catalyst must be maintained at a high level for high selectivity (*8*). These features have led to the suggestion that the oxidation process is of a 'redox' type in which chemisorbed hydrocarbon is oxidized by lattice oxygens which are then replaced by gas phase oxygen (*9*). More recent studies (*10, 11*) using isotopically labeled oxygen have supported this view of the overall mechanism and have also shown that the oxygen ions within the catalyst are highly mobile under the catalytic conditions (*10*).

The selective ammoxidation of alkenes to nitriles can also be carried out over the same catalysts that are used for straight oxidation (*12*), but less attention has been given to the mechanism of the ammoxidation process. One possible route involves the partial oxidation of the ammonia to oxides of nitrogen, followed by their reaction with propene, or with acrolein formed by selective oxidation of the propene, over the catalyst to give acrylonitrile (*13*). Some investigators have proposed that propene and ammonia chemisorb under oxidative conditions on the catalyst to give eventually surface radicals C_3H_y and NH_x, and these react to yield acrylonitrile by a direct surface route (*14*, *15*). Other investigators favor an indirect route in which propene is first oxidized to acrolein, which then reacts with a surface species containing nitrogen to give acrylonitrile (*16–18*).

The feasibility of these routes has been tested by low-pressure studies (*19*) of the rates, reaction orders, Arrhenius parameters, and selectivities of the ammoxidation of propene and of certain selected reactions which appear to be involved in the various proposed routes. It was decided to use catalysts for which the oxidation mechanism is well established, and most of the work was done with an unsupported bismuth molybdate catalyst, UBM4, with a Bi:Mo ratio of 0.73:1 which had been extensively studied for the oxidation of propene (*8*, *11*, *20*). Catalyst UBM4 is similar in composition to some commercial catalysts, but such catalysts contain several phases, and the identity and proportions of these seem to depend on the method of preparation. Thus there has been considerable controversy over the occurrence and role of the phases $Bi_2O_3 \cdot 3MoO_3$, $Bi_2O_3 \cdot 2MoO_3$ (Erman phase), and $Bi_2O_3 \cdot MoO_3$ (koechlinite phase); after this work was completed (*19*), three papers (*21–23*) were published which have clarified, among other points, the disputes over the Erman phase. However, it appeared earlier that studies similar to those on UBM4 should be attempted using a single, well-defined phase, and a sample (GS1) of the koechlinite phase with Bi:Mo = 2:1 was kindly supplied by Professor Dr. G. C. A. Schuit. The mechanism of selective oxidation of the butenes over this catalyst has been well-established (*9*), and the results described here show that the oxidation of propene over GS1 is very similar to that over UBM4. Quite unexpectedly, the ammoxidation of propene over GS1 shows some marked differences from that over UBM4—in particular, the activation energy is much lower (9 kcal mol^{-1} compared with 25 kcal mol^{-1}), and the selectivity for formation of acrylonitrile is much higher (95%, compared with 50%). These discoveries (*19*) unfortunately make it extremely unlikely that a single mechanism can be found for the ammoxidation of propene common to all active and reasonably selective bismuth molybdate catalysts, but they may be the starting point for investigations of exceptionally selective catalysts for the process, and for discovering reasons for the exceptional selectivity.

EXPERIMENTAL

Propene, acrolein, and oxygen were obtained and used as described previously (*11*). Nitric oxide and ammonia (Cambrian Chemicals, C.P. grade) were transferred from cylinders to storage bulbs on the line and then used as required. Acrylonitrile vapor was obtained from a reservoir of liquid acrylonitrile (B.D.H., saturated vapor pressure about 100 Torr at room temperature).

The catalyst UBM4 was prepared by a method described previously (*20*). $Bi(NO_3)_3$ (9 g) (Merck) was mixed with 45 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Merck) in a platinum crucible, and the green mixture was slowly heated in air to 300°C. The resulting yellow solid was cooled, ground, and heated in air at 600°C for 20 hr. Finally, the sample was activated in a stream of oxygen at 530°C for 20 hr. The Bi:Mo ratio was 0.73:1, and the specific surface area about 1 m^2g^{-1}.

The catalyst GS1 supplied by the Dutch workers had a Bi:Mo ratio of 2:1 and was prepared as follows (*9*). Freshly precipitated, thoroughly washed $BiO(OH)H_2O$ and H_2MoO_4 were allowed to react in boiling water while the total mass was stirred vigorously for 20 hr. After reaction, the solid was filtered and dried at 110°C overnight. The resulting yellow solid was calcined in air at 500°C for 2 hr. On cooling, it had a specific surface area of about 4 m^2g^{-1}.

The gas mixtures were prepared as required and, after a suitable time allowed for thorough mixing, were admitted into a thermostatted reaction vessel, about 45 cm^3 in volume, containing a known mass of the catalyst. Tests were made with different masses of the catalyst to ensure that all reported rates were measured under conditions where the total rate in the vessel was proportional to the mass of the catalyst present. This ensures that the reactions studied were genuine heterogeneous reactions, or were some mixture of heterogeneous reactions plus a homogeneous gas-phase reaction initiated by the catalyst surface. The latter can be discounted at these low pressures in the static system, because it was found that the homogeneous oxidation of acrolein, either in the presence or absence of propene, was more than forty times *faster* in the absence of the catalyst for similar reactant pressures. It is therefore clear that the homogeneous oxidations are severely inhibited by the catalyst under the experimental conditions where the gaseous chain-propagating radicals can diffuse easily to the surface; the effects might be very different in fast flow systems where the homogeneous oxidation might occur in any empty postcatalyst volume (*15*). Without such inhibition, it is difficult to see how high selectivity for formation of acrolein from propene, or of acrylonitrile from acrolein, could ever be found. Similar observations have been made by Callahan *et al.* (*14*).

The gas phase was analyzed continuously by an M.S. 10 mass spectrometer (A.E.I. Ltd.) via a capillary leak as described previously (*11*). It was possible by this means to follow the gas phase concentrations of all the major products and reactants, with the exception of NH_3 in propene–ammonia–oxygen systems for which the ammonia concentration was determined by glc (*19*). The reproducibility obtained from experiment to experiment was better than 99% for major products.

Orders of reaction were determined throughout by initial rate measurements. The reactant pressures used were typically 40, 20, and 10 Torr for each reactant in turn, with about 45 mg of catalyst present.

RESULTS

Feasibility of reaction routes via oxides of nitrogen. Preliminary experiments showed that the oxidation of ammonia over UBM4, at pressures around 20 Torr of each reactant and at temperatures around 400°C, yielded water and nitrogen almost exclusively, in agreement with the results of Aykan (*24*); oxides of nitrogen could not have exceeded one part in 10^4 of the reaction products under these conditions. However, during the reactivation of UBM4 after each oxidation of ammonia, using higher pressures of oxygen, nitrous oxide was formed. This suggests that the oxidation of ammonia at low oxygen pressures involves a fairly stable surface species containing nitrogen; it was also noticed that the rate of ammonia oxidation fell off rapidly as the reactants were consumed. The addition of propene to the ammonia–oxygen mixtures also reduced the rate of removal of the ammonia, but again oxides of nitrogen were not present in more than trace proportions in the gas phase. Therefore, they could be excluded as intermediates unless they proved to be extraordinarily active and selective reactants with propene or acrolein.

Nitric oxide did react with propene and with acrolein to give acrylonitrile, the reactions being first order in propene or acrolein and zero order in nitric oxide for all nitric oxide pressures up to equality with the other reactant. The rates of removal of propene or acrolein were, however, much slower than from corresponding mixtures of propene, ammonia, and oxygen or acrolein, ammonia, and oxygen (Table 1). In addition, the selectivities for production of acrylonitrile from propene or acrolein and nitric oxide were much lower than the values for the corresponding ammoxidation mixtures. Finally, propene and nitric oxide produced acrolein at a faster rate than they produced acrylonitrile, whereas, with propene, ammonia, and oxygen, the rate of acrolein production was less than 5% of that of acrylonitrile. These differences effectively exclude nitric oxide as a realistic intermediate.

Nitrous oxide did not yield any com-

TABLE 1
RATE CONSTANTS AND SELECTIVITIES FOR REACTIONS OVER BISMUTH MOLYBDATE CATALYSTS AT 400°C

Catalyst	Reaction mixture	Initial gas mixture composition ratio	k_1 at 400°C[a]	% Selectivity for	
				C_3H_3N	C_3H_4O
UBM4	NH_3/O_2	1:1	$3.1 \pm 0.3 \times 10^{-3}$ (NH_3)	—	—
	C_3H_6/NO	1:1	$7.7 \pm 0.7 \times 10^{-5}$ (C_3H_6)	30–40	40–50
	C_3H_4O/NO	1:1	$2.0 \pm 0.2 \times 10^{-4}$ (C_3H_4O)	10–25	—
	C_3H_6/O_2	1:1	$2.9 \pm 0.3 \times 10^{-4}$ (C_3H_6)	—	95
	$C_3H_6/NH_3/O_2$	1:1:1	$3.1 \pm 0.3 \times 10^{-4}$ (C_3H_6)	50	1–2
	$C_3H_4O/NH_3/O_2$	1:1:1	$9 \pm 1 \times 10^{-3}$ (C_3H_4O)	70	—
	C_3H_6/NH_3	1:1	5.8×10^{-5} (C_3H_6)	35–40	—
	C_3H_6	—	$6.4 \pm 0.6 \times 10^{-5}$ (C_3H_6)	—	85–90
GS1	C_3H_6	—	$2.0 \pm 0.2 \times 10^{-4}$ (C_3H_6)	—	95
	C_3H_6/O_2	1:1	$9 \pm 1.0 \times 10^{-4}$ (C_3H_6)	—	95
	$C_3H_6/NH_3/O_2$	1:1:1	$1.7 \pm 0.1 \times 10^{-3}$ (C_3H_6)	95	—
	$C_3H_4O/NH_3/O_2$	1:1:1	$4.5 \pm 0.4 \times 10^{-2}$ (C_3H_4O)	95	—
	C_3H_6/NH_3	1:1	$7 \pm 0.7 \times 10^{-4}$ (C_3H_6)	75–80	—

[a] k_1 is the specific first order rate constant in the equation $-dn_R/dt = k_1P_R$, where R is the reactant indicated; values in mole min^{-1} (g catalyst)$^{-1}$(atm R)$^{-1}$. UBM4 has a specific area of about 1 m^2 g^{-1} and GS1 of about 4 m^2 g^{-1}.

pounds with C–N bonds when mixed with propene or acrolein over UBM4. It is well known that nitrogen dioxide and higher oxides of nitrogen yield nitric oxide rapidly at the catalytic temperatures, both by decomposition and by oxidizing hydrocarbons (*25*), and so are also excluded as intermediates.

It therefore seemed very unlikely that oxides of nitrogen are reaction intermediates in the ammoxidation of propene or acrolein over UBM4.

Comparison of ammoxidation and oxidation reactions over UBM4. The results of a typical experiment with $C_3H_6:NH_3:O_2 = 1:1:1$ are shown in Fig. 1. It will be seen that the selectivity for production of acrylonitrile was about 50% throughout the reaction. Experiments showed that acrylonitrile itself was stable when exposed to the catalyst under the reaction conditions. The remainder of the nitrogen during the run could be accounted for as CH_3CN and HCN in equal amounts, as others have found (*14*, *26*), the amounts of CO plus N_2 being small although the background peak at 28 prevented accurate determination of CO and N_2; with this assumption, the carbon in the products was always within 5% of that in the reactants. An important point is that acrolein formed only a small proportion of the products, though relatively more after the oxygen was all consumed.

In agreement with the results of other investigations, the rate of removal of propene was first order with respect to propene and zero order with respect to oxygen and to ammonia for all mixtures with $C_3H_6:NH_3 \geqslant 1:1$. The specific first order rate constant in Table 1 can be compared with that for the selective oxidation of propene, which was shown to be first order in propene and zero order in oxygen. Not only were the rates very close to 400°C, but the activation energies are very similar. The activation energy for the rate constant for the oxidation reaction over the range 400–500°C, was 25 ± 2 kcal mole^{-1}. The activation energy for the ammoxidation reaction, determined from the rate constant for the rate of appearance of acrylonitrile at temperatures between 375 and 450°C, was also 25 ± 2 kcal mole^{-1} (Table 2); unless the selectivity changes markedly over this temperature range, the activation energy for

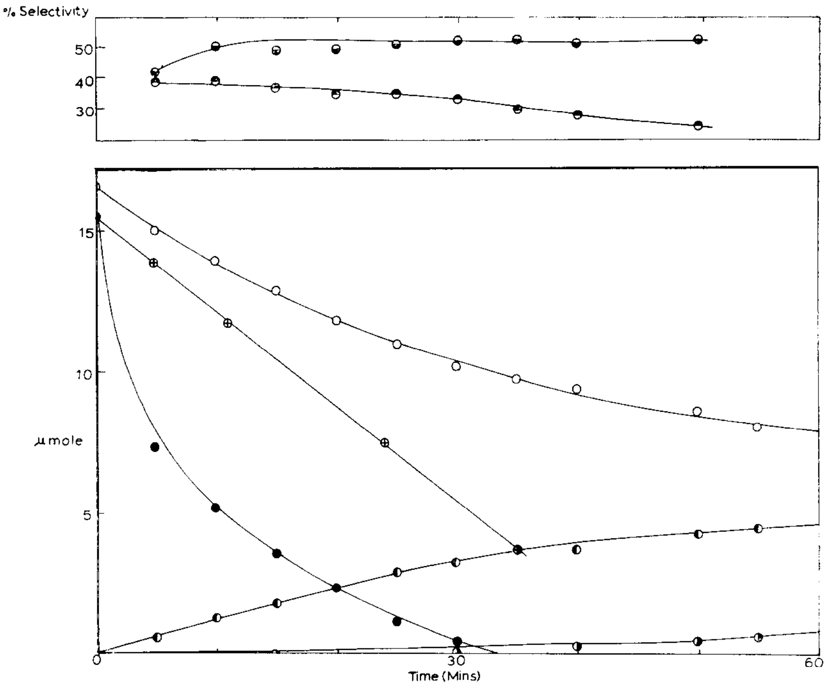


FIG. 1. *Lower part.* Amounts (μmoles) present in reaction vessel during the reaction of C_3H_6:NH_3:O_2 (1:1:1) over UBM4 at 400°C. (○)C_3H_6, (⊕)NH_3, (●)O_2, (◑)C_3H_4O, (◐)C_3H_3N. *Upper part.* Selectivity for the conversion of NH_3 to C_3H_3N (◓) and of C_3H_6 to C_3H_3N (◒).

propene removal in the ammoxidation reaction will be close to this value. The only realistic interpretation of these results is that the two reactions have a common rate-determining step, which in the case of the oxidation has been identified with the rate of dissociative chemisorption of the propene (*1–6*).

To obtain information about the route of the ammoxidation reaction following the initial step, comparisons were made of the rates of ammoxidation of acrolein and of propene. Typical results for the ammoxidation of acrolein are shown in Fig. 2. Initial rate measurements showed that the reaction was first order with respect to acrolein and zero order with respect to ammonia and to oxygen. The specific rate constant at 400°C is about thirty times greater than that for the ammoxidation of propene over this catalyst under comparable conditions (Table 1).

TABLE 2

ACTIVATION ENERGIES FOR REACTIONS OVER BISMUTH MOLYBDATE CATALYSTS

Reaction	Activation energies/kcal mole^{-1}	
	Over GS1	Over UBM4
$C_3H_6 \longrightarrow C_3H_4O$	18 ± 1 (95%)	29 ± 2 (95%)
$C_3H_6 \xrightarrow{O_2} C_3H_4O$	20 ± 2 (95%)	25 ± 2 (95%)
$C_3H_6 \xrightarrow{NH_3} C_3H_3N$	21 ± 2 (80%)	30 ± 3 (35–40%)
$C_3H_6 \xrightarrow{NH_3/O_2} C_3H_3N$	9 ± 1 (95%)	25 ± 2 (50%)

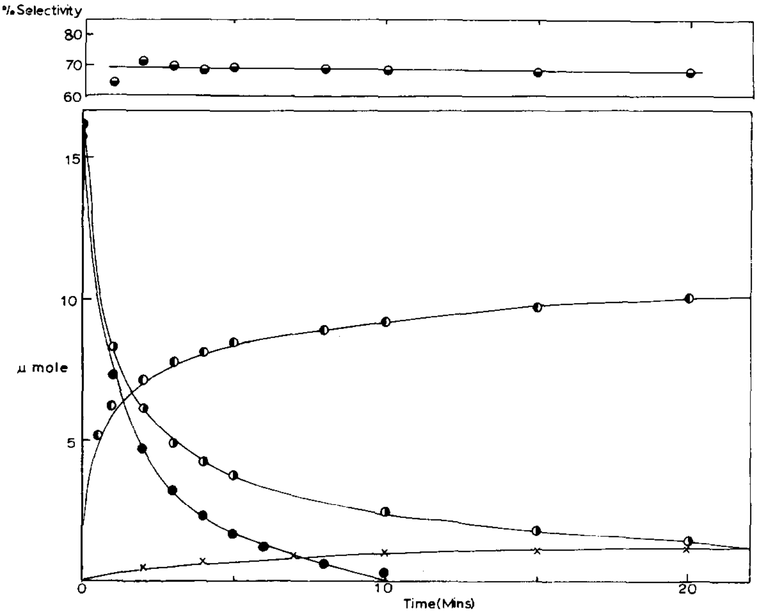


FIG. 2. *Lower part.* Amounts (μmoles) present in reaction vessel during the reaction of $C_3H_4O:NH_3:O_2$ (1:1:1) over UBM4 at 400°C. (◑)C_3H_4O, (●)O_2, (◐)C_3H_3N, (×)CH_3CN. *Upper part.* Selectivity for the conversion of C_3H_4O to C_3H_3N (◒).

Experiments were carried out to determine the mutual effects of acrolein and propene on their rates of removal in ammoxidation mixtures. It was found that the rate of ammoxidation of propene was not altered by adding acrolein, and the selectivity remained about 50%; this can also be seen from Fig. 1. It was also found that the rate of removal of acrolein was decreased somewhat by the addition of propene, but the selectivity for acrolein → acrylonitrile fell as shown in Fig. 3. To derive this plot, the acrylonitrile formed was corrected for that formed from the propene, using the experimental fact that the rate and selectivity for propene is unaffected by addition of acrolein. Unfortunately, the experimental accuracy became less satisfactory at ratios of propene:acrolein in excess of 10:1 but the most reasonable assumption is that the selectivity is about 40% in propene-rich mixtures.

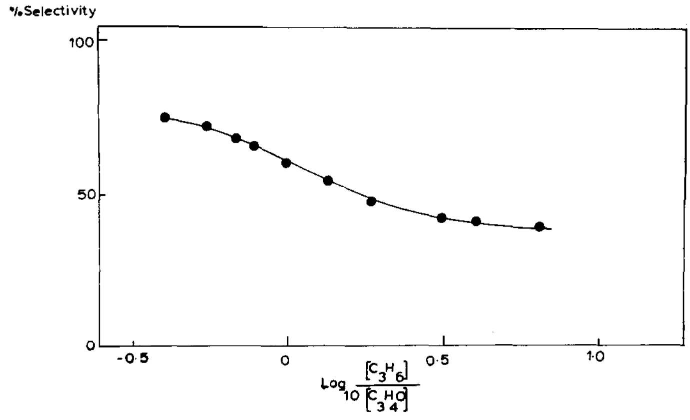


FIG. 3. Effect of added C_3H_6 on the percentage selectivity for the conversion of C_3H_4O to C_3H_3N.

These results can now be used to test the proposal that the route for production of acrylonitrile from propene, ammonia and oxygen mixtures is

$$\text{propene(g)} \rightarrow \text{allyl(chemisorbed)} \rightarrow \text{acrolein(g)} \rightarrow \cdots \rightarrow \text{acrylonitrile(g)}$$

If this were the sole route, the steady-state concentration of acrolein must be capable of yielding acrylonitrile at the rate observed for the ammoxidation of propene. At 400°C, using the data in Table 1, the rate of production of acrylonitrile is $0.50 \times 3.4 \times 10^{-4} \times P_{C_3H_6}$.

The production of acrylonitrile from a steady-state value of acrolein $((P_{C_3H_4O})_{ss})$ in the presence of propene must be *less than* the rate from the same pressure of acrolein in the absence of propene, i.e., $< 0.40 \times 9.0 \times 10^{-3} \times (P_{C_3H_4O})_{ss}$. Therefore,

$$\text{overall rate of production of acrylonitrile} = \text{rate of production of acrylonitrile from } C_3H_4O(ss)$$

and

$$0.50 \times 3.0 \times 10^{-4} \times P_{C_3H_6} < 0.40 \times 9.0 \times 10^{-3} \times (P_{C_3H_4O})_{ss}.$$

Therefore,

$$(P_{C_3H_4O})_{ss}/P_{C_3H_6} > 0.04.$$

It can be seen from Fig. 1 that the experimentally-found ratio is initially very much lower, and even after 40 min it is not larger than 0.03. Examination of the original data from many runs confirmed that the acrolein pressure was far too low in the early stages of the reaction for it to be a realistic intermediate for the conditions used over UBM4.

Experiments were also carried out to test whether propene and ammonia, in the absence of oxygen, can produce acrylonitrile. Some was produced but at a slower rate than for the same mixtures with equal partial pressure of oxygen present (Table 1). The activation energy (Table 2) was close to that for the reaction of propene with the catalyst UBM4.

The oxidation and ammoxidation reactions over GS1. The oxidation of 1:1 mix-

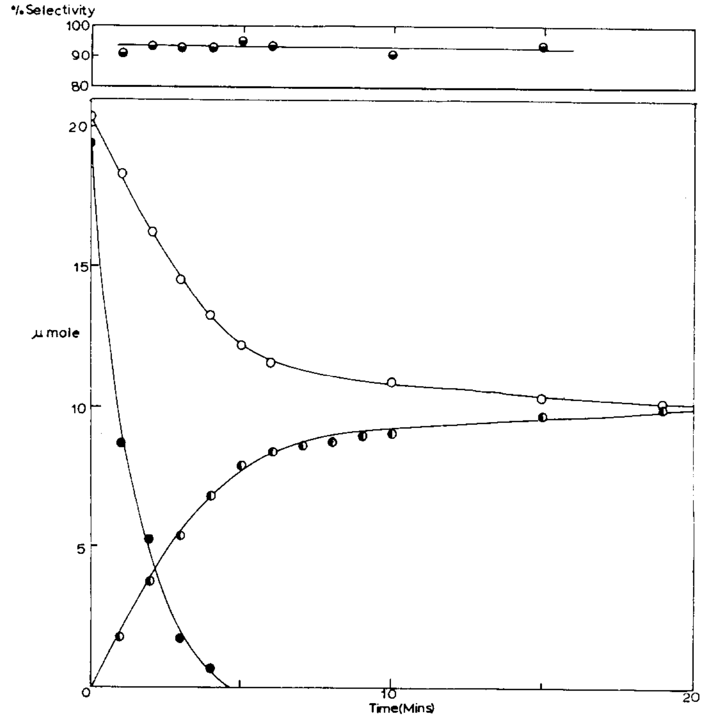


FIG. 4. *Lower part.* Amounts (μmoles) present in reaction vessel during the reaction of $C_3H_6:NH_3:O_2$ (1:1:1) over GS1 at 400°C. (○)C_3H_6, (●)O_2, (◐)C_3H_3N. *Upper part.* Selectivity for the conversion of C_3H_6 to C_3H_6N (⊖).

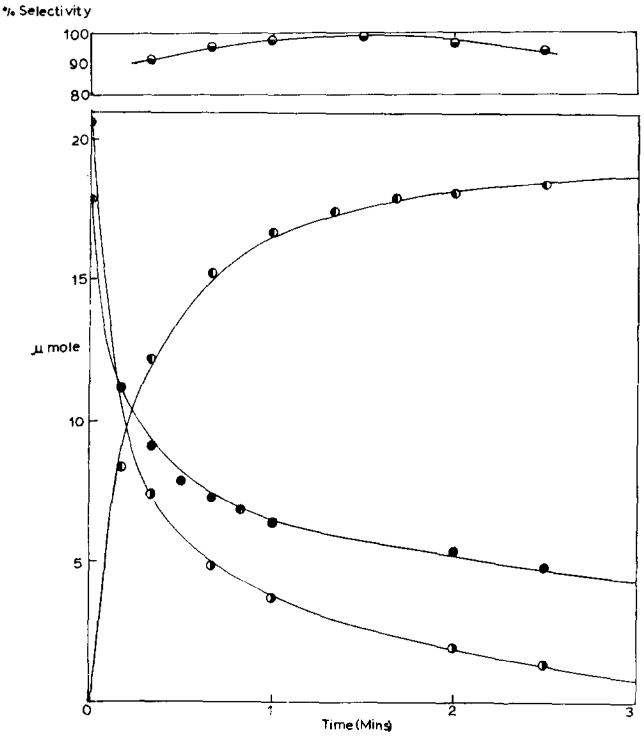


FIG. 5. *Lower part.* Amounts (μmoles) present in reaction vessel during the reaction of $C_3H_4O:NH_3:O_2$ (1:1:1) over GS1 at 400°C. (◑)C_3H_4O, (◐)C_3H_3N, (●)O_2. *Upper part.* Selectivity for the conversion of C_3H_4O to C_3H_3N (◒).

tures of propene and oxygen over GS1 produced acrolein with a very high selectivity (~95%), the reaction being first order in propene and zero order in oxygen, with an activation energy of about 20 kcal mole^{-1} (Table 2). The rate constant at 400°C was about three times that for the oxidation over UBM4 on a mass basis, but as the specific area of GS1 is about four times that for UBM4, on an area basis the two catalysts have about the same activities. The reaction of propene alone with GS1 also produced acrolein with about 95% selectivity, with an activation energy of about 18 kcal mole^{-1}.

Some typical results for the ammoxidation of propene using 1:1:1 mixtures are shown in Fig. 4 for 0.045 g of GS1 at 400°C. A notable feature of these results is the extremely high selectivity for formation of acrylonitrile which was close to 95% throughout the range of conversion studied, although there was a sharp fall in rate when the oxygen was consumed. From the initial rates, the reaction was found to be first order in propene and zero order in ammonia and in oxygen. The specific rate constant at 400°C was nearly twice that for the oxidation reaction over GS1 (Table 1). The activation energy for production of acrylonitrile was 9 ± 1 kcal mole^{-1}.

Investigation of the ammoxidation of acrolein over GS1, using various mixtures, showed initial rates which were first order in acrolein and zero order in the other reactants. Results for a 1:1:1 mixture are shown in Fig. 5, and the selectivity found was again extremely high (Table 1). It will be noticed that the oxygen is not consumed as rapidly as with propene, and correspondingly the rates do not fall off sharply at any point during the run. The rate constant is about thirty times that for the ammoxidation of propene over the same catalyst.

The reaction of 1:1 mixtures of propene and ammonia with GS1 produced acrylonitrile with a selectivity of about 75–80% at an initial rate about a half that of the normal ammoxidation mixture at 400°C, though the activation energy was considerably higher (Table 2).

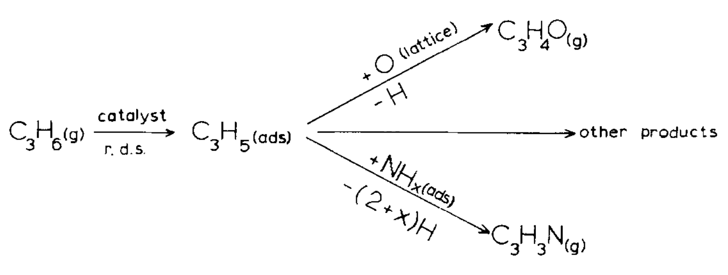
Discussion

Some fairly definite conclusions have emerged from the experiments upon the ammoxidation of propene over UBM4. It seems highly unlikely that oxides of nitrogen are realistic intermediates when using $C_3H_6/NH_3/O_2$ mixtures. The identity of rates of removal of propene in the oxidation and ammoxidation reactions over UBM4 at 400°C, together with the activation energies in Table 2 point to a common rate-determining step. From the earlier work on the oxidation (*1–6*), this identifies the rate-determining step for the ammoxidation of propene under the conditions used here as the dissociative chemisorption of the propene.

Little can be said about the later steps, except that it seems very unlikely that gaseous acrolein is an effective intermediate over UBM4. The experimental results showed that the concentration of acrolein in the gas phase was always much less than the steady-state value required if the route were mainly through gaseous acrolein. Thus most of the acrylonitrile must be formed from C_3H_5(ads) or C_3H_4(ads) by reaction with NH_x(ads), but it is impossible at this stage to say when the hydrogen atoms are oxidatively removed.

Over other bismuth molybdate catalysts, considerably different values have been reported for the ratio (rate of ammoxidation of acrolein)/(rate of oxidation of propene to acrolein) for similar reactant pressures. Thus Callahan *et al.* (*14*) have found the ratio 2:1 at 430°C. Shelsted and Chong (*16*) suggest a value of at least 10:1 at 390°C. Cathala and Germain (*15*) found 5:1 at 460°C (with higher values in the presence of steam). There is no steady trend with temperature, although the higher ratios occur at lower temperatures. With the highest ratio reported (30:1), the present results show that there is not enough acrolein present in the early stages of the reaction to make the indirect route through acrolein feasible. With lower ratios, even more acrolein should be present in steady state conditions, and in the absence of published reports of such amounts it seems likely that a direct route is generally favored.

With the catalyst GS1, the experiments on the oxidation of propene show, as expected, that the mechanism is extremely likely to be the same as over UBM4. The rate laws are the same, the specific rate constants per unit area of catalysts are roughly the same at temperatures around 400°C (over GS1, 1.75×10^{-4} compared with 2.90×10^{-4} mole min^{-1} m^{-2} $(atm\ R)^{-1}$ over UBM4), and the activation energies are similar. In addition, both catalysts react with propene alone to give acrolein very selectively, at very similar rates per unit area (Table 1). All these results point to the dissociative adsorption of propene as the rate-determining step for the oxidation to acrolein over GS1 as well as over UBM4.



If comparisons are made between the results for the ammoxidation of propene over the two catalysts, some results are remarkably similar. Thus, the rate laws are the same, and the specific rate constants per unit area are roughly the same at

400°C (over GS1, 3.75×10^{-4} compared with 3.0×10^{-4} mole min^{-1} m^{-2} (atm R)$^{-1}$ over UBM4. In addition, the ratios (rate constant for ammoxidation of propene)/(rate constant for ammoxidation of acrolein) are about 30 for each catalyst (Table 1). At first sight, these results seem to indicate very similar mechanisms for the ammoxidation of propene over the two catalysts. However, there are four very significant differences that point to different rate-determining steps for the ammoxidation of propene over GS1 and over UBM4.

(1) The significantly greater selectivity over GS1 compared with UBM4. (95% compared with 50% at 400°C).

(2) The rate of ammoxidation over GS1 is about twice the rate of oxidation over GS1 at 400°C; over UBM4 at 400°C these reactions have the *same* rate.

(3) The activation energy for ammoxidation over GS1 is much lower than over UBM4, measured from the temperature dependence of the rate constants for production of acrylonitrile.

(4) Mixtures of propene and ammonia give higher selectivities for acrylonitrile over GS1 than over UBM4, in the absence of gaseous oxygen (75–80%, compared with 35–40%).

Observation (*2*) must mean that the first step for the ammoxidation over GS1 is faster than the chemisorption of propene on to the catalyst in the absence of ammonia. Together with (*3*) and (*4*), it suggests that the ammonia may form an active intermediate (such as NH_x(ads)) over GS1 that reacts with propene upon chemisorption; the difference between GS1 and UBM4 may lie in the coverage of NH_x(ads) or the nature of NH_x(ads). Unfortunately, these possibilities could not be pursued in the present study, but it is clearly desirable to investigate further the causes of the exceptionally high selectivity found over GS1.

After this study was completed (*19*), Batist informed us that he had studied the ammoxidation of propene over the koechlinite catalyst using a flow system and had also found a very high selectivity to acrylonitrile using this catalyst in a high oxidation state. This work has since been published (*27*).

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