Interaction of Allyl Iodide with Molybdate Catalysts for the Selective Oxidation of Hydrocarbons

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The interaction of allyl iodide with MoO_3, Bi_2O_3, and molybdates of Bi, Co, and Mg has been studied in the temperature range of 270–480°C. Although practically inactive in the allylic oxidation of propylene, MoO_3 yielded 100% acrolein at 320°C, when in contact with allyl iodide. On Bi_2O_3, only 1,5-hexadiene and benzene were formed, whereas bismuth molybdate produced both oxygenated and nonoxygenated products. This confirms the multicenter model of allylic oxydation, the low-valent cation being responsible for activation of the hydrocarbon molecule and Mo–O polyhedra for insertion of oxygen. Stoichiometric $CoMoO_4$ and $MgMoO_4$ were inactive in the formation of acrolein from allyl iodide because the acrolein-like intermediate formed on the surface was unable to desorb. This indicates that the third condition of an active catalyst is the ability to desorb the oxygenated product by releasing the oxygen ion of the lattice sufficiently readily. When an excess of MoO_3 is present in these molybdates, they become active in the formation of oxygenated products.

INTRODUCTION

It is generally recognized (1–3) that selective oxidation of olefins to unsaturated aldehydes or acids on oxide catalysts takes place via the formation of an allylic intermediate in the first stage of the reaction, this step being rate determining in the overall process of oxidation. However, the nature of this intermediate, whether radical or cationic, as well as the type of its bonding to the surface, as a π- or σ-type complex, has been a matter of discussion. Moreover, no information is available on the reactivity of such allylic species at oxide surfaces. The presence of allyl radicals in the gas phase has been detected in the case of the interaction of propylene with manganese oxide at a pressure of 10^{-6} Torr, with the mixture of Mn_2O_3 and Mn_3O_4 as well as with ZnO (4). No radicals were observed in the presence of mixed-oxide catalysts

such as Bi–Mo–O and Mn–Mo–O systems, known as active and selective catalysts in partial oxidation, nor in the presence of Mn_3O_4, which is a deep oxidation catalyst. The studies of the ir spectra of propylene adsorbed on Bi_2O_3, MoO_3, and the mixed Bi–Mo–O oxide system diluted in the MgO matrix (5) showed that π-allylic species are present at the surface of the solution of Bi_2O_3 but could not be detected at the surfaces of other solutions.

Some years ago we advanced a multicenter model of the selective oxidation of olefins on mixed-oxide catalysts (6, 7). The main features of this model are: (i) Partial oxidation requires activation of the olefin molecule, but no activation of oxygen should take place; activation of oxygen leads to total oxidation. (ii) Activation of the olefin molecule, consisting of the abstraction of α-hydrogen and formation of

π-bonded allylic species, takes place on cationic active centers. In the case of molybdates, these centers involve such cations as Bi^{3+}, Co^{2+}, Ni^{2+}, etc. (iii) When no other centers are present at the surface, the π-allyl species either recombine to give dimers of the diene type or form polyenes by repetition of the first step on cationic active centers. (iv) Different active centers at the catalyst surface are required for the insertion of oxygen. Oxygen polyhedra of molybdenum are involved in the creation of these centers.

According to this model, the low activity of pure MoO_3 or $MgMoO_4$ in the oxidation of propylene has been ascribed to the absence, at their surface, of the first type of centers, capable of abstracting the hydrogen atom from the propylene molecule. Quantum-chemical calculations of the complexes formed on the surface of different oxide catalysts as a result of abstraction of the hydrogen and formation of the allyl radical (8) have shown that considerable transfer of π-electrons takes place. This occurs from the orbitals of the allylic ligand toward the metal involved in the active site of the first type in the case of transition-metal cations (Co, Fe, Ni), resulting in bonding and cationization of the allyl intermediate; whereas, on active centers containing Mg ion as the central atom, the allyl radical remained neutral, its bonding to the surface being very weak.

As in the majority of partial oxidation reactions the first step, consisting of the adsorption of the olefin molecule, is rate determining; studies of these reactions cannot yield any information on the next stages of the reaction.

One of the ways in which the discussed model could be confirmed and the reactivity of this intermediate complex could be studied in more detail would be to bypass the first step by generating the allyl radicals by some other more effective route. This can be effected by using allyl iodide, which readily decomposes into allyl radicals,

the strength of the C–I bond in C_3H_5I being 43.5 kcal/mol in comparison to 87.5 kcal/mol for the corresponding C–H bond in propylene (9). The first step of the selective oxidation is thus facilitated, making possible the examination of the conditions which are necessary for the insertion of oxygen in the next step of the reaction.

In the present work, the reaction of allyl iodide has been studied on the pure oxides MoO_3 and Bi_2O_3, as well as on molybdates of Bi, Co, and Mg.[1]

EXPERIMENTAL

The interaction of allyl iodide (Reakhim reagent, pure grade) with the oxide catalysts was studied by means of the pulse method. Using a microsyringe, 1-μl pulses of iodide were introduced into a stream of purified nitrogen, which was then passed over a sample of the catalyst, placed in a microreactor. Analysis of the products formed in the course of the reaction was performed by means of gas chromatography; the chromatographic columns were connected directly to the output of the microreactor. The liquid products (acrolein, benzene, 1,5-hexadiene) were analyzed on a 3-m column filled with 12% Carbowax on Chromosorb S. The temperature of the column was 80°C and the flow rate of nitrogen was 40 ml/min. Gaseous products (propylene, CO, CO_2) were analyzed on a 4-m column containing DMS at room temperature.

Prior to each set of runs at a given temperature, the samples were always heated in nitrogen for 30 min, and then 10 ml of oxygen were introduced in the form of 1-ml pulses. On such a pretreated sample, a series of the iodide pulses was introduced, measuring the distribution of products for

[1] After this work was completed, studies of the reactivity of allyl bromide with MoO_3 and bismuth molybdate were reported by Gamid-Zade et al. (23). The results are in full agreement with those described in the present work for allyl iodide.

TABLE 1

Characteristics of Catalysts

Catalyst	Method of preparation	Temperature and time of calcination	Surface area[a] (m^2/g)	Chemical composition after calcination[b]
MoO_3	Thermal decomposition of ammonium paramolybdate	500°C, 4 hr	2.43	MoO_3
Bi_2O_3	Commercial product	—	0.66	α-Bi_2O_3
Bi_2MoO_6	Co-precipitation of ammonium paramolybdate and bismuth nitrate solutions at pH 7	500°C, 5 hr	1.25	γ-Bi_2MoO_6
$CoMoO_4$	Co-precipitation of ammonium paramolybdate and cobalt nitrate solutions at pH 5,6, and then elution of the precipitate with H_2O	1200°C, 12 hr 400°C, 8 hr	1.22 12.6	b-$CoMoO_4$ a-$CoMoO_4$[c]
$CoMoO_4 \cdot 0.1\ MoO_3$	As above, without elution	400°C, 5 hr	8.39	a-$CoMoO_4$[c] + MoO_3
$CoMoO_4 \cdot 0.67\ MoO_3$	Impregnation of the precipitate with concentrated ammonium paramolybdate solution	460°C, 5 hr	9.75	a-$CoMoO_4$[c] + MoO_3
$MgMoO_4$	Recrystallization from filtrate obtained after solubilization of MgO and MoO_3 oxides taken in appropriate proportions in water at 100°C	550°C, 5 hr	2.77	$MgMoO_4$
$MgMo_{13}O_{10}$	As above	500°C, 5 hr	3.59	$MgMoO_4$ + $Mg_2Mo_3O_{11}$ + MoO_3

[a] Determined by BET method from the adsorption of krypton at liquid nitrogen temperature.
[b] From chemical and X-ray analysis.
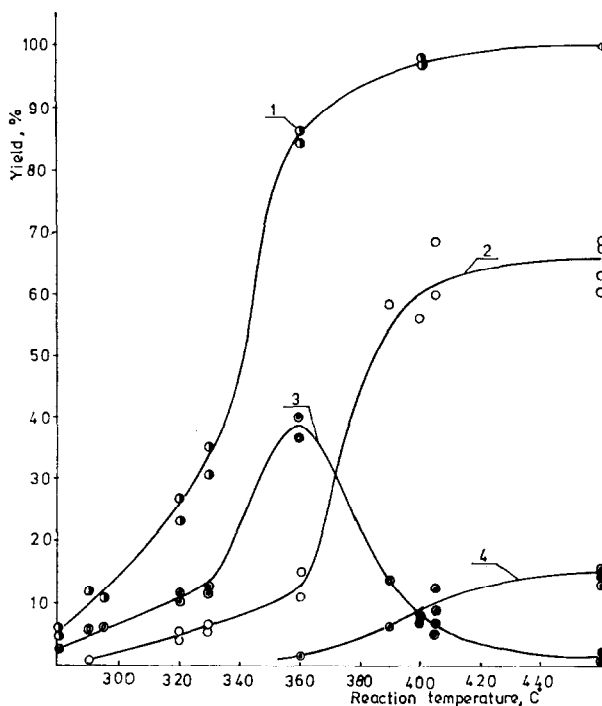[c] Partially transformed into b-$CoMoO_4$ after grinding.

Fig. 1. Homogeneous decomposition of allyl iodide: (1) total conversion (◑); (2) propylene (○); (3) 1,5-hexadiene (◎); 4-benzene (●).

each pulse. After completing a series of experiments at a given temperature, the samples were subjected to a number of oxygen pulses at a temperature of 460–480°C in order to burn off the eventual carbon deposit, and the amount of CO_2 evolved was recorded. The oxygen treatment was continued until no CO_2 was observed. The temperature was then lowered to that of the subsequent measurement, and the sample was kept at this temperature for 30 min in a stream of nitrogen and was standardized by again introducing 10 ml of oxygen. The list of catalysts used and the conditions of their preparation are given in Table 1. The volume of catalyst varied between 1 and 3 ml, ensuring a constant overall surface area for the reacting sample of 8 m^2/g, with the exception of Bi_2O_3, Bi_2MoO_6, and b-$CoMoO_4$, for which the overall surface area of each amounted to 1.5 m^2/g. As confirmed in separate experi-

ments, the difference in contact time had no essential effect on the selectivity values.

RESULTS

1. Blank Experiments for Decomposition of Allyl Iodide

Prior to examination of the interaction of allyl iodide with the catalyst, its decomposition in a reactor filled with glass beads, 0.2–0.5 mm in size, and pretreated in nitrogen for 30 min, was studied in the temperature range of 280–450°C and under the same flow conditions and with the same iodide dose as in subsequent catalytic studies.

The distribution of products obtained at different temperatures for the 3-ml volume of glass beads is shown in Fig. 1. At lower temperatures, the main product of the decomposition is 1.5-hexadiene, its yield increasing with temperature to about 350°C
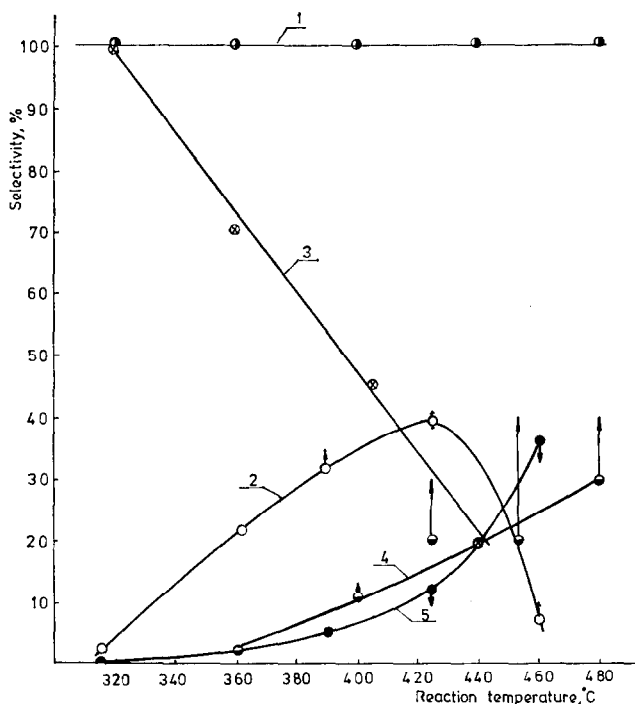
FIG. 2. Selectivity of the interaction of allyl iodide with MoO_3 as function of the reaction temperature; (1) total conversion (◑); (2) propylene (○); (3) acrolein (⊗); (4) acrylic acid (◒); (5) $CO + CO_2$ (●).

and then decreasing. At higher temperatures (>350°C) and high conversions, the yields of two other products, propylene and benzene, increase markedly.

The general pattern of decomposition and the types of products formed are in agreement with the data on the homogeneous decomposition of iodide performed in a static reactor at high temperatures (600°C) *(10)*.

2. MoO₃

The distribution of products obtained upon contact of the pulses of C_3H_5I with the surface of MoO_3 in the temperature range of 320–480°C is shown in Fig. 2. The conversion of iodide in this temperature range is 100%. The points marked in Fig. 2 pertain to the first pulse. For those products for which the amount changed with the number of pulses, the direction of the change and the yield observed after five pulses are indicated by the arrow.

At low temperatures, the main product of interaction of allyl iodide with MoO_3 is acrolein; its yield at 320°C was nearly 100%. Its amount remains practically constant in the first four to five pulses. Upon raising the temperature, the amount of acrolein decreases, this decrease being, to a large extent, compensated for by the increase in the yield of other products, namely, acrylic acid and carbon oxides.

The yield of acrylic acid increases markedly with the number of pulses. Thus, in contrast to the decomposition of iodide in the absence of catalyst, on the MoO_3 surface oxygenated products are formed. This indicates that oxygen of the MoO_3 lattice is readily incorporated into the allylic intermediate, even at low temperatures.

In the oxidation of propylene in the same temperature range, only very small amounts of products are formed: At 440°C, the conversion of C_3H_6 is 7%; the acrolein yield is 2%.

Among the nonoxygenated products of decomposition of allyl iodide on MoO_3, mainly propylene is observed. Only traces of benzene or hexadiene are found. The amount of C_3H_6 is considerably smaller than that obtained in the absence of the catalyst and reached a maximum at 420°C.

The decrease of the amount of propylene at higher temperatures may be due to oxidation to acrolein and acids. Only small amounts of C_3H_5I are adsorbed on the surface of MoO_3 in the irreversible form, removable in the form of CO_2 after exposure to oxygen. The irreversible sorption of C_3H_5I, calculated from the amount of CO_2 obtained when pulses of pure oxygen were injected on the surface after four to five pulses of the iodide, varied from 3.5 to 0.5% in the temperature range of 390–460°C.

The small extent of this sorption was confirmed by good carbon balances, which were close to 100%, even when only products in the gas phase were taken into account in the calculations.

3. Bi_2O_3

The distribution of products obtained upon interaction of allyl iodide with this oxide in the temperature range of 300–470°C is shown in Fig. 3; the conversion of iodide is again close to 100%. As seen from this figure, the main reaction products in this case are nonoxygenated compounds, such as hexadiene, benzene, and propylene, analogous to those obtained in the homogeneous pyrolysis of C_3H_5I.

However, in contrast to the blank reaction, where only a very small amount of conversion is observed below 350°C, the conversion on Bi_2O_3 is already 100% at 300°C, the main product being 1,5-hexadiene. This indicates that heterogeneous catalytic reaction takes place, Bi_2O_3 show-
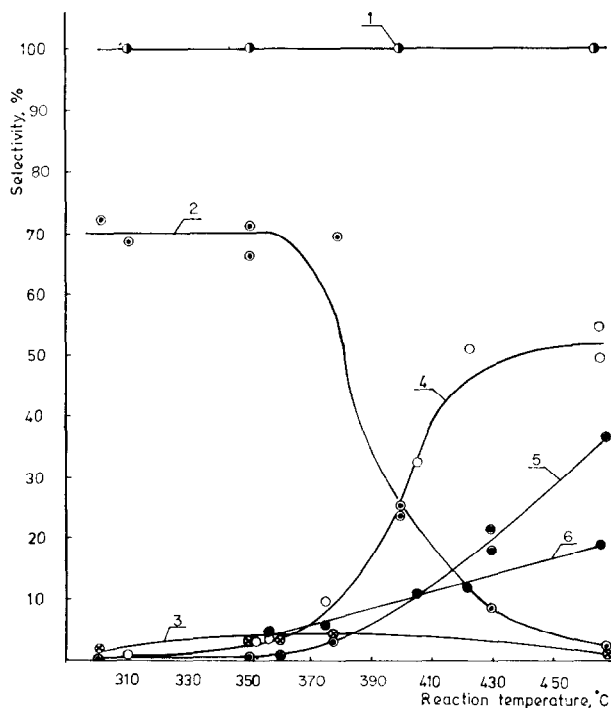

FIG. 3. Selectivity of the interaction of allyl iodide with Bi_2O_3 as function of the reaction temperature; (1) total conversion (◑); (2) 1,5-hexadiene (◎); (3) acrolein (⊗); (4) propylene (○); (5) benzene (◉); (6) $CO + 3O_2$ (●).
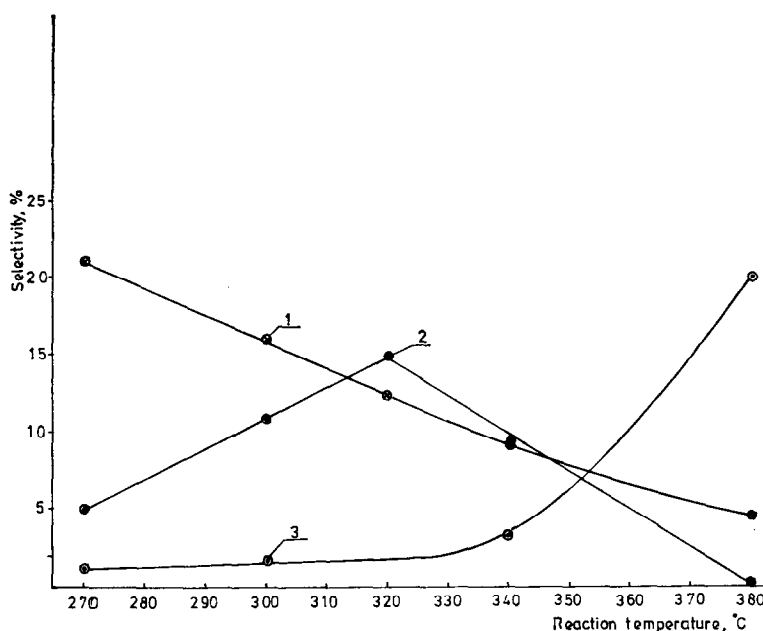
Fɪɢ. 4. Selectivity to oxygenated and nonoxygenated products of allylic oxidation at different temperatures in the interaction of allyl iodide with γ-Bi_2MoO_6; (1) acrolein ($\otimes$); (2) 1,5-hexadiene ($\circledcirc$); (3) benzene ($\bullet$).

ing high activity in the conversion of allyl radicals into 1,5-hexadiene.

The main oxygenated product is CO_2, the amount of which increases with temperature: Only small amounts of acrolein ($<5\%$) are observed. This indicates that the surface of Bi_2O_3 does not supply centers for insertion of oxygen into allylic species, leading to acrolein formation. The carbon balance in the case of Bi_2O_3 attains 100% only at higher temperatures and decreases with decreasing temperature. This would indicate the irreversible adsorption of C_3H_5I or products of its decomposition on the Bi_2O_3 surface at lower temperatures.

4. Bismuth Molybdate

The selectivities to various products obtained upon interaction of C_3H_6I with Bi_2MoO_6 (γ-phase), as a function of the reaction temperature, is shown in Fig. 4. The amounts of the different products change considerably with the number of pulses, particularly at lower temperatures.

The yield of C_3H_6 decreases, and that of hexadiene increases, whereas the yield of acrolein increases to a constant value reached in the first two to six pulses (depending on the temperature). The data presented in Fig. 4 pertain to the pulse for which the maximum yield of acrolein was attained. As seen from this figure, the amount of acrolein decreases on raising the temperature. In contrast to the reaction of propylene (11, 12) with bismuth molybdates, however, the interaction of allyl iodide also yields the nonoxygenated products of the reaction of the allylic intermediate, namely, hexadiene and benzene.

5. Cobalt Molybdates

The preparations of $CoMoO_4$ studied comprised stoichiometric cobalt molybdate (modifications a and b) as well as samples of $CoMoO_4$ containing some excess of MoO_3.

(a) Stoichiometric cobalt molybdate. The main product obtained after contacting C_3H_5I with b-$CoMoO_4$ is propylene, the

TABLE 2

Selectivity of the Interaction of Allyl Iodide with b-CoMoO$_4$

Product	Yield (%)										
	No. of pulses										
	1	2	1	2	3	1	2	3	1	2	1^a
	320°C		360°C			400°C			420°C		
C$_3$H$_6$	19.6	24.9	23.3	32.1	35.9	52.8	56.5	51.4	48.8	47.7	65.8
C$_6$H$_{10}$	0.5	tr	0.65	0.4	0.7	0.4	0.4	0.45	0.15	0.2	—
C$_3$H$_4$O	—	—	—	tr	0.4	—	—	—	tr	tr	—
C$_6$H$_6$	1.3	1.2	1.9	1.5	1.4	1.3	1.3	1.3	1.5	1.5	1.8
CO$_2$	0.6	tr	2.8^b	—^{c}	—^{c}	—^{c}	—^{c}	—^{c}	5.15	1.6	—^{c}

[a] After several pulses of acrolein and benzene.
[b] At 380°C.
[c] Not measured.

amount of which increases with rising temperature. Other products of the transformations of allylic intermediate, i.e., hexadiene and benzene, appear in negligible amounts. Only traces of acrolein are observed. The carbon balance of the products appearing after the reaction is poor: large amounts of irreversibly adsorbed products of the reaction of allyl iodide are deposited on the surface, as shown by the large amounts of CO$_2$ evolved when oxygen is pulsed on the cobalt molybdate surface after several pulses of iodide. The balance improves slightly on raising the temperature, as shown in Table 2, in which the amounts of products detected in the stream of the reactants leaving the reactor are summarized. Similar results were obtained in the case of a-CoMoO$_4$, which also turned out to be inactive in inserting oxygen into the allylic species, the yield of acrolein not exceeding 1%. Stoichiometric CoMoO$_4$ was found to be practically inactive in the oxidation of propylene (13).

The low yield of acrolein on stoichiometric cobalt molybdate, observed in the reaction with both propylene and allyl iodide, could be due to strong adsorption of acrolein. Experiments were then performed in which the surface of CoMoO$_4$ was saturated with acrolein by pulsing doses until a constant level of conversion of acrolein was obtained (besides the irreversible sorption of acrolein, some reaction also took place, consisting mainly in its polymerization and combustion), and, on such pretreated surfaces, the pulses of C$_3$H$_5$I were again introduced. The results obtained are shown in Table 3. As observed, after pretreatment of cobalt molybdate with acrolein, its yield in the interaction with the iodide at 320°C increased to about 6%. At higher temperatures, the effect of the increase, after covering the surface, is smaller, and the amount of acrolein formed decreases with the number of pulses of iodide. This result would indicate that, at lower temperatures, the lattice of CoMoO$_4$ may supply the small amount of oxygen capable of adding to the allyl species, provided that its surface is preliminarily blocked with irreversibly adsorbed acrolein.

(b) *CoMoO$_4$ with excess of MoO$_3$.* In view of the fact that stoichiometric CoMoO$_4$ appears to be practically inactive in the formation of acrolein from both allyl iodide and propylene, the interaction of C$_3$H$_5$I was studied for samples containing some excess of MoO$_3$. Such samples showed considerable activity in the oxidation of pro-

TABLE 3

Effect of Surface Blocking with Preadsorbed Acrolein on the Selectivity of the
Allyl Iodide Interaction with b-$CoMoO_4$

Reaction temperature (°C)	Reaction I[a]				Reaction II[b]		Reaction III[c]			
	No. of pulses	C_3H_6	C_6H_{10}	C_3H_4O	No. of pulses	C_3H_4O	No. of pulses	C_3H_6	C_6H_{10}	C_3H_4O
320	1	19.6[d]	0.5	—	1	87.5	1	17.5	5.2	6.4
	2	24.9	tr	—	2	69.5	2	19.9	2.8	6.0
					3	72.7	3	21.0	2.4	6.2
					11	16.4	4	18.6	3.0	5.7
360							1[e]	35.2	2.0	2.3
							2	35.5	2.4	2.4
	1	23.3	0.6	—	1	100.0	1	35.2	2.0	2.3
	2	32.1	0.4	tr	2	82.8	2	38.2	1.2	1.2
	3	35.9	0.7	0.4			3	41.5	1.1	0.8
	4	34.3	0.2	0.2			4	38.9	1.1	0.8
420	1[f]	23.5	—	tr	1	100.0	1	65.0	—	0.7
	2	45.2	—	0.3	2	98.0				
	3	50.6	—	0.4	11	75.0				

[a] (I) Reaction with C_3H_5I on an oxidized surface.
[b] (II) Blocking of the surface with acrolein expressed as percentage of acrolein disappearing from the gas phase.
[c] (III) Reaction with C_3H_5I on a surface blocked with acrolein.
[d] Values are percentage yields of products.
[e] Pulses without regeneration of the surface after Reactions I, II, and III at 320°C.
[f] After regeneration of the sample by heating in oxygen.

pylene to acrolein and acrylic acid, as compared with the stoichiometric molybdate (13).

The distribution of products for the sample containing a high excess of MoO_3 ($CoMoO_4$ + 0.67 MoO_3) is shown in Fig. 5. In contrast to stoichiometric $CoMoO_4$, the oxygenated products in this case are formed in large quantities. The acrolein yield decreases with increasing temperature and is compensated for by an increase in the yield of CO, CO_2, and acids. Among the nonoxygenated products, mainly propylene and benzene are found, the amount of the latter increasing with temperature to a level considerably higher than that observed upon interaction of the iodide with stoichiometric $CoMoO_4$.

The carbon balance in this case is about 100% at temperatures higher than 440°C; at lower temperatures the balance is poorer.

Similar results were obtained in the case of a sample with a smaller excess of MoO_3 ($CoMoO_4$ + 0.1 MoO_3), although the amount of acrolein was smaller in comparison with the MoO_3-richer sample. The amount of acrolein is sensitive to the extent of reduction of the surface. Figure 6 shows the results obtained when this sample was subjected to successive pulses of iodide, reoxidation with oxygen, and then pulses of the iodide–oxygen mixture, followed by pulses of the iodide again. The amount of acrolein formed decreases with the reduction of the sample; it is largest when oxygen is present in the reaction mixture.

6. Magnesium Molybdates

The interaction of C_3H_5I was studied for stoichiometric magnesium molybdate and for a preparation with the composition Mg:Mo = 1:3, which was shown, by X-ray analysis (14), to be a mixture of $MgMoO_4$, MoO_3, and the molybdate of Mg:Mo ratio 2:3. In the whole temperature range under study, stoichiometric $MgMoO_4$ produced practically only nonoxygenated compounds, among which propylene was the main
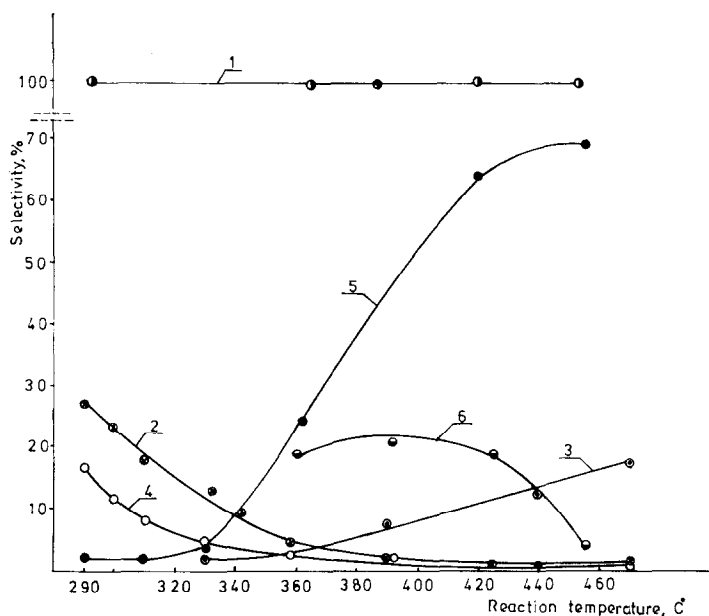
FIG. 5. Selectivity of the interaction of allyl iodide with a-CoMoO₄ + 0.67 MoO₃ as a function of the reaction temperature: (1) total conversion (◑); (2) acrolein (⊗); (3) benzene (◉); (4) propylene (○); (5) CO + CO₂ (●); (6) acrylic acid (◒).

product. Its amount increased with the number of pulses and was considerably higher than that observed in the blank reaction.

On the other hand, the amount of hexadiene, which reached a maximum of about 12% at 360°C and then decreased, was considerably smaller than that in the blank reaction. Only small amounts of benzene (1–2%) were observed over the whole temperature range. The acrolein yield did not exceed about 1% over the whole temperature range and increased to about 5% at 320°C after saturation of the surface with acrolein. Magnesium molybdate of composition 1:3 (Fig. 7), containing free MoO₃, shows a distribution of products similar to that of CoMoO₄, with an excess of MoO₃.

The amounts of oxygenated products, namely, acrolein and acrylic acid, exceed those of nonoxygenated ones. Among the latter products, only traces of hexadiene are formed. The carbon deposit in this case decreases with temperature; the amount of C₃H₅I irreversibly adsorbed changes from

18 to about 4% at temperatures of 385 and 440°C, respectively.

DISCUSSION

Important conclusions may be drawn from the comparison of the behaviors of Bi₂O₃ and MoO₃ in the reactions with propylene and allyl iodide. When allyl iodide is passed over MoO₃, practically total conversion is observed already at 310°C, with 100% selectivity to acrolein. Under the same conditions, MoO₃ was completely inactive with respect to propylene. On contacting allyl iodide with Bi₂O₃, total conversion at 310°C was also observed. In this case, however, 70% of the products formed was 1,5-hexadiene, and practically no acrolein was detected. Comparison with the results shown in Fig. 1 indicates that hexadiene was formed mainly as a result of heterogeneous reaction at the surface of Bi₂O₃, because at 310°C only about 20% conversion is observed in the blank reaction. In the reaction of propylene on Bi₂O₃,
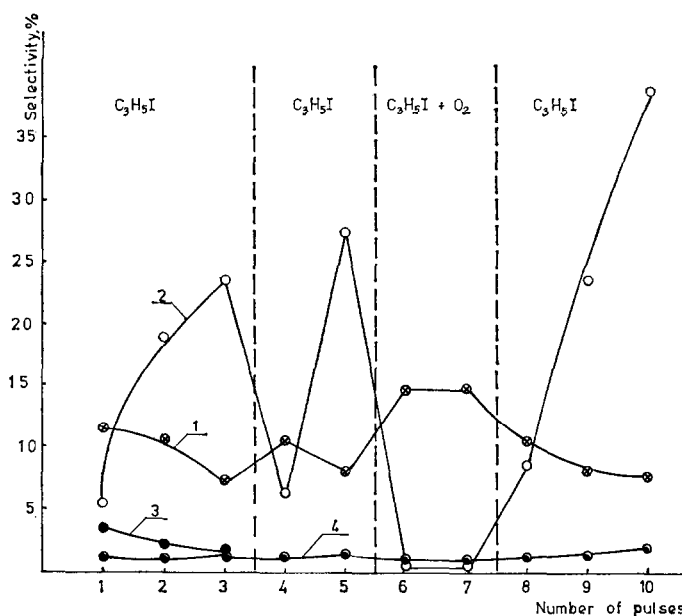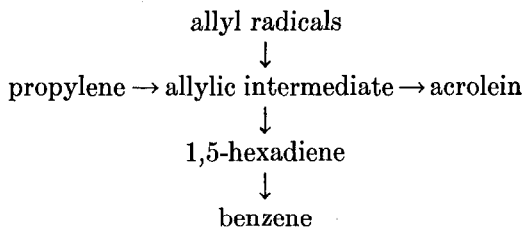
FIG. 6. Influence of the reduction of a-CoMoO₄ + 0.1 MoO₃ on the selectivity of its interaction with allyl iodide: (1) acrolein (⊗); (2) propylene (○); (3) CO₂ (●); (4) benzene (◉); Reaction temperature: 335°C.

1,5-hexadiene was also obtained as the product. These results confirm the validity of the multicenter model of molybdate catalysts which we have advanced (6, 7). Because the role of Bi-centers in selective oxidation catalysts is to generate allyl species, a change of the reactant from propylene to allyl radicals formed *in situ* in the reactor, as a result of the decomposition of allyl iodide, does not change the reaction pattern but merely gives a larger yield of 1,5-hexadiene. A different situation exists in the case of MoO₃. Its surface contains active centers which are able to perform the insertion of oxygen into the organic molecule; MoO₃, however, is inactive in propylene oxidation because no centers are available for efficient generation of allylic species. When, however, such species are formed by another route, their total conversion to acrolein at the MoO₃ surface takes place.

An efficient catalyst for the oxidation of propylene to acrolein, therefore, must be characterized by two functions namely, activation of propylene by formation and

bonding of allylic species and insertion of oxygen into the hydrocarbon molecule. In complex oxide catalysts, these functions are displayed by different lattice constituents, such as Bi–O and Mo–O polyhedra; however, it may be visualized that a single oxide may also have both kinds of centers present at the surface. The overall reaction may be described by a series of consecutive parallel steps:

$$\text{allyl radicals}$$
$$\downarrow$$
$$\text{propylene} \rightarrow \text{allylic intermediate} \rightarrow \text{acrolein}$$
$$\downarrow$$
$$\text{1,5-hexadiene}$$
$$\downarrow$$
$$\text{benzene}$$

Even when both kinds of active centers are present at the surface of the catalyst, as is the case in Bi₂MoO₆, the acrolein/diene ratio will depend on the ratio of the rate constants. In the case of oxidation of propylene, where adsorption of propylene is equivalent to its activation to the allylic intermediate, this is the rate-determining

step (15). Under such conditions, the surface of the catalyst is sparsely populated with allylic intermediates, since they rapidly react to acrolein, and, thus, the selectivity to this product is very high. When, however, the surface is contacted with allyl radicals generated in the gas phase by decomposition of allyl iodide, the coverage of the surface with adsorbed allylic intermediates may attain much higher values, and the probability that two such species will be adsorbed at adjacent centers and will recombine to form 1,5-hexadiene increases. Figure 4 shows that, in fact, the reaction of allyl iodide at the surface of Bi_2MoO_6 results in the formation of a certain amount of 1,5-hexadiene and benzene and, consequently, a much lower selectivity to acrolein than is observed in the oxidation of propylene.

The possibility of interpreting the selectivity of a catalyst in allylic oxidation is widely discussed in the literature, but, as yet, no satisfactory explanation has been offered as to the physico–chemical properties responsible for the ability of the catalyst to insert oxygen. Some time ago, Seiyama et al. (16) and Golodetz (17) advanced a hypothesis that the different behaviors of oxides may be related to their acid–base properties. Although this parameter may be of importance, its influence should be discussed only in respect to the ability to insert oxygen, as the activation of propylene resulting in formation of diene is performed by a great variety of oxides of very different acidity. However, insertion of oxygen is performed by very few oxides, although there are many other oxides of similar acidity, and the extremely high activity of MoO_3 in the insertion of oxygen in the reaction with allyl iodide rules out the concept (18) that MoO_3 modifies the acid–base properties of bismuth ions in bismuth molybdate catalysts.

When discussing the properties of an active catalysts, it should be borne in mind that the two functions mentioned
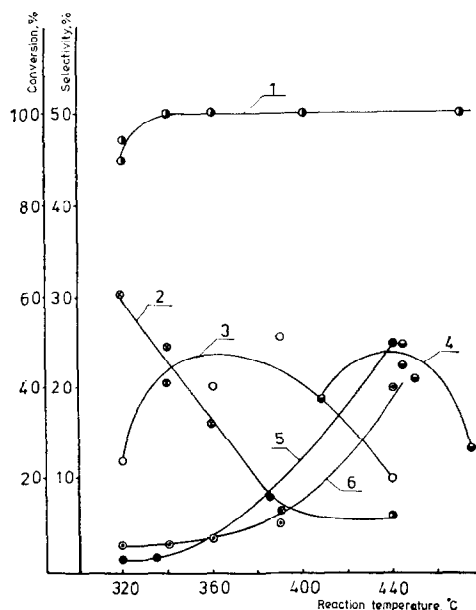

FIG. 7. Selectivity of the interaction of allyl iodide with $MgO-MoO_3$ catalyst of composition Mg:Mo = 1:3, as a function of the reaction temperature: (1) total conversion (◑); (2) acrolein (⊗); (3) propylene (○); (4) acrylic acid (◓); (5) CO + CO_2 (●); (6) benzene (◉).

above as a requirement for selective oxidation are necessary but not sufficient. Thus, as the result of both steps, oxygen ions are removed from the surface of the catalyst and must be replenished before the next elementary act can take place. This regeneration may occur by either direct oxidation of the active centers involved by gaseous oxygen or diffusion of vacancies into the lattice and their recombination with oxygen from the gas phase at other points. Apparently, this latter mechanism operates in the case of bismuth molybdate and MoO_3, in which the mobility of lattice oxygen is very high (21, 22). Under such conditions, the "dead time" of the active center is very short, and the catalyst shows high activity. However, this process of regeneration does not operate in cobalt molybdate.

Stoichiometric $CoMoO_4$ and $MgMoO_4$ are practically inactive in the reaction with both propylene and allyl iodide. On the

other hand, it has been found that $CoMoO_4$ strongly adsorbs large amounts of acrolein. At higher temperatures, reduction of the molybdate by acrolein takes place with the formation of CO_2 and simultaneous deposition of a carbonaceous deposit. Two observations are noteworthy (19): (i) Reduction with propylene proceeds at the same rate as with acrolein; and (ii) the ratio of the rate of reduction to the rate of coke deposition is constant, independent of the reducing agent and conditions of the experiment. This led to the conclusion that the reduction proceeds via the formation of a carboxylate-like complex, which undergoes decarboxylation, the hydrocarbon residue remaining at the surface in the form of a deposit. Such a mechanism for surface transformations of acrolein was confirmed by photoelectron spectroscopy (20). Summarizing our discussion, we may conclude that, on interaction of allyl iodide with $CoMoO_4$ and $MgMoO_4$, the allyl species which is π-bonded to the surface and which, in the first stage, forms the acrolein-like structure with the lattice oxygen ion, is unable to desorb, due to the inability of the lattice to release the oxygen ion sufficiently readily. The question remains open as to whether this is merely due to a high metal–oxygen bond energy or to a lack of some structural features making the process possible. The above model explains the fact that, on pulsing the allyl iodide to $CoMoO_4$, a very poor carbon balance is observed, and the large amounts of CO_2 evolved after pulsing oxygen confirm the conclusion that the surface is covered by irreversibly adsorbed species.

When MoO_3 is present at the surface of the molybdate, acrolein formation is observed in the reaction with allyl iodide. This may easily be explained by assuming that only lattice oxygen ions of MoO_3 participate in the formation of the acrolein-like intermediate, which is then rapidly desorbed from the surface of this phase. In

contrast, however, to the case of massive MoO_3, here the reaction results in the depletion of oxygen in the MoO_3 clusters, and the amount of oxygenated products decreases. In fact, the results presented in Fig. 6 clearly demonstrate that reoxidation has a pronounced influence on the activity of the surface in the reaction with allyl iodide. The activity of such preparations in the reaction with propylene could then be explained by assuming that Co cations are responsible for the generation of allyl species, which then migrate to the interface with MoO_3, where they are transformed into oxygenated complexes and are desorbed. However, as shown above, such catalysts can manifest their catalytic activity only under conditions in which their surface remains oxidized.

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