

## A MASS SPECTROMETRIC STUDY OF THE ALLYL RADICAL INTERACTION WITH OXIDES: MoO<sub>3</sub>

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Allyl radicals prepared by pyrolysis of 1,5-hexadiene or allyl bromide in a quartz pyrolyzer were directed at pressures of around 0.1 Pa through an unheated reactor filled loosely with pieces of MoO<sub>3</sub>. All components of the gaseous phase were analyzed by means of a mass spectrometer; the pyrolyzer and the catalytic reactor were placed in a high vacuum part of the mass spectrometer close to its ionization chamber so that unstable reaction products could also be detected. Acrolein was found to be the main product of the catalytic reaction between MoO<sub>3</sub> and allyl radicals; other products were propylene, CO and CO<sub>2</sub>. The above mentioned interaction of allyl radicals with unheated MoO<sub>3</sub> was compared with (i) the interaction of unheated MoO<sub>3</sub> with vapours of 1,5-hexadiene or allyl bromide heated below the respective temperature of pyrolysis; (ii) the interaction of MoO<sub>3</sub> heated to 510 K with unheated vapours of 1,5-hexadiene or allyl bromide. The difference between these three types of interactions and differences in the behaviour of 1,5-hexadiene and allyl bromide are discussed.

Attempts to estimate the role of free radicals in heterogeneous catalytic oxidation have been made for many years and comparisons of homogeneous and catalytic reactions have been discussed from this point of view. The participation of radicals in heterogeneous catalytic processes has been mainly assumed from indirect evidence, *e.g.*, from the measurement of differential temperatures<sup>1</sup> or from experiments based on post-catalytic volume changes<sup>2</sup>. The presence of free radicals on the surface of a catalyst was proved in many cases by the electron paramagnetic resonance method<sup>3</sup>. It has been shown recently by electron paramagnetic resonance that radicals formed on the catalyst can be detected in the gaseous phase after they were condensed in a liquid nitrogen trap<sup>4</sup>. The release of radicals from the surface into the gaseous phase was measured by means of a mass spectrometer in the propylene-manganese oxide system<sup>5</sup>. An extension of this study to other oxides, of different catalytic properties, has been described in our previous paper<sup>6</sup>.

It is a common shortcoming of the above mentioned papers that although the presence of radicals in the gaseous phase and on the surface was established, it is difficult to decide, whether the presence of the radicals is of a primary or secondary importance in the overall catalytic reaction mechanism. Our apparatus made it possible, after only minor modifications, to approach the problem from a different point

of view. We produced by pyrolysis a sufficient amount of a radical whose formation as an intermediate was assumed in a given catalytic mechanism; thereafter, in a separate region, we allow the radical to react with an unheated catalyst. The mass spectrometric detection made it possible to follow simultaneously both the products and the radical concentration. Such an experiment corroborates the assumed role of a radical in a catalytic reaction; however, it cannot be regarded as a full proof of such a mechanism.

In heterogeneous oxidation of propylene on oxide catalysts based on  $\text{MoO}_3$  acrolein is formed as the main product and the allyl radical is assumed to be the surface intermediate<sup>7</sup>. We prepared the allyl radical by pyrolysis of 1,5-hexadiene or allyl bromide; the radicals reacted then in the reactor with  $\text{MoO}_3$ . In several experiments, the  $\text{MoO}_3$  catalyst was moderately heated instead of the introduced vapours of 1,5-hexadiene or allyl bromide. These experiments allowed us not only to make comparisons with the more classical catalytic arrangement of temperatures, but they also served as a check of the influence of a partial heating of the catalyst caused by the heat transfer from the hot pyrolyzer to the reactor. High volatility of  $\text{MoO}_3$  did not allow to heat the catalyst to a higher temperature than 510 K.

We have discovered in the course of the experiments with allyl radicals that not only the radicals, but also unpyrolyzed vapours of 1,5-hexadiene or allyl bromide reacted in a special way with the unheated catalyst, when the vapours of these compounds were heated close to the temperature of their pyrolysis. Therefore, the results will be discussed in three parts: (i) the interaction of allyl radicals with unheated  $\text{MoO}_3$ ; (ii) the interaction of 1,5-hexadiene or allyl bromide, heated below the temperature of their pyrolysis, with unheated  $\text{MoO}_3$ ; (iii) the interaction of unheated vapours of 1,5-hexadiene or allyl bromide with heated  $\text{MoO}_3$ . Such a classification represents only a limiting case of the real temperature conditions in the experiments, but the observed differences in products show that we deal with three different types of interactions. A similarity between the dissociation energy of 1,5-hexadiene (45.7 kcal/mol) (ref.<sup>8</sup>) and allyl bromide (47.5 kcal/mol) (ref.<sup>9</sup>) made it possible to study the role of the halogen atom in the reaction.

## EXPERIMENTAL

Our experimental arrangement was originally used in the mass spectrometric detection of unstable gaseous products of heterogeneous catalytic oxidation. It was based on the arrangement of Lossing<sup>10</sup>, modified for the present work as shown in Fig. 1. A quartz tube of an inside diameter of 4 mm was placed in the high vacuum section of a mass spectrometer so that its end was 19 mm from the ionization chamber. Two heating elements made of 0.2 mm platinum wire were attached to the outside of the quartz tube (each element 30 mm long), with a 17 mm spacing between them. The introduced vapours enter the pyrolyzer (P), where they are pyrolyzed at temperatures up to 1070 K ( $T_2$ ). Products of the pyrolysis travel without significant recombination at pressures of about  $10^{-1}$  Pa towards the quartz reactor (R), filled with a catalyst. The reactor can be heated separately up to 1100 K ( $T_1$ ). The temperatures were measured by

Pt/Pt-Rh thermocouples. The thermocouple  $T_2$  remained permanently in the pyrolyzer, the thermocouple  $T_1$  was removed from the reactor after calibration. A small amount of the catalyst  $\text{MoO}_3$  (0.05–0.1 g) in the form of small plates ( $0.5 \times 1.0 \times 0.5$  mm) was used. The vacuum conductivity of the inlet part ( $228 \text{ cm}^3/\text{min}$ ) did not change after the catalyst was placed in the reactor. The flow rate calculated from the value of conductivity was  $228 \text{ Pa cm}^3/\text{min}$  (the average pressure at the entrance of the inlet tube was 1 Pa).

*Chemicals.* Molybdenum oxide  $\text{MoO}_3$  (Merck) was pressed into plates under the pressure of  $500 \text{ kg/cm}^2$ . Allyl bromide (Lachema) and 1,5-hexadiene (Fluka) were purified by distillation.

## RESULTS

### *Preparation of Allyl Radicals and Their Transport Towards the Reactor*

In order to know the composition of vapours leaving the pyrolyzer, it was necessary to test the pyrolysis of 1,5-hexadiene and allyl bromide in the absence of the catalyst. Fig. 2 shows the decomposition curves of both compounds, obtained after the vapours passed through the reactor, plotted against the temperature of pyrolysis. The 12 eV curve shows the formation of allyl radical from 1,5-hexadiene and represents a directly measured and normalized ion current of the radical. It was obtained by ionization of the radicals in the ionization chamber by electrons of very low kinetic energies, close to the ionization threshold. Under such conditions the mass spectrum is rather

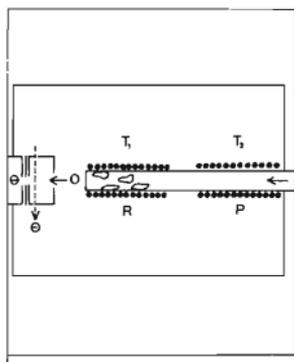


FIG. 1

Experimental Arrangement: Pyrolyzer (P), Reactor (R) and the Ionization Chamber of the Mass Spectrometer

$T_1$  and  $T_2$  are temperatures of the reactor and pyrolyzer, respectively.

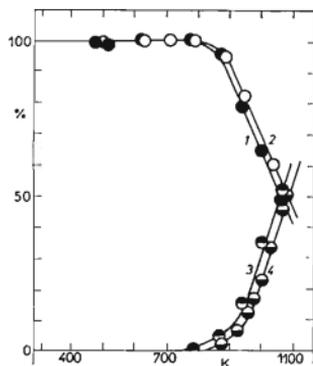


FIG. 2

Pyrolysis of 1,5-Hexadiene and Allyl Bromide Vapours and Allyl Radical Formation in the Pyrolyzer without  $\text{MoO}_3$  Catalyst in the Reactor

1 1,5-Hexadiene; 2 allyl bromide; allyl radical measured at: 3 30 eV; 4 12 eV.

simplified, however, a much lower ionization efficiency of non-pyrolyzed molecules (of a higher ionization potential) gives very misleading quantitative relations. For this reason we checked the concentration of radicals independently using mass spectra obtained at the ionization energy of 30 eV, applying the necessary corrections for the ion fragmentation. A reasonable agreement between both curves (at 12 eV and 30 eV) confirmed that the corrections performed at 30 eV were reliable and not influenced by a third compound. Fig. 2 shows that a 50% decomposition of 1,5-hexadiene leads to a production of the allyl radical, which is by one half lower than would correspond to the formation of 2 allyl radicals from one pyrolyzed molecule of 1,5 hexadiene. As no other products were observed and the necessary corrections for different ionization cross sections were carried out, we believe that the observed material balance discrepancy was caused by carbonization of the vapours in the pyrolyzer and by polymerization of allyl radicals in the ion source. This assumption is based on the experience that frequent cleaning of the entire system was needed, when working with the allyl compounds at high temperatures. The mass spectrum of the allyl radical obtained at 30 eV is shown in Table I.

The decomposition curve of allyl bromide (Fig. 2) shows a similar temperature dependence as the curve of 1,5-hexadiene, in agreement with the fact that both compounds have very similar dissociation energies. The curve of the allyl radicals formed from allyl bromide was identical with that one obtained for 1,5-hexadiene; therefore, it is not given in Fig. 2.

In the pyrolysis of allyl bromide, hexadiene can be observed as a recombination product of the allyl radicals. Small amounts of the recombination products (4% of the amount of introduced allyl bromide) were observed in experiments carried out in the absence of the catalyst. Simultaneously, hydrogen bromide (but not bromine) was detected. A relatively low recombination of allyl radicals results from the vacuum conditions. At pressures of the order of  $10^{-1}$  Pa products of the pyrolysis leaving the pyrolyzer in the direction towards the reactor suffer collisions with the wall, but their gas phase collisions are fairly rare. Heterogeneous reactions are usually slow and require that the adsorbed particles remain sufficiently long on

TABLE I

Mass Spectrum of the Allyl Radical

<i>m/e</i>	41	40	39	38	38	27	26
30 eV <sup>a</sup>	45	26	100	12	3	0	0
50 eV <sup>a</sup>	41	26	100	16	10	(0)	(7)

<sup>a</sup> Energy of ionizing electrons/eV.

the surface in order to have time to react. The main competition to the heterogeneous reaction is the process of desorption which prevails at the high temperature of the surface. Therefore, in our experiments the reactive particles did not react on the hot quartz walls on their way between the pyrolyzer and the reactor. A large surface area and the low temperature of the catalyst were then the main reasons, why we observed in our experiments mainly processes between the reactive particles and the catalyst. Several experimental evidences support our assumption that the vacuum conditions were not seriously influenced by the addition of the catalyst into the reactor, namely: (i) a part of the radicals penetrated through the catalyst into the ionization region of the mass spectrometer (Table II) – the radicals which either did not collide or did not react with the catalyst; (ii) the measured value of the flow conductivity of the inlet tube did not change when the catalyst was introduced into the reactor; to check, if this value was sufficiently sensitive to change when mechanical obstacles were put into the gas stream, we inserted either a piece of quartz wool or a glass tube with a narrowed end into the empty reactor; in both cases the flow conductivity dropped to about one third of its original value; (iii) significant amount of propylene, propadiene and benzene were observed in the pyrolysis of 1,5-hexadiene or allyl bromide under the conditions described sub (ii), when the residence time of particles in the reactor was increased; on the other hand, the above mentioned products were unimportant in normal experiments in which the glass obstacles were removed and replaced by the catalyst.

According to the results of high vacuum experiments of Lossing<sup>11</sup> we expected to observe in our experiments with allyl bromide mainly allyl radical dimer as the product. The formation of the dimer was significant at temperatures of the pyrolyzer above 770 K, but its production passed through a maximum at 970 K and at higher temperatures production of benzene, propylene and allene was observed together

TABLE II

Concentrations of 1,5-Hexadiene and Allyl Radical Measured after 1,5-Hexadiene Passed through the Pyrolyzer and the Reactor

Ionizing electron energy 12 eV, concentration as peak height (mm).

Temperature pyrolyzer, K	Empty reactor		MoO <sub>3</sub> Catalyst	
	hexadiene <i>m/e</i> 67	allyl <i>m/e</i> 41	hexadiene <i>m/e</i> 67	allyl <i>m/e</i> 41
470	45	1	45	1
1 070	22	480	15	163

with a steadily decreasing production of the allyl radical dimer. Propylene and allene could result from the allyl-allyl radical disproportionation, but the value reported for the ratio of the disproportionation/recombination rates of allyl radicals by Kerr<sup>12</sup> is very low (0.02). On the other hand, Haber<sup>7</sup> and Kunichika<sup>13</sup> described a significant formation of propylene, benzene and allene in experiments with allyl iodide. These experiments were carried out at higher pressures and temperatures of the catalyst.

### Reactions of Allyl Radicals with Unheated MoO<sub>3</sub>

Fig. 3 gives products obtained with vapours of 1,5-hexadiene, led through the pyrolyzer at the temperature  $T_2$ , interacting with unheated MoO<sub>3</sub>. At present, we shall concentrate on the temperature range above 870 K, in which allyl radicals are formed. The main product observed was acrolein, other detected products were propylene, carbon monoxide and carbon dioxide. The temperature dependence of the acrolein formation is similar to that of the allyl radical formation (Fig. 2), thus indicating a close connection between the two species. We were unable to avoid a partial heating of the reactor with the catalyst (up to 470 K) when the pyrolyzer was kept at a very high temperature. For this reason we carried out several experiments in which the catalyst was kept in a glass tube extension at the more distant end from the pyrolyzer.

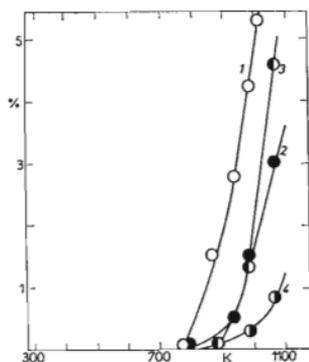


FIG. 3

Products of 1,5-Hexadiene Interaction with MoO<sub>3</sub>

Conversion vs temperature of pyrolysis; reactor not heated; maximum reactor temperature 470 K. 1 Acrolein; 2 propylene; 3 CO; 4 CO<sub>2</sub>.

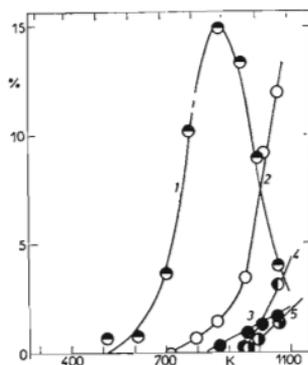


FIG. 4

Products of Allyl Bromide Interaction with MoO<sub>3</sub>

Conversion vs temperature of pyrolysis; reactor not heated; maximum reactor temperature 470 K. 1 1,5-Hexadiene; 2 acrolein; 3 propylene; 4 CO; 5 CO<sub>2</sub>.

Under these conditions the temperature of the catalyst remained safely below 370 K even at high temperatures of the pyrolyzer (up to 1070 K). The deep oxidation products were then mostly eliminated from the spectra, while acrolein remained as the dominant product. The participation of allyl radicals in the reaction with  $\text{MoO}_3$  can be seen from Table II. In the absence of the catalyst 1,5-hexadiene is pyrolyzed at 1070 K to about 50% (mass 67 — decrease of the peak height from 45 mm to 22 mm), while with the catalyst the original value drops to about 40% (peak height from 45 mm to 15 mm). Assuming that the process of pyrolysis was not influenced by the addition of the catalyst, we conclude that the difference between the peak height 22 mm and 15 mm is caused by the consumption of the 1,5-hexadiene molecules on the catalyst. A more significant effect than that one with the non-decomposed molecules can be observed with allyl radicals. Independently of the presence or absence of the catalyst in the reactor, the same amount of allyl radicals ought to be formed in the pyrolyzer from 1,5-hexadiene (mass 41 — peak height 480 mm in the spectra). The difference between this value and the value measured in the presence of the catalyst (190 mm) corresponds then to the interaction of allyl radicals with  $\text{MoO}_3$ .

The products obtained when vapour of allyl bromide passed through the heated pyrolyzer and then interacted with unheated  $\text{MoO}_3$  are given in Fig. 4. In the temperature range significant for the production of allyl radicals in the pyrolyzer

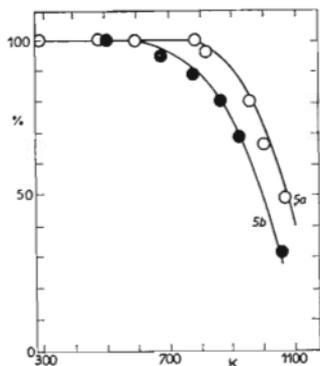


FIG. 5  
Pyrolysis of 1,5-Hexadiene Vapours  
5a Without  $\text{MoO}_3$  catalyst, 5b with  $\text{MoO}_3$   
catalyst in the reactor.

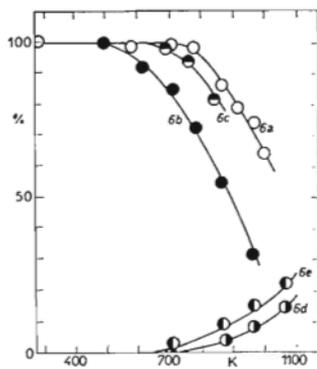


FIG. 6  
Pyrolysis of Allyl Bromide Vapours  
6a Without  $\text{MoO}_3$ ; 6b with  $\text{MoO}_3$ , first  
measurement; 6c with  $\text{MoO}_3$ , second  
measurement; 6d HBr, first measurement; 6e  
HBr, second measurement.

products as in Fig. 3 were observed: acrolein, carbon monoxide, carbon dioxide and propylene. In addition, hydrogen bromide was observed. The deep oxidation products (CO and CO<sub>2</sub>) were — as in the previous case (Fig. 5) — suppressed by the transfer of the catalyst to a larger distance with respect to the pyrolyzer. The formation of hexadiene, the main product formed below the temperature when allyl radicals were produced in the pyrolyzer, will be discussed in the next section.

*Reactions of Unheated MoO<sub>3</sub> with Vapours of 1,5-Hexadiene or Allyl Bromide Preheated below the Temperature of Their Pyrolysis*

Fig. 5 shows the dependence of the 1,5-hexadiene concentration on the temperature of the pyrolyzer measured both in the presence and absence of the catalyst in the reactor. The curve obtained with the catalyst in the reactor (curve 5b) is shifted by about 100 K to lower temperatures than the curve 5a obtained without the catalyst. The temperature shift between both these curves is relatively small and no corresponding products were observed in the interval 470–770 K.

Fig. 6 gives an analogous dependence for allyl bromide. The decomposition curves were obtained again in the absence of the catalyst (6a) and with the catalyst in the reactor (curve 6b). Curve 6c is a repeated measurement of the situation as in 6b. The observed temperature shift between curves 6a and 6b is about twice as large as in the case of 1,5-hexadiene. Moreover, a significant surface poisoning was observed after repeated measurements; as a result, a gradual re-shifting of the curve 6c from the position of the curve 6b almost up to the position of the curve 6a was observed. This fact is an evidence that the temperature shift between the curves

TABLE III

Main Products Formed in Interaction of Allyl Bromide or 1,5-Hexadiene with MoO<sub>3</sub>

Temperature, K		Allyl bromide	1,5-Hexadiene
pyrolyzer	reactor		
1 070 (allyl radical)	470	acrolein, CO, CO <sub>2</sub> , propylene	acrolein, CO, CO <sub>2</sub> , propylene
1 070 (allyl radical)	< 370	acrolein, propylene	acrolein, propylene
470–770	< 370	hexadiene	no products
270	470	acrolein	no products

5a and 5b on the one hand and 6a and 6b on the other hand is connected primarily with chemisorption effect and chemical reactions, rather than with a change of the vacuum regime caused by the addition of the catalyst into the flow. A substantial surface poisoning can also be seen from the measurements of the hydrogen bromide concentration: it increases in time with the number of repeated measurements.

It follows from Fig. 4 that hexadiene was the main product formed in the interaction with allyl bromide in the lower temperature region. The reaction started as early as at the temperature of the pyrolyzer of 470 K, earlier than any allyl radicals could be formed by pyrolysis in the gaseous phase. The temperature of the catalyst remained close to the room temperature. Naturally, the displacement of the catalyst to larger distances from the pyrolyzer had no effect on the composition of the products.

#### *Reactions of Unheated 1,5-Hexadiene or Allyl Bromide with Mildly Heated $\text{MoO}_3$*

In these experiments the catalyst was moderately heated to about 510 K. With 1,5-hexadiene no specific products were observed, while with allyl bromide about 3% of the conversion led to acrolein. In contrast with the acrolein formation described in the preceding section, in the present experiment no hexadiene formation preceded at lower temperatures the formation of acrolein. The products observed in the three above mentioned types of interactions are summarized in Table III.

## DISCUSSION

Large amount of papers on the interaction of radicals with molecules in homogeneous systems has been published and numerous quantitative kinetic and thermodynamic data have been reported in the last years<sup>12,14,15</sup>. The addition of a catalyst to a system containing free radicals, the main subject of this paper, rises several new problems. Chemisorption on an unheated catalyst and a changing surface poisoning are main obstacles of a quantitative evaluation of such experiments. It seems, however, that the presented approach — a study of the interaction of the catalyst with radicals prepared closely to the reactor — can provide valuable information on the mechanism of catalytic reactions.

In this paper we have described that the interaction of allyl radicals with  $\text{MoO}_3$  yields preferentially acrolein — the same product as obtained in the selective oxidation of propylene on the catalysts of the molybdate type under usual industrial conditions. Although the formation of acrolein from allyl radicals in our low pressure experiments agrees with the assumption that the allyl radical is an intermediate in the catalytic formation of acrolein in mixed Bi-Mo-O oxides<sup>7</sup>, such an agreement cannot be regarded as a full proof of such a mechanism.

Further evidence from methods which make it possible to study the character of the adsorbed allyl radical (electron paramagnetic resonance, infra-red spectroscopy) is required in the future.

We took a great care to confirm that the observed product — acrolein — was indeed connected with the interaction of the allyl radical with  $\text{MoO}_3$ . The evidence was discussed in the result section. In agreement with the assumed role of the allyl radical, the identical product — acrolein — was obtained independently of whether the allyl radical was prepared by pyrolysis of 1,5-hexadiene or allyl bromide.

More complicated results than those with allyl radicals were obtained on unheated  $\text{MoO}_3$  with vapours of allyl bromide, preheated below the temperature of its pyrolysis (pyrolyzer temperature 470–870 K). Hexadiene, which may result from the recombination of allyl radicals, was found to be the main product in this temperature range. Although under these conditions no allyl radicals were produced in the gaseous phase by pyrolysis, we cannot exclude that radicals were formed on the  $\text{MoO}_3$  surface from thermally activated allyl bromide. However, in the experiments described earlier allyl radicals yielded acrolein rather than hexadiene and we believe, therefore, that the formation of hexadiene from allyl bromide does not necessarily proceed through an allyl radical intermediate. Direct evidence can be, of course, obtained only by an analysis of the surface complex.

A clear difference between 1,5-hexadiene and allyl bromide can be seen in the third type of interaction, heated  $\text{MoO}_3$ /unheated vapours. While allyl bromide yielded acrolein, with 1,5-hexadiene no specific products were observed. The role of bromine atoms in these experiments seems to be evident; either they modify the surface or they enable an easier bond formation between the catalyst and the molecule. For these reasons it is not possible to draw any simple correlations between the rate of acrolein formation and the dissociation energies of the reagent molecules<sup>16,17</sup>.

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