MASS SPECTROMETRIC STUDY OF ALLYL RADICAL, ALLYL BROMIDE AND 1,5-HEXADIENE INTERACTIONS WITH OXIDES; COBALT SUBOXIDE Co_3O_4

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Products of (*a*) allyl radical interaction with unheated Co_3O_4, (*b*) thermally activated 1,5-hexadiene or thermally activated allyl bromide with unheated Co_3O_4, (*c*) moderately heated Co_3O_4 with unheated 1,5-hexadiene or allyl bromide were studied under Knudsen flow conditions. Cobalt suboxide Co_3O_4, a typical catalyst of deep oxidations, yielded acrolein in reaction with allyl radicals as early as at the room temperature of the catalyst. A similar acrolein formation was also observed in the allyl radical interaction with other oxides exhibiting different catalytic properties. It appears that acrolein is in general the primary product of the allyl radical interaction with the oxides. The results are discussed and compared with previous data obtained with MoO_3.

In the interaction of MoO_3 with allyl radicals, prepared by pyrolysis of 1,5-hexadiene or of allyl bromide, acrolein was formed as the main product[1]. This result is in agreement with the assumption that acrolein can be produced on MoO_3, once a formation of the allyl radical is possible on the surface of the catalyst[2]. According to the authors, in industrial catalysts Bi^{3+} ions catalyze such allyl radical formation, while MoO_3 — owing to its special structure — acts as an oxygen donor to allyl radicals in the step of the acrolein formation. We have measured the interaction of allyl radicals with some other oxides possessing different catalytic properties in order to find out, whether the acrolein formation is characteristic only of the MoO_3/allyl radical interaction. Our main attention in this paper is concentrated on reactions proceeding on Co_3O_4, a typical catalyst of a deep oxidation type.

In our previous study[1] of MoO_3 it was observed that – together with allyl radicals – non-pyrolyzed allyl bromide reacted partially on the catalyst, too, if its vapours were heated to temperature higher than 470 K. It was also found that – in contrast with 1,5-hexadiene – unheated allyl bromide formed acrolein in the interaction with midly heated (510 K) MoO_3. In this paper we have studied: (*a*) the interaction of allyl radicals with unheated Co_3O_4; (*b*) the interaction of unheated Co_3O_4 with vapours of 1,5-hexadiene or allyl bromide (both heated below their point of pyrolysis); (*c*) the interaction of unheated vapours of 1,5-hexadiene or allyl bromide with mildly heated Co_3O_4.

EXPERIMENTAL

The experimental arrangement was described in our previous paper[1]. A quartz pyrolyzer and a quartz reactor were located inside the vacuum part of a mass spectrometer, close to the ionization source. Vapours of 1,5-hexadiene or allyl bromide passed through the pyrolyzer which could be heated to temperatures up to 1 070 K. At this highest temperature about 50% of the molecules were pyrolyzed to yield allyl radicals. The pyrolyzed mixture entered the reactor containing the catalyst under a pressure of the order of 0·1 Pa. The reactor could be heated independently. Due to the heat transfer, a temperature rise of the reactor up to 470 K was observed when the pyrolyzer was heated to about 1 070 K. To check the effect of the temperature rise of the catalyst, in several experiments the catalyst was placed into a thin glass tube extension, located outside the reactor at the more distant end with respect to the pyrolyzer. Under these conditions the temperature of the catalyst remained always safely below 370 K. In order not to change the vacuum conditions after the insertion of the catalyst into the reactor, only small amounts of the catalyst (0·05—0·1 g), loosely packed in the reactor, were used.

RESULTS

The interaction of allyl bromide with Co_3O_4. Fig. 1 shows products obtained in the interaction of Co_3O_4 with allyl bromide which was passed through the pyrolyzer heated up to 1070 K. Carbon dioxide, 1,5-hexadiene, and acrolein were the main

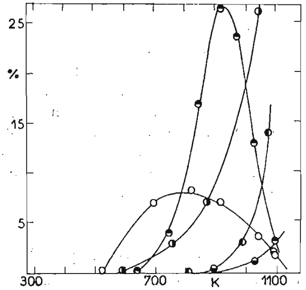

FIG. 1

Products of Interaction of Allyl Bromide with Co_3O_4

Conversion (%) *vs* temperature of pyrolysis (T_2); reactor unheated, its maximum temperature rise to T_1 470 K; ○ acrolein, ◓ 1,5-hexadiene, ◑ CO_2, ◐ CO, ◒ HBr.

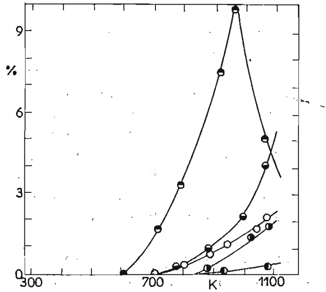

FIG. 2

Products of Interaction of Allyl Bromide with Co_3O_4 with the Catalyst Kept in the Extension Tube

T_2 Temperature of pyrolysis; reactor unheated, its maximum temperature rise to T_1 — below 370 K; symbols for products same as in Fig. 1.

products in the lower part of the temperature region (up to 900 K). At temperatures higher than 900 K, where allyl radicals begin to be formed in significant amounts by pyrolysis[1], a strong decrease of hexadiene and acrolein concentrations, with an increase of carbon dioxide and carbon monoxide amounts, was found. Small amounts of HBr and propylene (not shown) were observed, too.

Fig. 2 describes the results of an experiment whose conditions differ from those of the first experiment (Fig. 1) in that the catalyst was kept outside the reactor in a small glass tube extension at the more distant end with respect to the pyrolyzer. In this arrangement the catalyst was only gently heated by the heat transfer from the pyrolyzer and its temperature stayed always below 370 K, even though the pyrolyzer was heated up to 1070 K. The amount of deep oxidation products is strongly reduced. Hexadiene, the selective product of the interaction of allyl bromide on Co_3O_4, shows a significant maximum in dependence on the temperature; however, contrarily to Fig. 1, the amount of acrolein increases steadily up to the highest temperatures of the pyrolyzer. It is probable that the decrease of the amount of acrolein (formed by the reaction of thermally excited allyl bromide) is overshadowed by the formation of acrolein in another process, in the interaction of allyl radicals with Co_3O_4. An analogous acrolein formation was described earlier in the case of the interaction of allyl radicals with MoO_3. However, such acrolein formation from the allyl radical was strongly suppressed on Co_3O_4 at temperatures above 900 K (Fig. 1), because at those temperatures allyl radicals and allyl bromide were preferentially oxidized to carbon monoxide and carbon dioxide.

There is another difference which can be observed, when comparing the results in Fig. 1 and Fig. 2: though in the latter case (Fig. 2) only one half of the amount of the catalyst was used (and in agreement with this the total amount of products formed is lower than in the former case, Fig. 1), the amount of HBr is nearly twice as large in the results in Fig. 2, inspite of the smaller amount of the catalyst. Since HBr molecules are formed in the pyrolyzer in a concentration independent of the amount of the catalyst, this higher HBr concentration in the latter case is due to a lower chemisorption.

Fig. 3 shows the relative amount of products found in the interaction of the Co_3O_4 catalyst (heated to 470 K) with allyl bromide vapours introduced through the pyrolyzer kept at the room temperature. These temperature conditions correspond more closely to an usual catalytic arrangement. Also, in this way we could check the effect of the temperature rise of the catalyst by the heat transfer from the pyrolyzer. The results show that although allyl bromide was mostly oxidized to CO_2, still a small amount of acrolein was formed. However, hexadiene – the main product of the interaction of preheated allyl bromide (Fig. 1 and Fig. 2) – was not observed in the experiment described in Fig. 3.

The interaction of 1,5-hexadiene with Co_3O_4. Only deep oxidation products were observed when 1,5-hexadiene was pyrolyzed at 1070 K; this temperature of the pyrolyzer led to a rise of the reactor temperature to 470 K. When the catalyst was kept in the extension tube at a temperature safely below 370 K, the deep oxidation products were strongly suppressed and small amounts of acrolein and propylene were observed. In the medium temperature range of the pyrolyzer (470–800 K), below the temperature of hexadiene pyrolysis, no acrolein formation was found. When the arrangement was reversed and non-heated vapours of hexadiene were admitted to the catalyst heated to 470 K, only deep oxidation products were observed.

The interaction of allyl radicals with other oxides. Several qualitative experiments were carried out earlier in the basically same experimental arrangement. The interaction of allyl radicals, prepared by pyrolysis of 1,5-hexadiene, was studied with oxides of different catalytic properties: a catalyst of a selective oxidation (Bi—Mo—O) catalysts of dimerization and aromatization (Bi_2O_3, ZnO), catalysts of deep oxidation (CuO, MnO_2, NiO). All these oxides yielded acrolein at those temperatures of the pyrolyzer, when allyl radicals were formed.

Table I shows products obtained with 1,5-hexadiene and allyl bromide on Co_3O_4 and MoO_3. Products are listed in a sequence according to decreasing intensities.

DISCUSSION

It has been shown in our previous paper[1] that allyl radicals yield acrolein on MoO_3 practically at the room temperature of the catalyst. At temperature above 470 K products of deep oxidation are partially formed on MoO_3. The present result show that allyl radicals yield acrolein on Co_3O_4 at the room temperature, too, but above 470 K of the catalyst exclusively deep oxidation products (CO and CO_2) are formed.

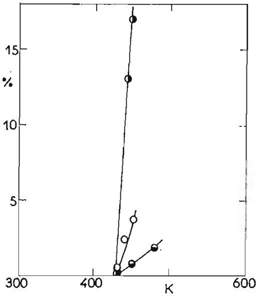

FIG. 3

Products of Interaction of Allyl Bromide with Co_3O_4

T_1 Temperature of reactor containing Co_3O_4; pyrolyzer unheated; symbols for products same as in Fig. 1.

Acrolein formation was also observed in the allyl radical interaction with other unheated oxides of different catalytic properties. It seems that acrolein formation from the allyl radical is not limited to those special catalysts only which yield acrolein under normal (industrial) conditions. More likely, acrolein is produced as a product of the allyl interaction with oxides in general, as a result of a specific complex formation.

An interesting difference can be noticed in the behaviour of 1,5-hexadiene and allyl bromide on a cold catalyst, if the vapours were preheated to a temperature below the temperature of their pyrolysis. While in the system MoO_3/allyl bromide hexadiene appeared as the main selective product, in the system Co_3O_4/allyl bromide two significant selective products (hexadiene and acrolein) are formed. In an attempt to explain this behaviour one might assume that oxygen, more loosely bound in Co_3O_4 than in MoO_3, is able in the case of Co_3O_4 to participate partly in the formation of the allylic surface complex; as a result, after desorption both acrolein and hexadiene (a product of recombination) are observed. In our previous measurements[1] with allyl bromide/MoO_3 and 1,5-hexadiene/MoO_3 it was not possible to decide, whether both compounds (*i.e.* 1,5-hexadiene and allyl bromide) formed a similar type of the surface complex on MoO_3, since only one specific product (hexadiene)

TABLE I

Products of Interaction of 1,5-Hexadiene and Allyl Bromide with Co_3O_4 and MoO_3[a]

	Co_3O_4	MoO_3
Allyl radical (catalyst max. 470 K)	CO_2, CO, HBr, propylene	acrolein, CO, HBr, propylene
Allyl radical (catalyst less than 370 K)	CO_2, acrolein, HBr, propylene	acrolein, HBr, propylene
1,5-Hexadiene heated (catalyst less than 370 K)	no products	no products
Allyl bromide heated (catalyst less than 370 K)	hexadiene, acrolein	hexadiene
1,5-Hexadiene cold (catalyst 470 K)	CO_2, CO	no products
Allyl bromide cold (catalyst 470 K)	CO_2, acrolein, HBr	acrolein

[a] Products listed in a decreasing order of intensities.

was observed in the interaction with allyl bromide. In the case of the interaction with 1,5-hexadiene we had no way of distinguishing the hexadiene-reactant from the hexadiene-product, if hexadien were also formed. The situation with Co_3O_4 is different, since two products, hexadiene and acrolein, are observed in the interaction with allyl bromide. When the allylic complex formed on Co_3O_4 from allyl bromide and 1,5-hexadiene were of the same character, one would expect acrolein to be formed also in the 1,5-hexadiene/Co_3O_4 interaction. This is, however, not the case. Possibly a higher polarizability of allyl bromide enables an easier formation of the surface complex, possibly bromine atoms modify partly the surface of the catalyst.

Experiments in which unheated vapours interacted with a moderately heated Co_3O_4 made some interesting comparisons possible. The gently heated catalyst did not react with unheated 1,5-hexadiene, while it reacted with unheated allyl bromide, yielding a small amount of acrolein. This result – the formation of one selective product, acrolein – is different from the previous result, where thermally activated allyl bromide yielded with unheated Co_3O_4 two selective products, acrolein and hexadiene. Let us assume that in both cases allyl bromide forms a surface complex of a similar character. Then in the system cold Co_3O_4 catalyst/heated allyl bromide oxygen only partly participates in the surface complex and both products, hexadiene and acrolein, are present after desorption in the gaseous phase. In the system heated Co_3O_4 catalyst/unheated allyl bromide gentle heating of the catalyst to temperatures below 370 K leads to a complete oxygen incorporation into the surface complex; consequently, only acrolein is present in the gaseous phase as the main product. However, if in this latter system the catalyst is heated to temperatures close to 470 K, not only a full oxygen incorporation into the complex, but also a complete complex dissociation takes place; strong CO and CO_2 evolution results and only traces of acrolein are present in the gaseous phase. Under these latter conditions, 1,5-hexadiene reacts on Co_3O_4 to form only deep oxidation products CO and CO_2.

On the basis of the results of the previous and this paper we believe that similar studies of the interaction of radicals with a catalyst, which allow an approach to the first steps in the over-all catalytic mechanism, can provide further useful information.

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