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Organic Polymers: Correlation between Their Structure and Catalytic Activity in Heterogeneous Systems

IV. Oxidative Dehydrogenation: A Comparison between the Catalytic Activity of an Organic Polymer and That of Some Molybdate Catalysts*

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The molybdates of Bi, Co, and Ni were compared as catalysts with an organic polymer containing benzoquinone groups. Limonene, 1-menthene, and 4-methyl-4-ethyl-1-cyclohexene served as substrates. The substrates were passed over the freshly oxidized solids at 300° and 350°C and product compositions were measured with time. Experimental results are consistent with an initial transfer of hydrogen from substrate to catalyst for all materials concerned, but with the molybdates hydride transfer seems to occur and with the organic polymer, hydrogen atom transfer. Molybdates of Co and Ni cause disproportionation and isomerization reactions, and gaseous hydrogen is evolved. Bi molybdate gives mainly dehydrogenation and formation of water. The organic polymer causes dehydrogenation, and to some extent disproportionation and isomerization reactions. These phenomena are discussed in the light of the bond strength between catalyst and transferred hydrogen.

Acrylonitrile, if passed together with limonene, suppresses the disproportionation reaction over Co molybdate. The catalytic activity of the organic polymer does not fall below that of the inorganic catalysts.

INTRODUCTION

Quinones are known to be strong dehydrogenating agents in organic chemistry. They are mostly used in solution together with the substrate to be dehydrogenated. Heating at reflux for hours and sometimes days causes transfer of hydrogen from the substrate to the quinone, by which hydroquinone is formed. The mechanism of this reaction has been studied extensively (*1*).

If a quinone unit is incorporated into a thermostable polymer, hydrogen transfer may also occur from a substrate in the gas phase to the solid polymer. The hydrogen transferred to the solid may be removed by air oxidation. This means that these polymers can act as catalysts in oxidative dehydrogenation (*2*), when a substrate and air or oxygen are passed simultaneously over the catalyst.

The way we studied reactions of this kind previously (*3*, *4*) was to pass organic model compounds over the polymer in the absence of air and to study the composition of the effluent with time until the polymer had become inactive as a catalyst, because of saturation with hydrogen. After removal of the hydrogen by air, the dehydrogenation could be repeated. As recent studies (*5–8*) on the mechanism of the catalytic activity of molybdate catalysts, which have become important for oxidation, ammoxidation, and dehydrogenation reactions, also suggest a transfer of hydrogen from substrate to catalyst, we thought that a comparative study of organic and inorganic catalysts,

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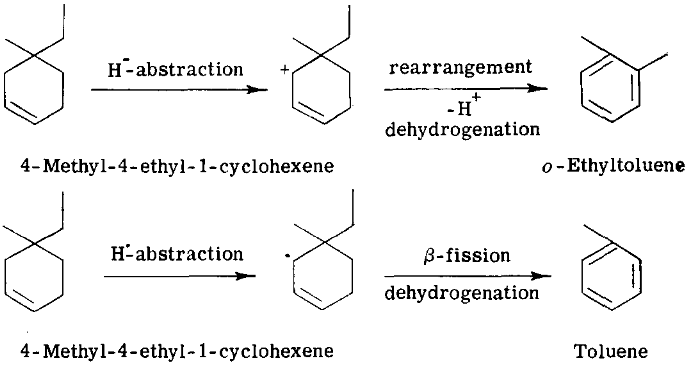
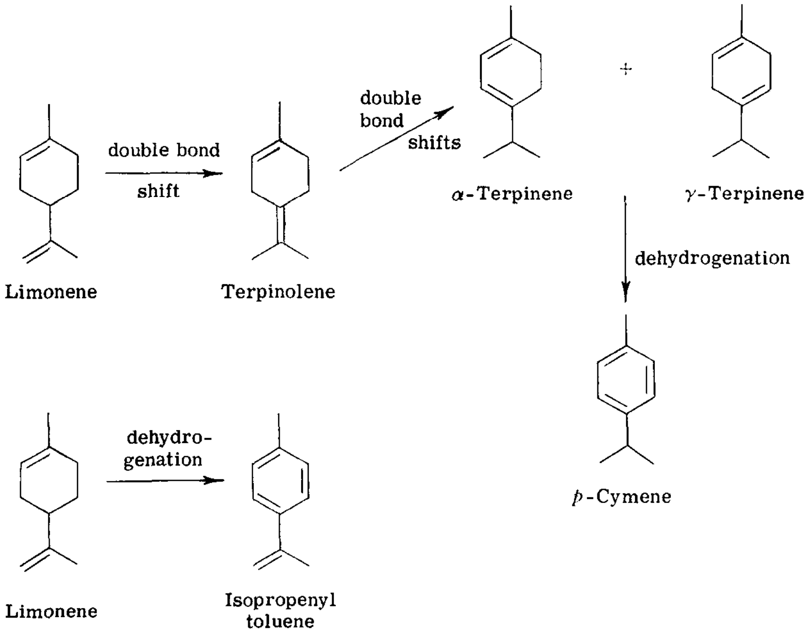
using the method mentioned, might give information on the mechanism of both. This was borne out by experiment. We used the three model compounds and the catalysts described below.



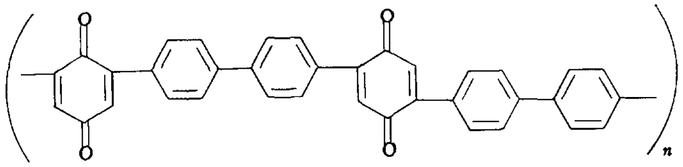
Limonene. This is a cyclic diolefin, which dehydrogenates easily and because of double-bond shifts may give a series of products that all can be identified by gas chromatography.



1-Menthene. This is a cyclic monoolefin, having the same carbon skeleton as limonene, but being a monoolefin it dehydrogenates less easily.

4-Methyl-4-ethyl-1-cyclohexene. This is a gem compound having a methyl and an ethyl group at the same carbon atom of the cyclohexene ring. To permit dehydrogenation to an aromatic compound, either the methyl or the ethyl group has to leave. We showed previously (*3*) that for compounds of this kind, the reaction product can be indicative for the kind of H abstraction which occurs.

Organic catalyst. As the catalyst containing quinone groups we used the polymer obtained by treating diazotized benzidine with benzoquinone (*9*) giving the structure



This polymer is red. During the hydrogen transfer reaction its color changes to yellow-brown. That we are concerned here with a quinone–hydroquinone transition can be seen in Fig. 1. The characteristic absorption for a quinone group in the infrared at 1660 cm^{-1} has disappeared in the material that has taken up hydrogen from the substrate. After reoxidation it reappears together with the red color.

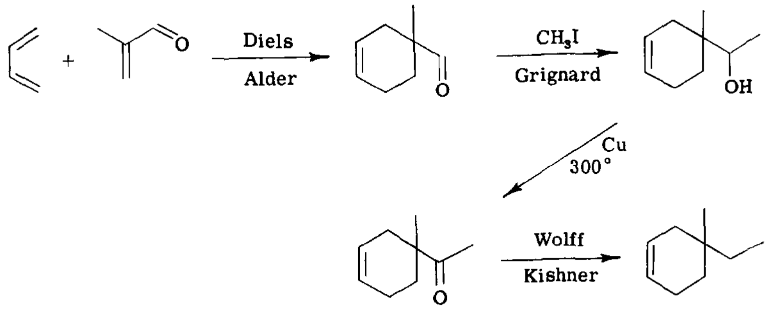
Molybdate catalysts. Bi, Co, and Ni molybdates were studied, the molar ratio between metal ion and molybdenum being 1.

METHODS

Catalysts. The molybdates were prepared by coprecipitation of equivalent aqueous solutions of the metal nitrate and ammonium molybdate in the presence of an equivalent quantity of aqueous ammonia. Bismuth nitrate decomposes in water and therefore was dissolved in an equivalent of dilute acetic acid and coprecipitation was done in the presence of two equivalents of aqueous ammonia. The organic catalyst was prepared according to ref. (*9*).

Catalytic reaction. Catalysts were heated in a vertical Pyrex tube and the liquids introduced at the upper end by means of a syringe pump of variable speed.

Materials. 1-Menthene (Givaudan, Delawanna, N. J.) and limonene (Fluka A. G., Switzerland) were passed over a column of Merck acid-washed alumina before use. 4-Methyl-4-ethyl-1-cyclohexene was synthesized according to ref. (*11*) by the sequence



The only step that causes trouble is the dehydrogenation over copper catalyst, where the catalyst is poisoned rapidly for unknown reasons and has to be changed frequently.

Analysis. All hydrocarbons with the menthene skeleton could be analyzed by gas

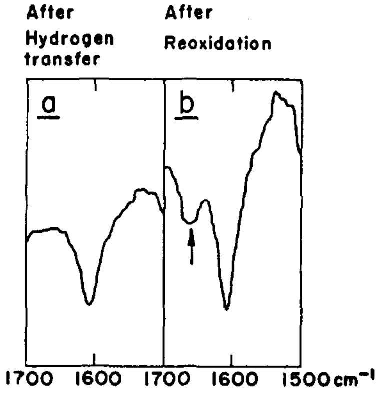


FIG. 1. Infrared absorption in the region 1700–1500 cm^{-1} of the organic catalyst, using the KBr pellet technique. (a) After hydrogen has been transferred from subtrate to catalyst (no quinone adsorption). (b) After removal of hydrogen by air oxidation (quinone adsorption).

chromatography on a 10-m column, containing 6 m of Carbowax 4000 and 4 m of silicone oil on Chromosorb. If the mixture passes first over the Carbowax and then over the silicone oil at 175° total separation is obtained. Relative retention times, taking *p*-cymene as 1 were as shown in the table.

7.8-Menthene	0.665
3-Menthene	0.705
2-Menthene	0.74
1-Menthene	0.825
α-Terpinene	0.86
Limonene	0.905
γ-Terpinene	0.94
p-Cymene	1
Terpinolene	1.12
Isopropenyltoluene	1.51

The products of 4-methyl-4-ethyl-1-cyclohexene were analyzed as reported previously over β,β-oxydipropionitrile at 90°C (*3*).

RESULTS

Reactions were run at 300° and 350°C. Liquid feed rates were in all cases 0.9 ml/hr. Catalysts were compared on a basis of equal volume (15 ml) which corresponds to 7.5 g of the inorganic material, but only 3 g of the organic material.

Samples were taken according to a rigid scheme: After the liquid feed was started, the very first drop appearing at the reactor outlet was taken with a microsyringe and this was taken as the zero point on the time scale of the graphs. After that samples were taken at regular intervals by a microsyringe, so the values shown in the graphs give the composition of the mixture as it comes out of the reactor at the time indicated.

After the composition of the effluent had become more or less constant, the liquid feed was disconnected and the catalyst oxidized. Oxidation of the organic catalyst was done by air at 20 ml/min, $\frac{1}{2}$ hr at 150°, $\frac{1}{2}$ hr at 250°, and $\frac{1}{2}$ hr at 300°. In this way the transferred hydrogen was recaptured as water and the catalyst did not decompose. After completion of the oxidation the liquid feed was started again and only when results before and after oxidation were identical was the experiment considered to be significant.

The inorganic catalysts were oxidized at 450°C, because in their case decomposition is no problem. An interesting phenomenon was discovered here: the molybdates are brightly colored materials. As soon as the reaction with the substrate was started they became dullish green. If after reaction air was passed at 300°C, water was produced, but the color did not change. A catalyst thus treated recovered its original activity. The bright color could only be restored by oxidation at 450°C, but oxidation at 450°C of a sample already treated with air at 300°C did not change its catalytic activity. This

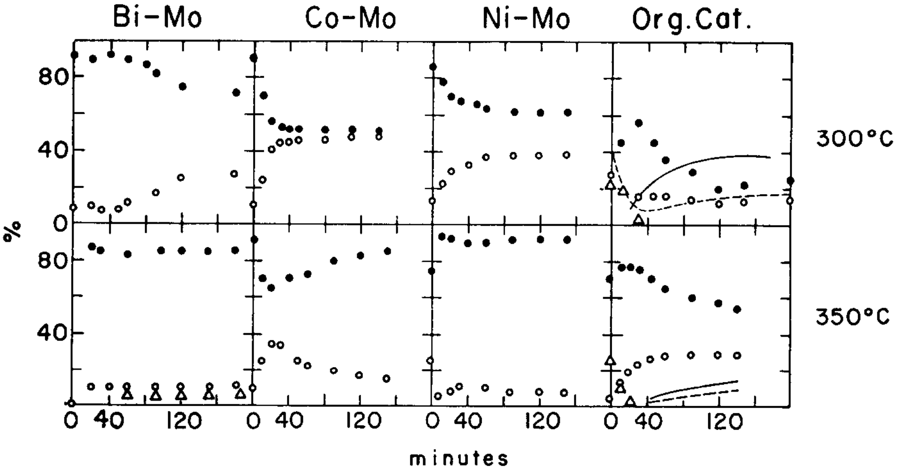
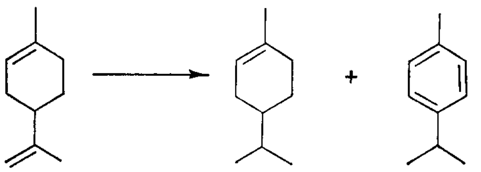


FIG. 2. Product compositions with time when limonene is passed over different catalysts at 300°C and at 350°C: ●, *p*-cymene; ○, menthenes; △, *p*-isopropenyltoluene; – – –, limonene; ——, limonene isomers.

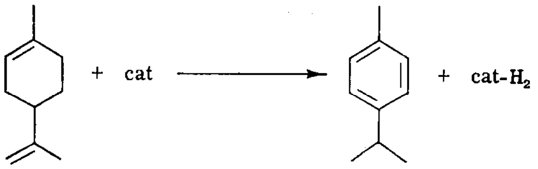
simple experiment shows several things: The production of water during oxidation at 300°C shows that hydrogen had been transferred to the catalyst during the dehydrogenation of the substrate. Restoration of activity upon oxidation shows that hydrogen transfer from substrate to catalyst is connected with catalytic activity. The fact that on heating from 300° to 450° the original color can be recovered without change in activity shows that catalytic activity is not connected with the color change.

In Fig. 2 results obtained according to the above method are given for limonene.

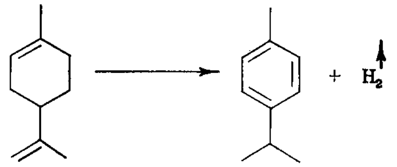
The inorganic catalysts give only two products, menthene and *p*-cymene, according to the disproportionation reaction



and no unreacted limonene. If this were the only reaction that occurs one would expect a 1:1 mixture of the two products, as is indeed found with Co molybdate at 300°, after 1 hr reaction. At shorter reaction times more *p*-cymene than menthenes is found, which can be explained by hydrogen transfer to the catalyst:



As mentioned before the hydrogen can be recovered from the catalyst by oxidation at 300°C. So the behavior of Co molybdate at 300°C is according to expectation: with a freshly oxidized catalyst the main product is *p*-cymene; because of the hydrogen transfer to the catalyst it becomes less active for dehydrogenation and the disproportionation reaction takes over until in the end a 1:1 mixture of *p*-cymene and menthenes is found. The Ni molybdate at 300° and 350° and Co molybdate at 350°C do not reach the 1:1 mixture and this is because of a third reaction:



By measuring the quantity of hydrogen formed it could be proven that this reaction is responsible for the higher than 50% content of the *p*-cymene in the mixture.

These reactions explain the products obtained with Ni and Co molybdate. With Bi molybdate also more *p*-cymene than menthene is found, but no hydrogen is evolved. Water is found instead and it seems that here the catalyst is slowly stripped of its oxygen, because of hydrogen transfer and subsequent elimination of water. At 350°C, this catalyst also forms some isopropenyltoluene in addition to *p*-cymene and menthenes.

The organic catalyst behaves differently: with the freshly oxidized catalyst at 300° appreciable quantities of isopropenyltoluene are formed in addition to *p*-cymene and unreacted limonene. When the catalyst has taken up some hydrogen the isopropenyltoluene gives way to menthene and limonene isomers. At 350° the disproportionation reaction is seen to gain in importance; no gaseous hydrogen and no water are formed however.

In Fig. 3 are given the results for 1-menthene. The results for this less reactive olefin confirm those for limonene. The inorganic catalysts initially give high conversions of *p*-cymene because of hydrogen transfer to the catalyst, but activity rapidly decreases. In the case of Ni molybdate and Co molybdate at 350° activity does not go to zero, but remains at a constant value, which can be accounted for by hydrogen evolution. In this case the change of mechanism can be followed. In the beginning no hydrogen is evolved, as it is all taken up by the catalyst; only when conversion decreases and *p*-cymene formation approaches its constant value, does hydrogen start to be evolved. Ni and Co molybdates show a high activity for double-bond shifts, as is expressed in the high percentage of menthene isomers; Bi molybdate does it to a far smaller degree. The

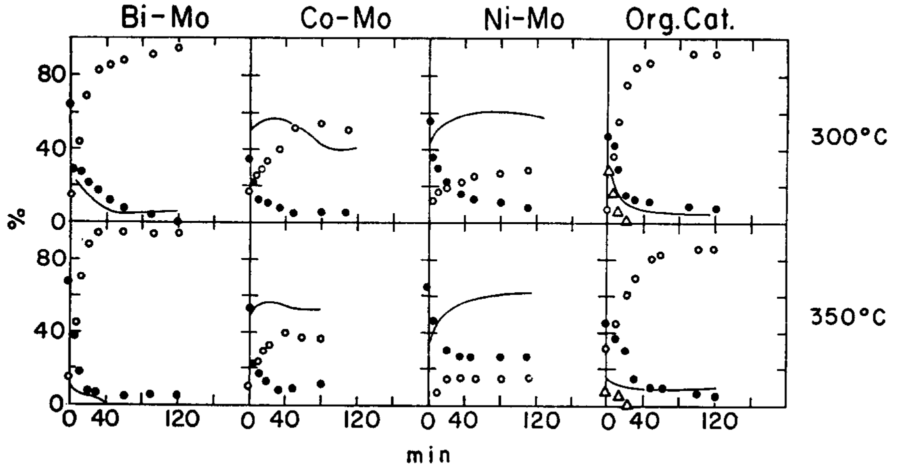


FIG. 3. Product compositions with time, when 1-menthene is passed over different catalysts at 300° and 350°C: ●, *p*-cymene; ○, 1-menthene; ——, menthene isomers; △, *p*-isopropenyltoluene.

organic catalyst is capable of forming the tetraolefin isopropylene-toluene also from the monoolefin menthene. The formation of isomers is comparable to that obtained with Bi molybdate, and *p*-cymene formation approaches zero with the saturation of the catalyst.

In Fig. 4 we give the remarkable results for 4-methyl-4-ethyl-1-cyclohexene. While the organic catalyst gives toluene as the sole product, the inorganic catalysts give no toluene (except in small quantities with Bi molybdate at 350°) but only 2-ethyltoluene With Ni and Co molybdate even 3- and 4-ethyltoluene are formed.

The molybdate catalysts appear to be acidic: next to the extensive double-bond shifts found with limonene and menthene, they show alkyl 1–2 shifts and even 1–3 and 1–4 shifts with Co and Ni. The organic catalyst does not show acidity. We interpret the toluene formation as hydrogen atom abstraction, a result also found for iron and chromium oxide catalysts (*3*).

In all the limonene and menthene experiments, isomers formed were analyzed sepa-

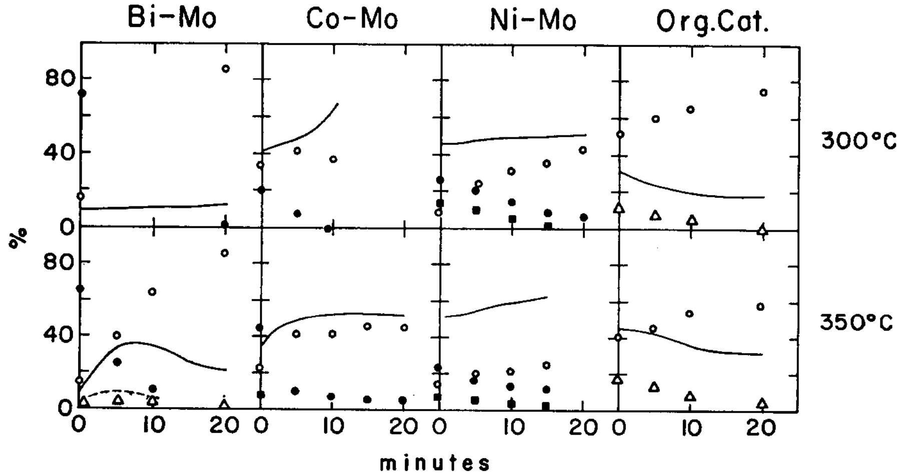


FIG. 4. Product compositions with time, when 4-methyl-4-ethyl-1-cyclohexene is passed over different cataylsts at 300° and 350°C: ●, 2-ethyltoluene; ○, 4-methyl-4-ethyl-1-cyclohexene; ——, isomers of 4-methyl-4-ethyl-1-cyclohexene; - - -, ethylbenzene; △, toluene; ■, 3- and 4-ethyltoluene.

TABLE 1

PRODUCT COMPOSITION WITH TIME FOR LIMONENE OVER THE ORGANIC CATALYST AT 350°C

Time (min)	7,8-Menthene	3-Menthene	2-Menthene	1-Menthene	α-Terpinene	γ-Terpinene	Terpinolene	Isopropenyltoluene	p-Cymene	Limonene	Not identified
0	1.9	1.9	—	1.1	—	—	—	26.6	68.5	—	—
5	1.4	4.1	0.8	3.0	—	—	—	17.1	73.6	—	—
10	1.2	6.9	1.5	4.5	—	—	—	7.8	78.1	—	—
20	1.0	10.2	1.8	7.0	—	—	—	2.3	78.7	—	—
30	1.2	11.7	2.3	8.3	—	—	—	—	76.5	—	—
45	1	13.3	3.0	9.6	1.5	—	—	—	70.5	0.8	—
60	1	13.3	3.3	9.6	4.6	—	—	—	65.6	1.3	1.3
90	0.9	13.5	3.7	10.4	5.5	—	1.2	—	60.2	2.8	1.8
120	0.8	13.2	3.4	10.4	6.8	0.8	1.8	—	56.3	3.4	2.6
150	0.6	12.6	3.9	10.2	7.4	1.2	2.4	—	54.2	4.8	2.7

rately. In the graphs only the sum of limonene and menthene isomers is given for clarity. In Table 1 the full analysis results are given for limonene over the organic catalyst, at 350°, where limonene as well as menthene isomers are found.

DISCUSSION

The main conclusion to be drawn from the experimental results is that dehydrogenation on both types of catalyst occurs initially by hydrogen transfer from substrate to catalyst. This agrees with conclusions reached by others for molybdate catalysts. Tracer experiments showed that in propylene oxidation over molybdate catalyst, a symmetrical allyl intermediate (*5*) is formed, and kinetic evidence also suggests that reduction of the catalyst is rate-determining in the oxidative dehydrogenation over Bi molybdate (*7*b).

The second conclusion, that quinone catalysts are active via radical abstraction and molybdate catalysts by hydride abstraction, is in disagreement with some published results. In a comparative study on the behavior of different olefins over Bi molybdate it has been found that 4,4-dimethyl-1-pentene gives 2,3-dimethylpentadiene under oxidizing conditions over Bi molybdate instead of the expected aldehydes or ketones. Even 3,3-dimethyl-1-butene, where no primary allyl abstraction is possible, gave mainly the diene (*6*). This is in perfect agreement with our results that the catalyst causes double-bond shifts as well as alkyl shifts. On the other hand more recent work on the mechanism of dehydrogenation over Bi molybdate suggests the adsorbed intermediate to be a hybrid between R^-–Mo^{6+} and $R^·$–Mo^{5+} (*7*). In terms of organic chemistry this means that the adsorbed intermediate would be either an allylic carbanion or radical. With our model compound 4-methyl-4-ethyl-1-cyclohexene these intermediates would be expected to give either ethylbenzene or toluene (*3*), which are only found in small quantities.

This means that evidence presented here and previously (*5*, *6*) is more in agreement with a carbonium ion intermediate than a carbanion or radical.

The toluene found on reaction of 4-methyl-4-ethyl-1-cyclohexene over the quinone catalyst is in apparent contradiction with evidence found on liquid-phase quinone dehydrogenation, where, using the same kind of gem intermediates, a rearranged product was formed, which was taken as the main argument for a carbonium ion mechanism (*1*). It has been suggested that the carbonium ion is formed in a two-step mechanism (*10*).

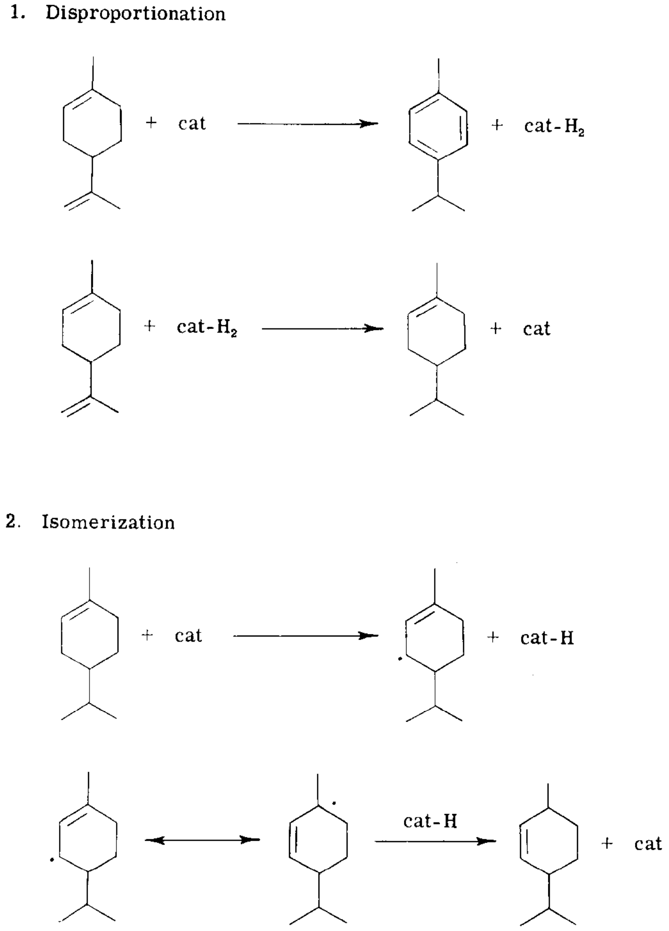
(a) $$RH_2 + Q \rightarrow RH^· + QH^·$$

(b) $$RH^· + QH^· \rightarrow RH^+ + QH^-$$

In solution the radicals RH·formed in step (a) may be stable enough at the temperatures used to react further in a second electron transfer. However under our conditions of 300–350°C there is a good chance that the radical decomposes by β-fission, before it can undergo a second electron transfer. This seems to be the most logical explanation for the difference between hydrogen transfer by quinone in solution and in the gas phase. In agreement with this view is the fact that free radicals may also be obtained in solution by hydrogen transfer to a quinone if the free radical is a comparatively stable one (*10*).

The model compound 4-methyl-4-ethyl-1-cyclohexene has thus given us the general information that all three molybdates are acidic and the organic catalyst is not.

The results obtained with limonene and menthene enable a further differentiation. Without going into any details about the specific mechanism of the reaction one can imagine the following representation for the disproportionation and isomerization reaction:


1. Disproportionation

2. Isomerization

The fact that Co and Ni molybdates give disproportionation as the main reaction with limonene, and isomerization as the main reaction with menthene, and the fact that gaseous hydrogen is evolved, lead us to believe that the hydrogen that is transferred from substrate to catalyst is only loosely bound. The hydrogen bound to the catalyst is easily given off, either to a reactant olefin (disproportionation) or to an allylic intermediate (isomerization), or two hydrogen atoms bound to the surface recombine to form gaseous hydrogen.

Bismuth molybdate behaves as the most selective catalyst, if our goal is dehydrogenation. As the reason for this we see the fact that either because of a strong oxygen–hydrogen bond or a weak catalyst–oxygen bond, transferred hydrogen is constantly removed as water, so no hydrogen is available for disproportionation or isomerization processes.

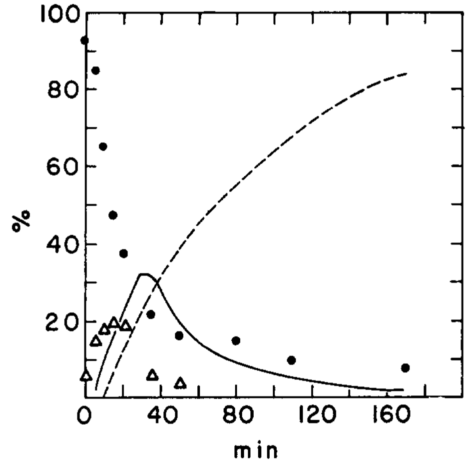


FIG. 5. Product composition of the limonene fraction when a 1:1 mixture of acrylonitrile and limonene is passed over Co molybdate at 300°C: ●, *p*-cymene; ----, limonene; —, menthene isomers; △, *p*-isopropenyltoluene.

In the organic catalyst we know the oxygen to be bound securely as the quinonic —C=O bond, and no water is found in the reaction product. However, the hydrogen of the hydroquinone is seen to be sufficiently labile to give isomerization as well as disproportionation; the disproportionation is less prominent, however, than that found with the inorganic catalysts and therefore we find isomerization also in the case of limonene.

So it has been possible to fingerprint the different catalysts. Ni and Co molybdate cause acid-catalyzed shifts, disproportionation, isomerization, and hydrogen evolution. The Bi molybdate also causes acid-catalyzed shifts, but the other reactions are greatly suppressed. The organic catalyst does not cause acid-catalyzed shifts, but in other respects is somewhat less selective than the Bi molybdate. Its catalytic activity does not fall much below that of Bi molybdate however, certainly not if we take into account that we compare 3 g of organic catalyst with 7.5 g of the inorganic catalyst. So the organic catalyst takes an honorable place between long established inorganic catalysts and might be superior for certain purposes.

One additional phenomenon of Co molybdate is worth reporting: because we pictured the disproportionation reaction as a hydrogen transfer from catalyst to olefin, we thought it must be possible to perform hydrogen transfer from one olefin to another by passing a mixture of two olefins. This did not materialize unfortunately, but something else happened.

In Fig. 5 the product composition is given when a 1:1 limonene-acrylonitrile mixture is passed over Co molybdate at 300°C. The acrylonitrile exerts a profound influence on the product composition of the limonene, but does not react itself, and the expected propionitrile is not found. Disproportionation is entirely suppressed and we find dehydrogenation and isomerization instead. Furthermore the catalyst did not develop its dullish green color but remained brightly colored. We have no ready explanation for this phenomenon, but it is interesting enough to be reported as such.

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