Reactions of Alkynes and Dienes on Magnesium and Other Metal Films

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Summary Alkynes and dienes undergo self-hydrogenation on magnesium and other metal films apparently through an interaction between adsorbed alkynes or dienes and a hydrocarbon residue, probably a polymer, deposited on the metal surface.

Although the self-hydrogenation of ethylene on transition metal catalysts is well-known, self-hydrogenation of other olefins[1–3] and of acetylene[2,4,5] has been less widely studied. Reactions of higher alkynes and dienes with metals in the absence of hydrogen or deuterium have never been investigated to our knowledge.

We report that if an alk-1-yne, an alk-2-yne, or a 1,2-diene is added to a magnesium film without hydrogen, the gaseous reaction products contain the corresponding olefin(s) and isomers of the starting material. These reactions were observed in the temperature range 0—200° with the following compounds: allene, propyne, but-1-yne, but-2-yne, buta-1,2-diene, pent-2-yne, penta-1,2-diene, and hex-1-yne. Conjugated dienes (buta-1,3-diene, isoprene) also undergo reduction but no isomerization and the formation of the saturated hydrocarbon is not observed, except in trace amounts (however acetylene reduction on magnesium at 150° is non-selective). The only gaseous secondary products are lighter olefinic hydrocarbons in very small amounts. Olefins are not reduced on magnesium under the same conditions, except in trace amounts.

Although reduction and isomerization of alkynes and allenes always take place simultaneously, we shall deal here mainly with reduction since isomerization seems to be an independent reaction occurring by a different mechanism.[6]

The reactions observed on magnesium also occur on alkali metal films. With the latter, olefin formation can be explained by metallation. However, on magnesium, unlike on alkali metals, no addition compound was formed by further adsorption of an alkyl halide, and metallation does not occur.

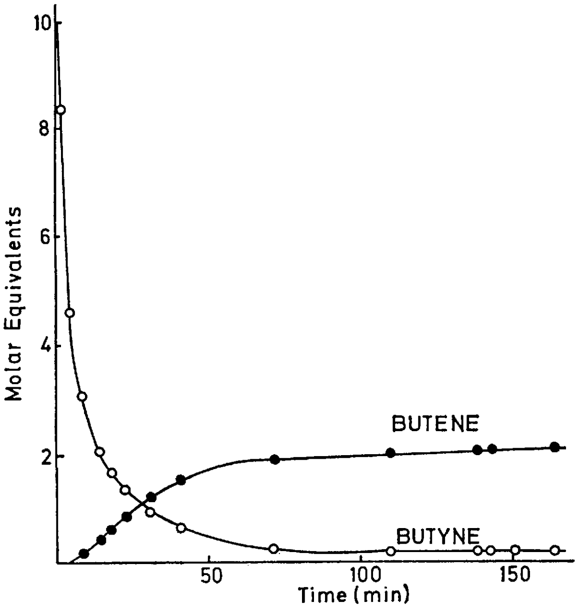

FIGURE. *Reaction of but-1-yne on a magnesium film at 135°: Change of the gas phase composition* versus *time (mass-spectrographical data).*

No evidence could be found for the intermediacy of species similar to diene–magnesium compounds.[7–10] Firstly their synthesis, in THF medium, is never accompanied by olefin formation in significant amounts.[10] Secondly, in conditions (THF solution, ethylene dibromide as catalyst) under which isoprene–magnesium is readily formed, no reaction could be obtained from magnesium and hex-1-yne or penta-1,2-diene, while all three hydrocarbons react similarly with magnesium films. Thus, olefin formation from dienes or alkynes does not proceed *via* organo-magnesium compounds.

A rapid and strong adsorption of the starting compound occurs at the beginning of the reaction. A typical product *versus* time curve obtained at 135° for but-1-yne, the most reactive of the four C_4H_6 isomers, is shown in the Figure: *ca.* 80% of the initial butyne cannot be recovered as butene, but remains in the adsorbed state. This suggests the formation of a hydrocarbon polymer.

No hydrogen is detectable in the gas phase at any stage of the reaction at this temperature (no tests for hydrogen were made at lower temperatures). This shows that the formation of olefins does not involve molecular hydrogen.

If the gaseous products, containing unreduced starting compounds and olefins, are trapped and removed after 10—15 minutes at 150°, a further desorption of gases occurs over a period of several hours; these consist entirely of olefins. Thus olefins arise, at least in part, from adsorbed and not gaseous alkynes or dienes, and adsorption of these last is irreversible.

If, after completion of olefin evolution followed by prolonged pumping, a second dose of reactant is admitted on the same film, only very small amounts of olefins are formed.† Thus the process of olefin formation is not repeatable.

These observations are consistent with the fact that self-hydrogenation of alkynes and dienes does not occur on the metal itself, but by an interaction between adsorbed molecules and a hydrocarbon residue strongly held on the surface.

Further investigations showed that but-1-yne reduction does not occur only on magnesium: it also occurs (tests performed at room temperature) on many metallic films, in fact on all the ones investigated: Ca, Al, Au, Zn, Fe, Ni, Co, Pt, and Pd. These different metals are active to different extents in this process. On some of these, the reduction is non-selective and variable amounts of n-butane are also formed. On most of them, isomerization of but-1-yne takes place simultaneously.

Thus, many metallic surfaces, even those, like magnesium, which are not able to promote self-hydrogenation of ethylene or other olefins, and which have no catalytic properties for hydrogenation, can exhibit similar behaviour in the self-hydrogenation of alkynes and probably of dienes.

Self-hydrogenation of these compounds is caused not by an intrinsic property of any given metal or group of metals, but by the formation of an active species probably highly unsaturated, and possibly polymeric in nature on the surface of the metal.

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† However isomerization is not poisoned and occurs to the same extent as on a clean film.

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