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Mechanohydrogenation

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Abstract. Treatment of naphthalene and biphenyl with alumina and hydrogen in a vibratory mill for about 5h at ambient temperature gives up to 75 % and 15 % of tetralin and phenylcyclohexane respectively. This suggests that the previously reported[1] disproportionation of naphthalene and biphenyl to give tetralin and phenylcyclohexane by analogous treatment *under nitrogen* proceeds at least partially by a step involving molecular hydrogen. However, these observations are not general because identical mechanical treatment of *trans*-stilbene under hydrogen gave *less* bibenzyl than under nitrogen.

We have recently reported[1] that treatment of a number of hydrocarbons in a vibratory mill with approximately ten-fold weight of silica or alumina under nitrogen, air, or oxygen resulted in complete conversion to graphite, but that at an intermediate stage significant quantities of partially reduced products *e.g.* tetralin from naphthalene and phenylcyclohexane from biphenyl were also observed when alumina was the inorganic matrix.

In principle, one could postulate three broad classes of mechanism for the disproportionation reactions resulting in partially reduced products:

(i) The partially reduced compounds could arise via a stepwise transfer of hydrogen atoms.

(ii) Alternatively, they could arise from electrocyclic transfer of *pairs* of hydrogens, given that under mechanochemical conditions it may be possible for a molecule to undergo quite unusual processes.[2]

(iii) Finally, as stoichiometry requires the production of molecular hydrogen to account for all the original carbon being converted to elemental carbon, the partially reduced intermediates, such as tetralin from naphthalene, could result from "mechanocatalytic" hydrogenation. This mechanism is not attractive because alumina is not a likely candidate for a hydrogenation catalyst, but at least there was an indication that the reduction was matrix specific (it does not occur with silica[1]). Furthermore, this mechanism was testable by simply replacing nitrogen with hydrogen as the atmosphere and this forms the basis of this report. The remainder of the experimental procedure was exactly as reported previously.[1]

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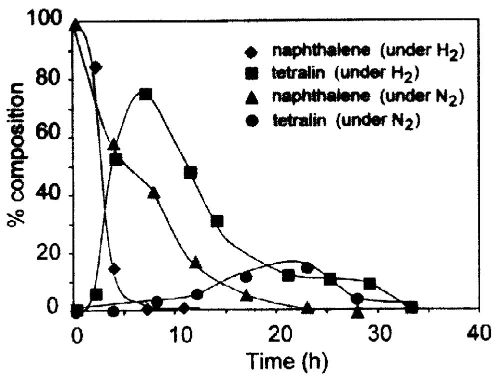

Figure 1. Treatment of naphthalene with alumina under H_2 and N_2.

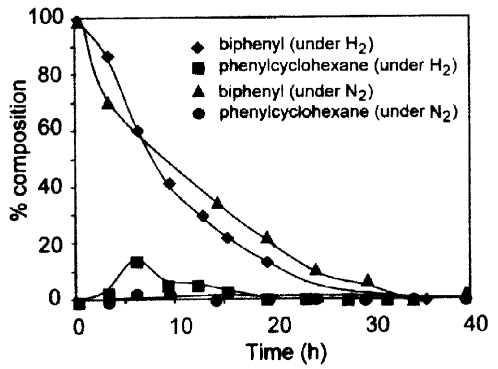

Figure 2. Treatment of biphenyl with alumina under H_2 and N_2.

Figures 1 and 2 show that a very marked increase in the transient yields of tetralin and phenylcyclohexane is observed when nitrogen is replaced by hydrogen thus giving support to the mechanism proposed under *(iii)*. However, these observations are not general because the effect is *reversed* for the transient conversion of *trans* stilbene to bibenzyl.

The "mechanohydrogenation" reactions of naphthalene and biphenyl are highly sensitive to the nature of alumina used as the matrix/catalyst: in general basic alumina gives higher yields of the reduced products and the material used for the runs in Figures 1 and 2 was SIGMA A-8878 (Lot 126H3421), Activity Grade 1, W-2:Basic, which was heated at 390° for 12 hours and was used as soon as it cooled in a desiccator.

The only results reported in the literature which might qualify as examples of "mechanohydrogenation" concern the hydrogenation of benzene[3] over cobalt and of coal[4] where grinding substantially increased the heavy oil products.

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