Molecular Queueing in Catalytic Hydrogenation

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DURING study of the heterogeneous catalytic hydrogenation of allenes (5% Pd–$BaSO_4$, n-pentane), the competitive situation between but-3-ynoic acid and buta-2,3-dienoic acid was examined. Selectivity of hydrogenation, generally associated with selectivity of adsorption on the catalyst surface, was high enough among the two starting compounds and three olefinic products to suggest the description "molecular queueing". The matter is summarised in Figure 1, constructed from g.l.c. analysis of small samples withdrawn at intervals. Analysis as methyl esters (CH_2N_2) employed 10% poly(ethyleneglycol adipate) as stationary phase (50°).

But-3-ynoic acid is first semi-hydrogenated with only slow attack on buta-2,3-dienoic acid. On disappearance

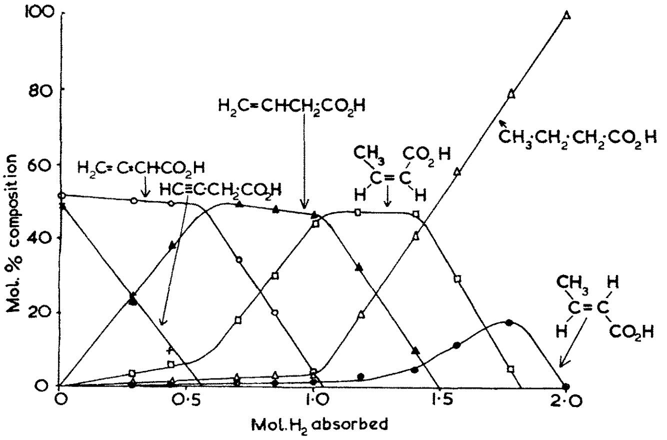

FIGURE 1. *Hydrogenation of a mixture of but-3-ynoic acid and buta-2,3-dienoic acid.*

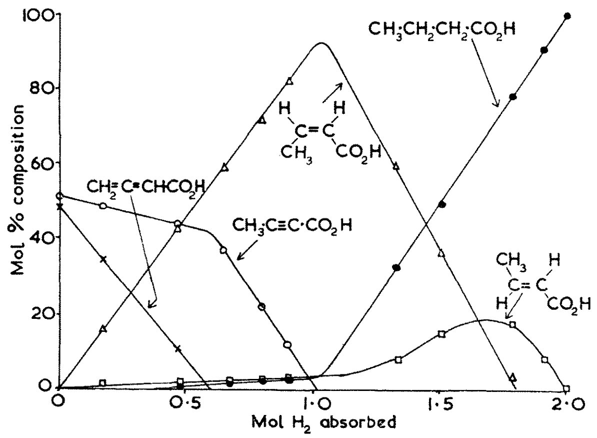

FIGURE 2. *Hydrogenation of a mixture of but-2-ynoic acid and buta-2,3-dienoic acid.*

of the acetylene, the allene is semi-hydrogenated to *cis*-but-2-enoic acid, this and the but-3-enoic acid from the acetylene being little affected. Removal of the allene then brings about hydrogenation of but-3-enoic acid with no appreciable hydrogenation of the *cis*-but-2-enoic acid. With the disappearance of the former, *cis*-but-2-enoic acid is removed by a competitive process of hydrogenation and stereomutation to *trans*-but-2-enoic acid. Maximal concentration of the latter is reached as the last *cis*-olefin disappears. The *trans*-olefin is then hydrogenated with completion of the hydrogen uptake.

In the competitive system (Figure 2) involving but-2-ynoic acid and buta-2,3-dienoic acid the allene is now hydrogenated faster than the acetylene, though the selectivity of attack is lower than in the previous case. Both give the same product, *cis*-but-2-enoic acid, which follows a pattern of hydrogenation similar to that above. The selectivity pattern in both systems would probably be improved by using partially poisoned catalyst systems. "Molecular queues" involving a larger number of species are envisaged.

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