Non-Saytzeff Dehydration of 2-Methylpentan-2-ol over γ-Al_2O_3

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Summary Dehydration of diluted 2-methylpentan-2-ol over γ-Al_2O_3 shows a primary product distribution of at least 70% terminal olefin, which is possibly isomerised in a secondary reaction.

Alcohol dehydration over alumina is reputed to give rise to a typical Saytzeff product distribution.[1-3] Primary product studies and use of alkali-treated catalyst (in order to exclude isomerisation)[2,3] exhibited a similar, though less pronounced, orientation.

We found that dehydration of 2-methylpentan-2-ol at 314 °C over an acid γ-Al_2O_3 catalyst with full isomerising ability, yielded primary product compositions of at least 70% terminal olefin. The catalyst (50—60 mesh) was prepared by the method of Havestadt and Fricke.[4] The alcohol was diluted with the appropriate amount of nitrogen to obtain the desired vapour phase concentrations.

The figure shows the percentage alk-1-ene, in the total product obtained, as a function of contact time, at two different mole fractions. Also shown is the isomerisation of 94·0% 2-methylpent-1-ene over the same catalyst under comparable conditions.

The percentage alk-1-ene decreases markedly with contact time to give ultimately a typical Saytzeff distribution. The rate of this decrease is a function of alcohol concentration and it is more or less paralleled by the rate of isomerisation of the terminal olefin.† The highest percentage alk-1-ene determined was 65·3. Extrapolation to zero contact time cannot be made reliably but a lower limit of 70% may be safely assumed.

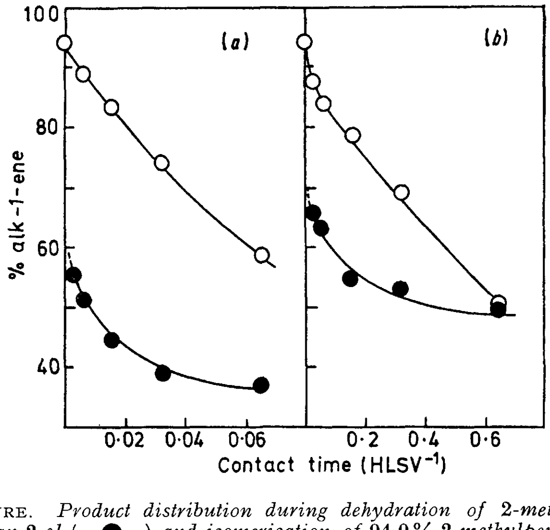

Figure. *Product distribution during dehydration of* 2-*methylpentan*-2-*ol* (—●—) *and isomerisation of* 94·0% 2-*methylpent*-1-*ene* (—○—) *over* γ-Al_2O_3 *at* 314 °C. *Mole fractions in the vapour phase feed are:* (*a*) $x_{alcohol} = 0{\cdot}22$, $x_{olefin} = 0{\cdot}23$; (*b*) $x_{alcohol} = x_{olefin} = 0{\cdot}028$. *Products were analysed by g.l.c.*

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† As a referee pointed out, it has not been proved that isomerisation can also occur in the presence of the alcohol. Any conclusions regarding the primary process, however, are of necessity not influenced by the knowledge of the nature of the secondary reactions leading to the changed product distribution. The demonstration of the isomerising ability of the catalyst preparation is also important to characterise the catalyst surface as one with the strongly acid sites intact.[2b]

Our data do not exclude the occurrence of a carbonium ion mechanism, *e.g.* at high alcohol concentrations. At low mole fractions, however, a different mechanism seems to be operative, presumably involving both acid and basic sites of the catalyst,[5] and which should be in agreement with either a Hofmann orientation, as found also over ThO_2,[6] or no orientation at all (statistical distribution). The above results are significant, the more so as they were obtained with a tertiary alcohol, at a relatively high temperature, and over an acid catalyst preparation, all factors which are commonly thought to promote an E_1-like mechanism and a typical Saytzeff distribution.

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