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NOTES

Diene Disproportionation Reactions

In 1964 Banks and Bailey reported the discovery of a new catalytic reaction in which linear olefins were disproportionated to homologs of shorter and longer carbon chains (*1*). For example, propylene was disproportionated to give ethylene and 2-butene. Mechanistically these disproportionation reactions can be explained by a four-center mechanism or the analogous quasi-cyclobutane intermediate suggested by Bradshaw, Howman, and Turner (*2*). Disproportionation reactions are not limited to monoolefins; dienes also disproportionate. This note discusses a number of reactions where dienes are disproportionated.

EXPERIMENTAL

The catalyst was prepared by impregnating a tungsten oxide–silica catalyst (7% WO_3–93% SiO_2) (*3*) with a sodium carbonate solution. After drying and activating the catalyst contained 0.19 wt % sodium oxide.

Five ml of catalyst was placed in a stainless steel reactor mounted in an electric furnace. The catalyst was pretreated in place, usually for 1 hr with dry air at 590°C followed by flushing with nitrogen as the reactor cooled to run temperature. The olefinic feed was passed through a flow control valve, an alumina drying tube, a flow meter, and the reactor. The product was collected in a Dry Ice trap for analysis. The pressure of the system was atmospheric. Phillips' pure grade hydrocarbons were used for the feeds.

Samples of the product were analyzed periodically with a GLC column. The product analyses reported here were of samples collected at the end of 3 hr. The samples were introduced into the GLC column at pressures below 30 mm Hg to ensure vaporization of the heavier hydrocarbons.

RESULTS AND DISCUSSION

1,3-Butadiene → Ethylene and Cyclohexadiene. Butadiene can be disproportionated to yield ethylene and cyclohexadiene, an isomer of hexatriene. To be consistent with the four-center mechanism butadiene should yield ethylene and hexatriene. Experimentally, however, the hexatriene undergoes cyclization to cyclohexadiene. Conditions for this run were as follows: temperature, 538°C; space rate, 26 WHSV; feed, butadiene. Analysis of the product showed, on a weight basis, 29% ethylene, 4% propylene, 12% butenes, 28% cyclohexadiene, and 27% vinylcyclohexenes. Butadiene conversions varied from 3% to 5% during the run.

1,3-Pentadiene disproportionates more readily than butadiene with the product containing a large variety of monoolefins and dienes.

1,3-Butadiene plus Propylene → Ethylene and 1,3-Pentadiene. Butadiene and propylene disproportionate to yield ethylene and 1,3-pentadiene, the products expected from the four-center mechanism theory. Conditions for this run were as follows: temperature, 538°C; space rate, 20 WHSV; feed, 46% propylene and 54% butadiene. Analysis of the product showed 10% ethylene, 22% butenes, 22% *trans*-1-3-pentadiene, 14% *cis*-1-3-pentadiene, and 32% butadiene dimers. Feed conversion was 24% and selectivity to ethylene and pentadienes 46%.

1,3-Butadiene plus trans-2-Butene →

Propylene and 1,3-Pentadiene. This reaction is similar to the preceding reaction except that propylene is one of the products instead of ethylene. Conditions for this run were as follows: temperature, 538°C; space rate, 18 WHSV; feed, 45% *trans*-2-butene and 55% butadiene. Analysis of the product showed 6% ethylene, 48% propylene, traces of pentenes, 19% *trans*-1-3-pentadiene, 10% *cis*-1-3-pentadiene, and 17% butadiene dimers. Conversion of the feed was 39% and selectivity to propylene and 1,3-pentadiene, 77%.

1,3-Butadiene plus Isobutene → Ethylene and 4-Methyl-1,3-Pentadiene. Disproportionation of dienes is not limited to straight-chain reactants. Conditions for this run were as follows: temperature, 538°C; space rate, 22 WHSV; feed, 51% isobutene and 49% butadiene. Analysis of the product showed 31% ethylene, traces of propylene and butenes, and 69% 4-methyl-1,3-pentadiene. Conversion was 5%.

2-Methyl-1,3-pentadiene and 3-methyl-1,3-pentadiene were obtained by disproportionating *trans*-2-butene with isoprene. Conversion was 2%.

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Group VIII Metal-Catalyzed Condensation of Alcohols to High Molecular Weight Ketones

INTRODUCTION AND BACKGROUND

A catalytic reaction was recently reported which distinguished between rhodium metal and $(RhCl_6)^{-3}$ anion in the liquid phase; the chlorine complex would dehydrogenate 2-propanol to acetone but the metal did not (*1*). We have been interested in finding a test which could show whether the metal-complex, used to prepare a supported heterogeneous catalyst, survived the catalyst pretreatment. We found that the gas phase 2-propanol reaction could not distinguish between a chlorine containing noble metal catalyst and one which had the chlorine removed by a chemical reaction. However, we wish to report the formation of higher molecular weight ketones from 2-propanol using alumina supported Group VIII metal catalysts.

The homogeneous base-catalyzed condensation of acetone is a well known reaction (*2*); the condensation products contain olefinic unsaturation. In 1913 it was reported that acetone condensation over a heterogeneous nickel catalyst gave products similar to the base catalyzed reaction (*3*). Ipatieff and Haensel (*4*) found that a $Cu-ZnO-Al_2O_3$ catalyst was effective for the condensation of alcohols and ketones, but they concluded that only catalysts having *both* dehydrogenation and dehydration properties could effect condensation. Kawamoto (*5*) observed small amounts of condensation products formed by a side reaction during the dehydrogenation of 2-propanol over copper catalysts. Bursian *et al.* (*6*) studied the conversion of 2-propanol over a $Pt-Al_2O_3-Na$ catalyst at