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

340°C, a higher temperature than used in our study, and did not report the formation of condensation products. A recent patent teaches that 2-propanol forms acetone when passed over Group VIII metals on "non-acidic" alumina but does not mention the formation of higher weight ketones (the absence of water implied little condensation to higher weight ketons) (*7*). Another patent related to the production of higher ketones from acetone and hydrogen; in this case it was necessary to have both aldolization/dehydration and palladium catalysts (*8*).

Experimental

Materials

Catalysts. Catalysts prepared for this study were Group VIII metals supported on "non-acidic" alumina. The latter—as prepared by the method of Pines and Chen (*9*)—contains 0.5% potassium, and was found to produce minimal typical acidic reactions with hydrocarbons, even at 500°C. The support was impregnated with the hexachlorometallic complex (in amounts required to give a catalyst containing 0.6 wt % metal) dissolved in the volume of water required to fill the alumina pore volume. A portion of each metal-alumina catalyst was heated to 120°C in nitrogen, held at 120° in hydrogen for two hours, then heated to 482°C and held at this temperature for 4 hours in hydrogen, and finally cooled to room temperature in nitrogen. The reduced metal-alumina catalysts were washed twice with ammonium hydroxide (about 2% NH_3) to reduce the chlorine content to a low level. Final compositions contained 0.6% Pt, 0.3% Rh, and 0.29% Pd on "non-acidic" alumina. Organic reactants (Reagent grade) were obtained from standard commercial sources and were used without further purification.

Apparatus and Procedure

The simple flow apparatus consisted of a motor-driven syringe for liquid feed, a Vycor glass reaction tube wound with nichrome heater wire and fitted with a thermocouple well, a water-cooled condenser, liquid collector, and gas flow meters. A preheater section (30 cc of 8–14 mesh quartz chips) preceded the catalyst bed (5 cc). All runs were made at 1 atm, 220°C, and L. H. S. V. 0.3 in the absence of added hydrogen.

Analyses

Initial analysis was by GLC (silicone gum rubber column). Fractions corresponding to the main product peaks (II, III, IV) were trapped and analyzed by mass spectroscopy (Consolidated Electrodynamics Corp. Model 21-103, inlet temperature 350°C, 70 and 7 eV). Fragmentation patterns for II and III were in excellent agreement with published spectra for 4-methyl-2-pentanone and 2,6-dimethyl-4-heptanone, respectively (*10*). Infrared and nuclear magnetic resonance spectra were consistent with the mass spectral assignments. An unidentified tetrameric ketone, IV (parent mass corresponding to $C_{12}H_{24}O$) was also detected. Olefins were sought for, but not detected in significant quantities.

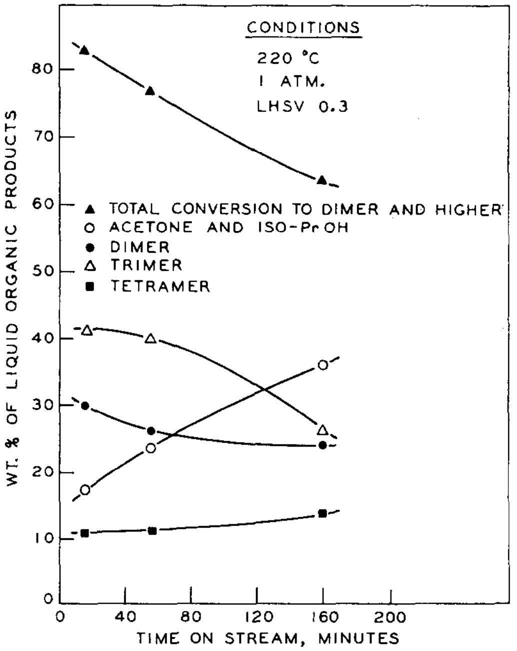


FIG. 1. Conversion data and product distribution for reaction of 2-propanol over 0.6% Pt/Al_2O_3.

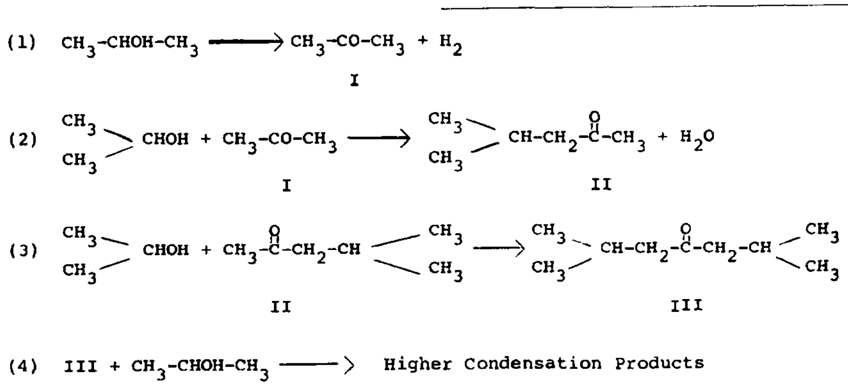
RESULTS AND DISCUSSION

Data for the vapor phase reaction of 2-propanol over a 0.6% Pt/Al_2O_3 catalyst are shown in Fig. 1. Total conversion of alcohol to C_3-through C_{12}-ketones was over 90% initially, but decreased rapidly to under 65% at 160 min (catalyst aging). The major products—all non-olefinic—were acetone (I), 4-methyl-2-pentanone (II), 2,6-dimethyl-4-heptanone (III), and an unidentified tetramer, $C_{12}H_{24}O$ (IV). Selectivity for trimer (III)—relative to dimer (II) and tetramer (IV)—decreased with time on stream.

In a reaction under similar conditions with a 0.3% Rh/Al_2O_3 catalyst, about 84% initial (16 min) conversion, of 2-propanol to a mixture of ketones I, II, III, and IV (weight ratios 1.0:1.9:1.6:0.3, respectively) was obtained. Also under similar conditions, reaction of 2-propanol over a 0.29% Pd/Al_2O_3 catalyst, gave nearly quantitative initial conversion of 2-propanol to a mixture of ketones II, III, IV, and unknown high boiling products (weight ratios 1.0: 2.0:0.25:1.8 (3 components), respectively). Traces only of acetone (I) were detected.

Several runs with other alcohols were made using the 0.3% Rh/Al_2O_3 catalyst at 200°C: with *n*-propanol, only 5% conversion to ketones, mainly II, was obtained. Neither *tert*- or 2-butanol gave any high molecular weight products; dehydration to octenes was the major reaction path for 2-octanol.

The condensation products of 2-propanol are consistent with—but do not require—the reaction mechanism proposed by Kawamoto (*5*) to explain his by-products. Thus, we may visualize the sequence:



$$(1)\quad CH_3\text{-}CHOH\text{-}CH_3 \longrightarrow \underset{I}{CH_3\text{-}CO\text{-}CH_3} + H_2$$

$$(2)\quad (CH_3)_2CHOH + \underset{I}{CH_3\text{-}CO\text{-}CH_3} \longrightarrow \underset{II}{(CH_3)_2CH\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3} + H_2O$$

$$(3)\quad (CH_3)_2CHOH + \underset{II}{CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH(CH_3)_2} \longrightarrow \underset{III}{(CH_3)_2CH\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH(CH_3)_2}$$

$$(4)\quad III + CH_3\text{-}CHOH\text{-}CH_3 \longrightarrow \text{Higher Condensation Products}$$

We favor the above scheme rather than aldol-type condensation to form mesityl oxide followed by hydrogenation. In our experiments, only traces of mesityl oxide were observed in the liquid products. It is unlikely that the small amount of hydrogen partial pressure permissible by the stoichiometry of these experiments would be sufficient to saturate the quantities of mesityl oxide required.

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