

NOTE

REACTIONS OF ALCOHOLS WITH PLATINUM SALTS. TRENDS IN ISOMER RATIOS OF THE COORDINATED OLEFINIC PRODUCTS*

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Platinum-olefin complexes are generally prepared by treatment of a platinum(II) compound with an olefin¹⁻⁴. The platinum-ethylene complex has frequently been prepared by the alternative procedure of using a platinum(IV) compound with ethanol^{2,3,5,6}. This investigation explored the generality of the platinum(IV) reaction with other alcohols and determined the location and configuration of the double bond in the olefinic products***.

RESULTS

1-Butanol and 2-butanol reacted when heated with the soluble sodium hexachloroplatinate(IV) to form alcohol soluble compounds of coordinated olefins^{5,8-12}. Insignificant amounts of free olefins were released during the heating; the byproducts produced were analogous to those known to be obtained from the reaction with ethanol^{13,14}.

Both the type of alcohol and the reaction conditions influenced the position and the configuration of the double bond formed. At 60-70° for 18 h, 1-butanol produced only the 1-butene complex; in a few exploratory runs at higher reaction temperatures (70-105° for 7 h) moderate amounts of the 2-butene complexes were also formed.

With 2-butanol, the reaction at 60-70° for 18 h produced a mixture of the isomeric complexes of 1-butene, *cis*-2-butene and *trans*-2-butene. In these experiments as the temperature of heating over the final 12 h period was increased slightly around the 70° median, the relative amounts of 1-butene to 2-butene decreased from 44% to 36%, while the *trans*- to *cis*-2-butene ratio increased from 1.6 to 2.0. At higher temperatures extensive precipitation of platinum black occurred, therefore the reac-

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*** In only one instance⁷ was this reaction applied to another alcohol (amyl), with no report of the olefin isomer that was produced.

tion was further studied at a fixed temperature (60°) as a function of time (up to 36 h). It was found that the total yield of butenes increased only up to about 18 h, while the relative amounts of butene isomers varied continuously with increasing time (Fig. 1), in a direction similar to that already noted with increasing temperature.

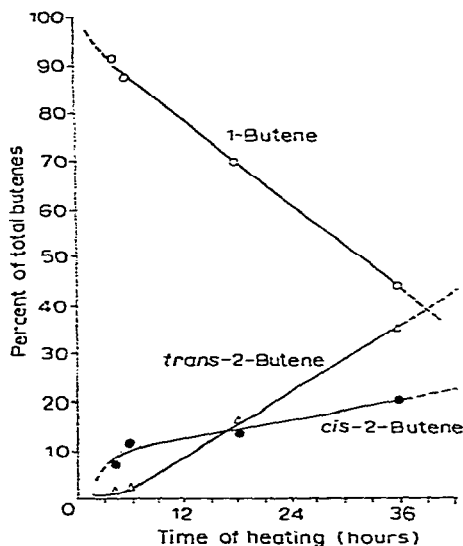


Fig. 1. Variation of isomer ratio with time at 60° for the reaction of 2-butanol with sodium hexachloroplatinate(IV). Values plotted are averages of several individual experiments.

The olefin forming reaction did not occur between *tert*-butyl alcohol and the essentially insoluble sodium hexachloroplatinate(IV), although the reaction mixture turned heterogeneously gelatinous. Either this insolubility* or the inability of a tertiary alcohol to reduce the platinum(IV) of the starting reagent to platinum(II) found in platinum-olefin complexes would explain the failure of the reaction. Attempts to investigate the reaction of *tert*-butyl alcohol with a platinum(II) salt—already in the proper oxidation state for olefin coordination—were inconclusive because the potassium tetrachloroplatinate(II) used was insoluble in the alcohol.

DISCUSSION

Alteration of the ratio of the various butene isomers continued after total yield of butenes became constant. Isomerization is indicated by these results. This isomerization occurred at a lower temperature with 2-butanol than with 1-butanol, even though a 1-butene complex was initially formed in both cases. Participation of the solvent alcohol in the isomerization is thus very probable. This hypothesis is consistent with several facts reported in the literature. The butene complexes do not isomerize in the solid state^{8,9}; uncoordinated olefins are isomerized by catalytic amounts of the platinum-ethylene complex only in the presence of certain cocatalysts,

* The importance of reagent solubility was demonstrated by the failure of 1-butanol to react when heated with insoluble potassium hexachloroplatinate(IV).

the most common of which are alcohols¹⁵; in alcoholic solutions certain platinum-olefin complexes are converted to ether derivatives by net addition of an alcohol molecule to one of the double bonds⁴.

The mild conditions employed in the reactions of butyl alcohols with sodium hexachloroplatinate(IV), as well as the proportions of isomeric butenes obtained, suggest that the mechanism for olefin formation differs from that of the usual acid-catalyzed dehydration of alcohols¹⁶. The platinum-olefin complexes favored at the early stages of reaction and at lower temperatures contain those olefin isomers which coordinate most strongly to platinum(II)¹⁷. The subsequent olefin isomerizations are in the direction that favor the more thermodynamically stable olefins¹⁸.

EXPERIMENTAL

Reagents

Commercial butyl alcohols were distilled before use. Potassium hexachloroplatinate(IV) and potassium tetrachloroplatinate(II) (Fisher Scientific Co.) were used without further purification. Sodium hexachloroplatinate(IV) was obtained from the hexahydrate (J. Bishop & Co.), prepared from chloroplatinic acid hexahydrate (Fisher), or prepared from platinum metal. The platinum metal was purified and converted to hydrated chloroplatinic acid¹⁹. The acid was converted to hydrated sodium hexachloroplatinate(IV)⁶. The hydrated salt from all sources was dried briefly at 105°, recrystallized from absolute ethyl alcohol²⁰, and dried *in vacuo* at 110–130° for 6–9 h.

General procedure

The procedure consisted of three stages: The formation of the platinum-olefin complexes, the removal and analysis of liquids from the reaction mixture, and the decomposition of the complexes to liberate the olefins for analysis.

One mmole of the dried platinum salt and 25–35 ml of alcohol were heated and stirred in an apparatus suitably equipped to retain or trap volatile materials. Except where noted otherwise, the temperature of the reactants was raised to 60° ± 2° for 6 h, then raised to 70° ± 2° for an additional 12 h. These conditions essentially consumed all of the starting platinum salt without appreciable formation of platinum metal. The orange reaction mixture turned yellow, while sodium chloride precipitated¹⁴.

The excess of alcohol and the volatile byproducts¹³ were then removed by vacuum distillation, conducted below 50° and not carried to dryness to minimize decomposition of any complexes. The condensates collected from the olefin-producing reactions were acidic¹³ and were neutralized with aqueous sodium bicarbonate prior to analysis of all condensates by GLC. A four-meter column of 25% carbowax 20 M on HMDS-treated Chromasorb W was used at 100°.

The solids remaining in the reaction flask were then treated with aqueous alkaline cyanide ion to decompose any platinum-olefin complexes. Cyanide displaces ethylene quantitatively from platinum complexes⁵ and displaces butenes without isomerization⁹. The butenes were swept by helium through a drying tower and into a liquid nitrogen trap. The olefins were weighed and analyzed by GLC on an 18-meter column of dimethyl sulfolane on Chromopak, at room temperature. The mole ratios of isomeric butenes were determined from peak areas, after correcting for differences

in thermal detector response for each compound²¹. The butenes were further characterized by conversion to their known dibromides²² and by gas chromatographic comparison with authentic samples on the carbowax column at 150°.

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