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Deuterium Labeling Studies in the Transfer Hydrogenation of Ketones and in the Disproportionation of Diphenylcarbinol over Alumina[1]

In the previous papers in this series (*1*), transfer hydrogenation of aldehydes and ketones over Na^+-doped alumina at about 300°C has been shown to be a facile reaction (*2*). Stereochemical studies have shown that the reaction involves the direct transfer of a hydrogen from the carbinol carbon of an adsorbed alcohol molecule to the carbonyl carbon of an adsorbed aldehyde or ketone (*3*). The present paper describes deuterium labeling studies which confirm the direct hydrogen transfer mechanism for the transfer hydrogenation of ketones as well as for the disproportionation and the transfer hydrogenolysis of diphenylcarbinol (*4*).

The alumina and 2.2% Na^+/Al_2O_3 were prepared by procedures reported earlier (*4*). Experimental techniques for the catalytic reactions have been previously reported (*3*, *4*).

2-Propanol-2-*d* was prepared by the reduction of acetone in the presence of Raney nickel by deuterium generated by the electrolysis of heavy water (*5*). The isotopic purity of the sample was 92% as determined by mass spectrometry.

Diphenylcarbinol-*d* was prepared by the Na–D_2O reduction of benzophenone in dry ether at room temperature. To 9.1 g of benzophenone in 50 ml of dry ether were added 7 g of sodium metal in wire form followed by 12 ml of D_2O (99.5%) which was added dropwise with stirring maintaining the temperature at about 25°C, over a period of 40 min. The system was protected from atmospheric moisture. The mixture was stirred for 1 hr more after adding an additional 3 ml of D_2O. The aqueous alkali layer was separated, the ether solution was washed with very dilute hydrochloric acid and dried over anhydrous sodium sulfate, and the solvent was removed. The product contained in addition to diphenylcarbinol some benzophenone and diphenylmethane. The yield of diphenylcarbinol was 95% based on gas chromatographic estimation. Two recrystallizations from ethanol yielded pure diphenylcarbinol (ir spectrum: 2114 cm^{-1}, medium, benzylic C–D stretch; no C–H band at 2866 cm^{-1}; no O–D band at 2500 cm^{-1}. NMR spectrum: no benzylic proton at δ 5.45; at δ 2.9, singlet, 1 H, due to O–H). By a comparison of the 14-eV mass spectra of undeuterated and deuterated diphenylcarbinol, the isotopic purity of the latter was estimated to be 98%.

Diphenylmethane-*d* and dephenylmethane-d_2 were prepared as authentic samples for product identification purposes by the hydrogenolysis of diphenylcarbinol-*d* by Na–H_2O and Na–D_2O, respectively, in dry benzene at 60°C. To diphenylcarbinol-*d* (1.8 g) in 20 ml of dry benzene were added 2.3 g of sodium wire, followed by 4 ml of either H_2O or D_2O added dropwise with stirring while maintaining the temperature at 60°C. The mixture was stirred for an additional 1 hr and worked up as described for diphenylcarbinol-*d*. The yield of diphenylmethane was 60%. The samples

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[1] Part V of a series entitled "Hydrogen Transfer Reactions." For Part IV, see Venkatasubramanian, N., Ramana, D. V., and Pillai, C. N., *J. Catal.* **51**, 40 (1978).

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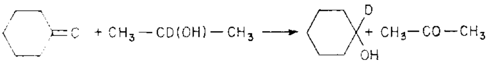
were characterized by ir, NMR, and mass spectrometry.

The catalytic reaction products were analyzed by gas chromatography, and pure samples were isolated by preparative gas chromatography. Isotopic purities were estimated by ir, NMR, and mass spectrometry.

2-Propanol-2-*d* of 92% isotopic purity (*5*) was used to reduce 4-methyl-2-pentanone and cyclohexanone over 2.2% Na^+/Al_2O_3 at 300°C. The 4-methyl-2-pentanol and cyclohexanol formed, respectively, were isolated by preparative gas chromatography and analyzed by ir, NMR, and mass spectrometry. In both cases about 92% of the alcohol was monodeuterated at the carbinol carbon.



$$CH_3\text{-}CO\text{-}CH_2CH(CH_3)_2 + CH_3\text{-}CD(OH)\text{-}CH_3 \rightarrow CH_3\text{-}CD(OH)\text{-}CH_2CH(CH_3)_2 + CH_3\text{-}CO\text{-}CH_3$$

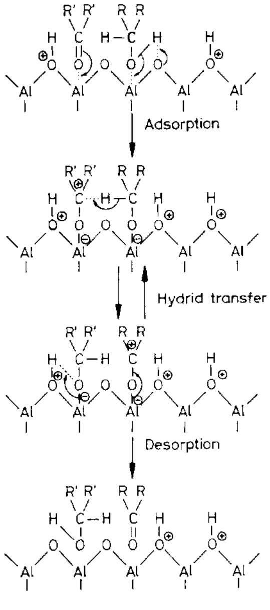


FIG. 1. Formal representation of the hydrid transfer mechanism.

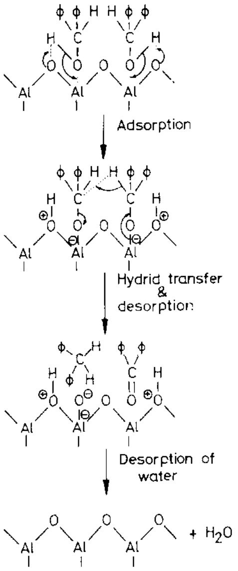


FIG. 2. Disproportionation of diphenylcarbinol by hydrid transfer.

This indicated that the reduction of the ketones over alumina took place exclusively by a direct hydrid transfer mechanism, as suggested previously (*1, 3*). A somewhat speculative representation of this process assuming the alumina surface to be composed of oxide and hydroxide ions and exposed aluminum ions, is given in Fig. 1. Bonds linking oxygen and aluminum are represented only for convenience in electron bookkeeping. Formal charges arising from the interaction of the substrates with the surface are also indicated for the same purpose. An alternate mechanism involving an initial dehydrogenation of the donor alcohol followed by the hydrogenation of the ketone by the hydrogen so formed would have led to the incorporation of hydrogen as well as deuterium at the carbinol carbon, as represented by the following equations:

$$CH_3\text{-}CD(OH)\text{-}CH_3 \xrightarrow{\text{catalyst}} CH_3\text{-}CO\text{-}CH_3 + HD$$

$$2R\text{-}CO\text{-}R + 2HD \longrightarrow R\text{-}CD(OH)\text{-}R + R\text{-}CH(OD)\text{-}R$$

A related reaction was the disproportionation of diphenylcarbinol quantitatively into diphenylmethane, benzophenone, an water over pure (undoped) alumina at 300°C (*3*).

$$2(C_6H_5)_2CH(OH) \rightarrow C_6H_5\text{–}CH_2\text{–}C_6H_5 + C_6H_5\text{–}CO\text{–}C_6H_5 + H_2O$$

The disproportionation could take place by a direct hydrid transfer process or by a two-step, dehydrogenation–hydrogenolysis mechanism. The direct hydrid transfer process is represented in Fig. 2.

The present study describes the differentiation of these two pathways by the use of diphenylcarbinol-*d*. The former mechanism demands exclusive formation of dephenylmethane-d_2, whereas the latter predicts the formation of an equimolar mixture of mono- and dideuterated diphenylmethane. Disproportionation of diphenylcarbinol-*d* of 98% isotopic purity, over several samples of undoped alumina at 300°C under conditions reported previously (*4*), yielded in most cases diphenylmethane-d_2 of isotopic purity as expected of reaction taking place exclusively by the hydrid transfer mechanism. However, this was not reproducible on all samples of alumina, though all the samples were prepared by the same procedure, namely, hydrolysis of aluminium isopropoxide. In one case the diphenylmethane formed was found to be 40% monodeuterated and only 60% dideuterated. Even in this case the unreacted dephenylcarbinol was found to retain its original isotopic purity, ruling out the possibility of a reversible dehydrogenation of the carbinol. An irreversible dehydrogenation followed by a fast hydrogenolysis, cannot be ruled out as a competing mechanism at least on certain catalyst samples.

In the presence of a hydrogen donor like isopropyl alcohol over alumina at 300°C, in addition to the normal disproportionation of diphenylcarbinol described above, a cross-disproportionation between the two reactants ("transfer hydrogenolysis") according to the equation given below also took place.

$$C_6H_5\text{–}CH(OH)\text{–}C_6H_5 + CH_3\text{–}CH(OH)\text{–}CH_3 \rightarrow C_6H_5\text{–}CH_2\text{–}C_6H_5 + CH_3\text{–}CO\text{–}CH_3 + H_2O$$

When 2-propanol-2-*d* was used as the donor in this reaction, appreciable quantities of di-, tri-, and tetradeuterated diphenylmethane were obtained in addition to the expected undeuterated and monodeuterated products. The mass spectral fragments confirmed that the hydrogens of the phenyl rings had been exchanged for deuterium. No rational explanation can be offered for this observation at this stage. The same catalyst sample was first exposed to D_2O vapor at the reaction temperature and then the disproportionation of diphenylcarbinol was carried out. The diphenylmethane formed was free of deuterium.

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