Direct Transfer of Hydrogen or Deuterium in the Cannizzaro Reaction

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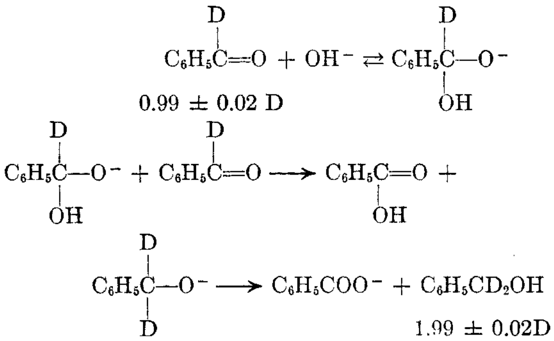
In 1938 Fredenhagen and Bonhoeffer[2] observed that deuterium-free benzyl alcohol is produced on effecting the Cannizzaro reaction of benzaldehyde with potassium hydroxide in the presence of deuterium oxide. They concluded therefore that the aldehydic hydrogen is transferred directly from one aldehyde molecule to another without involving an exchange with the medium. However, because of the possible equilibrium represented by equation 1 (and further equilibrations), an undetected exchange might have occurred involving the DOH hydrogen which is known to be more reactive than deuterium.[3] The ratio of the potassium hydroxide to deuterium oxide was approximately 1:1.8.

$$KOH + D_2O \rightleftarrows KOD + DOH \qquad (1)$$

The conclusion of the earlier workers has now been confirmed under conditions that essentially exclude the possible equilibrium represented by equation 1. Thus, deuterium-free benzyl alcohol was obtained from the Cannizzaro reaction of benzaldehyde with sodium deuteroxide in deuterium oxide and deutero methanol (equation 2). This reagent was prepared from deuterium oxide and commercial sodium methoxide which contained only a small amount of sodium hydroxide.

$$2\ C_6H_5CHO \xrightarrow[D_2O,\ CH_3OD]{NaOD} \underset{0.00\ D \pm 0.02\ D}{C_6H_5CH_2OH} + C_6H_5COONa \qquad (2)$$

Of probably more significance, the aldehydic deuterium of benzaldehyde-d$_1$ was found to undergo direct and quantitative transfer from one molecule to another on effecting the Cannizzaro reaction of this aldehyde with potassium hydroxide in ordinary water. Thus, the resulting benzyl alcohol contained two deuterium atoms per molecule within the limits of the analytical method.[4] Presumably the deuterium is transferred as the deuteride ion; one of the current mechanisms by which this may occur is represented by equations 3 and 4.[5]



$$\underset{0.99 \pm 0.02\ D}{C_6H_5\overset{D}{C}{=}O} + OH^- \rightleftarrows C_6H_5\underset{OH}{\overset{D}{C}}{-}O^- \qquad (3)$$

$$C_6H_5\underset{OH}{\overset{D}{C}}{-}O^- + C_6H_5\overset{D}{C}{=}O \longrightarrow C_6H_5\underset{OH}{C}{=}O +$$

$$C_6H_5\underset{D}{\overset{D}{C}}{-}O^- \longrightarrow C_6H_5COO^- + \underset{1.99 \pm 0.02D}{C_6H_5CD_2OH} \qquad (4)$$

EXPERIMENTAL

Reaction of benzaldehyde with sodium deuteroxide. To 21.0 g. (0.35 mole of active reagent)[6] of a freshly opened, carefully dried, sample of Mathieson Company sodium methoxide was added, under nitrogen with cooling, 30.0 g. (1.5 mole) of deuterium oxide (99.8%). To the resulting solution of sodium deuteroxide in deuterium oxide and deutero methanol contained in a flask was added under nitrogen 32.0 g. (0.3 mole) of freshly distilled benzaldehyde, and the flask was stoppered. The mixture was shaken, and allowed to stand at room temperature for 2 days. The solid mass was dissolved in water, and the mixture was extracted with ether. The solvent was removed from the ethereal extracts, and the residue was distilled to give 9.4 g. (58% yield) of benzyl alcohol, b.p. 95° at 10 mm., n_D^{25} 1.5386; reported n_D^{20} 1.53955.[7] No deuterium was detected on analysis of a sample of this product.

Benzaldehyde-d$_1$. This compound was prepared by the method of Wiberg[8] employing double amounts of the reactants and omitting the treatment with sodium bisulfite. Benzil (20.0 g., 0.01 mole) was reduced with 2 g. (0.05 mole) of lithium aluminum deuteride (Metal Hydrides, Inc.) in ether (refluxed 2 hours), and 18.0 g. (0.084 mole) of the resulting 20.9 g. of dihydrobenzoin-d$_2$ was cleaved with 39.0 g. of lead tetraacetate[9] (stirred 2 hours). There was obtained 12.05 g. (67%) of benzaldehyde-d$_1$, b.p. 157–158°, and at the same temperature on redistillation. It contained 0.99 ± 0.02 D per molecule.

Reaction of benzaldehyde-d$_1$ with potassium hydroxide. To a cooled solution (ice-bath) of 5.6 g. (0.1 mole) of potassium hydroxide in 5 ml. of water was added under nitrogen 6.0 g. (0.055 mole) of benzaldehyde-d$_1$, and the flask was stoppered. After shaking, the mixture was allowed to stand at room temperature for 2 days. The resulting solid was dissolved in 20 ml. of water, and the mixture was extracted with three 10-ml. portions of ether. The combined ethereal extracts were dried over magnesium sulfate and, after filtering, the solvent was removed. The residue was distilled to give 3 g. of crude benzyl alcohol-d$_2$, b.p. 94–96° at 10 mm. Redistillation yielded pure benzyl alcohol-d$_2$, b.p. 96° at 10 mm., n_D^{25} 1.5390; reported for benzyl alcohol n_D^{20} 1.53955.[7] This product contained 1.99 ± 0.02 D per molecule.

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[2] Fredenhagen and Bonhoeffer, *Z. phys. Chem.*, **A181**, 379 (1938).

[3] Wilson, *J. Chem. Soc.*, 1550 (1936); Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934).

[4] See Hill, Judge, Skell, Kantor, and Hauser, *J. Am. Chem. Soc.*, **74**, 5599 (1952).

[5] For a recent evaluation of the mechanisms, see Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 706. Also see L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 350.

[6] The reagent was found by the differential titration method to contain approximately 89% sodium methoxide.

[7] *International Critical Tables*, Vol. 7, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 40.

[8] Wiberg, *J. Am. Chem. Soc.*, **76**, 5372 (1954).

[9] Fieser, *Experiments in Organic Chemistry*, D. C. Heath and Co., New York, N. Y., 1941, p. 436.