The Deuteroxide-catalyzed Hydrogen Exchange of Dimethyl Sulphoxide. Preparation of Diperdeuteromethyl Sulphoxide, $(CD_3)_2SO$

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WE have observed that dimethyl sulphoxide (DMSO) undergoes hydrogen exchange in the presence of sodium deuteroxide under very mild conditions. Even at a deuteroxide concentration of 0·01M and at room temperature, a 10% D_2O—90% DMSO solution equilibrates hydrogen and deuterium within one hour. In a preliminary rate study, the rate of exchange was measured by following the appearance of OH absorption in the infrared spectrum (2·9μ). At a deuteroxide concentration of 0·002M in 10% D_2O—90% DMSO by volume the initial (pseudo first order) rate constant is $2 \cdot 3 \times 10^{-4}$ sec.$^{-1}$ at 28°C (ambient temperature). The rate increased linearly with deuteroxide-ion concentration over the range studied (0·001—0·003M). The rate of exchange also increased as the water content of the medium was decreased: at 0·001M-NaOD a change from 10% D_2O—90% DMSO to 5% D_2O—95% DMSO increased the rate about ten-fold.

This ready hydrogen exchange affords a convenient and inexpensive method for the preparation of deuterated dimethyl sulphoxide.[1] The deuteroxide-catalyzed equilibration between DMSO and D_2O is simply allowed to occur a sufficient number of times and the exchanged water is removed by fractional distillation. In one experiment, a $(CH_3)_2SO$—D_2O solution containing equimolar proportions of hydrogen and deuterium and 0·1M in NaOD was heated at 100° for 1 hour before removal of the water at 50 mm. pressure. The residue was further equilibrated six times with successive equivalent portions of D_2O, and finally distilled. The product contained practically no hydrogen as shown by its n.m.r. spectrum and exhibited the characteristic infrared frequencies reported for $(CD_3)_2SO$.[2]

Previous work on hydrogen exchange at carbon alpha to the sulphoxide group has shown that the deuteroxide-catalyzed exchange in D_2O is extremely slow.[3] The rapid exchange in DMSO solution is presumably due to the greatly enhanced reactivity of bases in this medium.[4]

This observed exchange is in accord with the intermediate formation of the methylsulphinyl carbanion:

$$OH^- + CH_3{\cdot}SOCH_3 \rightleftarrows CH_3{\cdot}SO{\cdot}CH_2^- + H_2O$$

Previously the methylsulphinyl anion had been obtained by reaction of sodium hydride with DMSO[5] or directly from alkali metals and DMSO.[6] A small equilibrium concentration of the anion was shown to be formed on addition of potassium t-butoxide to DMSO.[7] In view of these stringent conditions used to generate the methylsulphinyl anion, its formation in aqueous DMSO solutions is unexpected.

Since the equilibrium basicity for the DMSO–water system, as measured by the H_- acidity function, is now available[8], it should be informative to extend the hydrogen exchange data to wider solvent compositions.

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