

## The Deuterioxide-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 deuterioxide under very mild conditions. Even at a deuterioxide 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 ( $2.9\mu$ ). At a deuterioxide concentration of 0.002M in 10%  $D_2O$ —90%

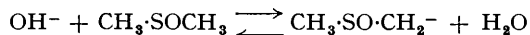
DMSO by volume the initial (pseudo first order) rate constant is  $2.3 \times 10^{-4} \text{ sec.}^{-1}$  at 28°C (ambient temperature). The rate increased linearly with deuterioxide-ion concentration over the range studied (0.001—0.003M). The rate of exchange also increased as the water content of the 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.<sup>1</sup> The deuterio-catalyzed equilibration between DMSO and D<sub>2</sub>O is simply allowed to occur a sufficient number of times and the exchanged water is removed by fractional distillation. In one experiment, a (CH<sub>3</sub>)<sub>2</sub>SO—D<sub>2</sub>O 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<sub>2</sub>O, 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<sub>3</sub>)<sub>2</sub>SO.<sup>2</sup>

Previous work on hydrogen exchange at carbon alpha to the sulphoxide group has shown that the deuterio-catalyzed exchange in D<sub>2</sub>O is extremely slow.<sup>3</sup> The rapid exchange in DMSO solution is presumably due to the greatly enhanced reactivity of bases in this medium.<sup>4</sup>

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



Previously the methylsulphinyl anion had been obtained by reaction of sodium hydride with DMSO<sup>5</sup> or directly from alkali metals and DMSO.<sup>6</sup> A small equilibrium concentration of the anion was shown to be formed on addition of potassium t-butoxide to DMSO.<sup>7</sup> 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*<sub>-</sub> acidity function, is now available<sup>8</sup>, it should be informative to extend the hydrogen exchange data to wider solvent compositions.

(Received, March 29th, 1965.)

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<sup>2</sup> F. A. Cotton, R. Francis, and W. D. Horrocks, jun., *J. Phys. Chem.*, 1960, **64**, 1534.

<sup>3</sup> W. E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 1955, **77**, 521. However, exchange occurs readily with Bu<sup>+</sup>OK—Bu<sup>+</sup>OD, cf. D. E. O'Connor and C. D. Broadus, *J. Amer. Chem. Soc.*, 1964, **86**, 2267; D. J. Cram and S. H. Pine, *ibid.*, 1963, **85**, 1096.

<sup>4</sup> D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfeld, *J. Amer. Chem. Soc.*, 1961, **83**, 3678; J. E. Hofmann, R. J. Muller, and A. Schriesheim, *ibid.*, 1963, **85**, 3000; A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.

<sup>5</sup> E. J. Corey and M. Chaykovski, *J. Amer. Chem. Soc.*, 1962, **84**, 866.

<sup>6</sup> A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 1964, 108.

<sup>7</sup> The equilibrium constant for the process with potassium t-butoxide in anhydrous DMSO was found<sup>6</sup> to be 1.5 × 10<sup>-7</sup>.

<sup>8</sup> R. Stewart and J. P. O'Donnell, *Canad. J. Chem.*, 1964, **42**, 1681; E. C. Steiner and J. M. Gilbert, *J. Amer. Chem. Soc.*, 1965, **87**, 382.