

## The Chemical Shift of the Hydroxide Ion

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IN an n.m.r. study of aqueous solutions of acids and bases, Gutowsky and Saika<sup>1</sup> showed that if the proton chemical shift was assumed to be the weighed mean of the H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup>, OH<sup>-</sup> shifts respectively, then the  $\tau$ -values of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> were both about  $-5$  p.p.m. Although this value for H<sub>3</sub>O<sup>+</sup> is consistent with later experimental estimates in other solvents,<sup>2,3</sup> no other experimental estimate of the chemical shift of OH<sup>-</sup> seems to have been reported. Musher<sup>4</sup> has obtained theoretical estimates in good agreement with the above values using an electrostatic model. Here we present evidence that this value for the chemical shift of OH<sup>-</sup> is in error by 13 p.p.m.

The proton magnetic resonance spectra of solutions of tetramethylammonium hydroxide in dry ammonia at room temperature were recorded at 40 Mc./sec. using cyclopentane as internal

standard. We shall assume that  $\tau = 8.491 \pm 0.002$  p.p.m. for cyclopentane, which we find for a dilute solution in CCl<sub>4</sub> containing Me<sub>4</sub>Si, in good agreement with the literature value ( $8.49 \pm 0.02$  p.p.m.).<sup>5</sup> The tetramethylammonium ion was identified as a well resolved 1:1:1 triplet,  $J = 0.61 \pm 0.02$  c./sec., at  $\tau = 6.58 \pm 0.01$  p.p.m., exactly the values we find for a solution of tetramethylammonium chloride in dry ammonia. The spectra of the solutions of tetramethylammonium hydroxide, but not those of tetramethylammonium chloride, showed a sharp line at  $\tau = 7.88 \pm 0.01$  p.p.m., of approximately 1/12 the total intensity of the tetramethylammonium signal. Thus we assign this to OH<sup>-</sup>. In confirmation of this assignment saturated solutions of tetramethylammonium and lithium hydroxide gave weak signals at  $\tau = 7.890 \pm 0.005$  and  $7.701 \pm 0.003$

p.p.m. respectively in 1,2-dimethoxyethane containing a little  $\text{Me}_4\text{Si}$  as internal standard. Neither signal was found in a blank. The 1,2-dimethoxyethane was dried over potassium anthracene, the ammonia over potassium, and vacuum-line techniques were used throughout. A small amount of sodamide was added to the solutions in ammonia to remove the last traces of water; this caused the ammonia triple-line spectrum to collapse to a broad single line in the expected manner.<sup>6</sup>

There seems to be a simple qualitative explanation for the aqueous solution results. Hydrogen-bonding invariably gives rise to a large low-field shift for the proton involved. Whereas it is unlikely that the  $\text{OH}^-$  proton H-bonds to anything, in aqueous solution about three water molecules will be strongly H-bonded to the oxygen atom of the  $\text{OH}^-$  ion. A low-field shift of about

4 p.p.m. per H-bond would result in a weighed mean proton chemical shift consistent with the observed values, since the value assigned here to  $\text{OH}^-$  is about 3 p.p.m. to high-field of water. This model also rationalises the small solvent dependence of the  $\text{OH}^-$  chemical shift found above; although ion pairing probably predominates for lithium hydroxide in 1,2-dimethoxyethane, the chemical shift assigned to  $\text{OH}^-$  in this system differs by only  $-0.2$  p.p.m. from the tetramethylammonium hydroxide value.

However it is still possible to argue qualitatively that the strong electrostatic field should reduce the shielding of the  $\text{OH}^-$  proton relative to  $\text{H}_2\text{O}$ , since  $\tau = 9.7$  p.p.m. for water in the gas phase,<sup>7</sup> to high-field of the value assigned here to  $\text{OH}^-$ .

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