The Disproportionation of HOD in the Liquid Phase

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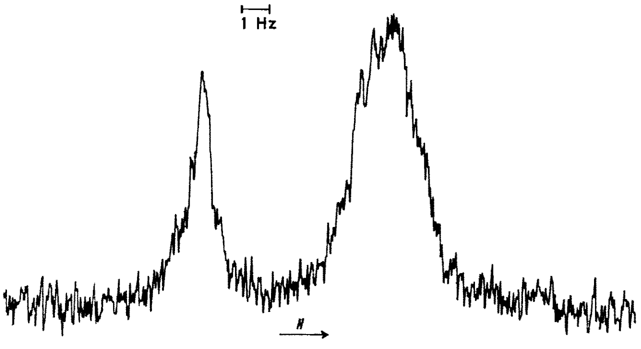
Summary. The equilibrium constant for the reaction $H_2O + D_2O \rightleftharpoons 2HOD$ in perdeuterioacetone as solvent has the value 3·94 ± 0·12 at 20°.

THE equilibrium $H_2O + D_2O \rightleftharpoons 2HOD$ is important in the treatment of solvent isotope effects in mixtures of D_2O and H_2O.[1] The value of the equilibrium constant K in the gas phase has been determined by mass spectrometry[2,3] and also calculated by statistical-mechanical methods from spectroscopic data.[4] From a consideration of the vapour pressure of H_2O-D_2O mixtures[6] it may be concluded that the difference between gas-phase and liquid-phase results should be insignificant. The experimental determinations and some of the calculations favour a value in the range 3·75—3·85 at 25° but some workers[5] have deduced lower figures (3·4—3·7). In the context of solvent isotope effects this discrepancy is significant. Most workers have used the statistical value (4·000) for K, a procedure which is justified[7] provided the true value is not substantially lower than 3·7. Indirect measurements of K in the liquid phase support[7,8] a figure around 3·8, but there has been no previous direct determination of K in the liquid phase with a precision sufficient to distinguish between alternative values.



FIGURE

Holmes, Kivelson, and Drinkard[9] have pointed out that the value of K can be deduced from the relative intensities of the ^{1}H n.m.r. signals of the species HOD and H_2O under conditions of slow proton exchange. Their measurements, with a 40 MHz instrument, did not fully resolve the two signals but were stated to be consistent with a value $K = 4·0 \pm 0·4$. The current availability of spectrometers of higher field strength has promoted a re-investigation of the problem; the preliminary results are now reported.

Using a solution of isotopically mixed water (H : D = 0·36, *ca.* 0·4 M) in purified $(CD_3)_2CO$ as solvent, we found excessive overlap between the two signals of interest at a frequency of 100 MHz but an essentially complete separation at 220 MHz (although the 1 : 1 : 1 triplet structure of the HOD signal, which is clearly observed at lower fields, is not very distinct at 220 MHz) (see Figure). The chemical shift of HOD is 0·032 ± 0·001 p.p.m. upfield from the H_2O signal. For a quantitative evaluation of the ratio of the signal intensities, separate scans were run with due regard to the instrumental factors governing quantitative uses of n.m.r. spectrometry.[10] The scans were averaged by use of a "d-mac Pencil Follower", type PF 10,000 Mark IB, for digitising the spectra at 0·1 Hz intervals, the maximum of the H_2O signal being taken as origin. This method of accumulation of spectra was preferred to that using a computer for averaging transients, because of movement of the signals due to the two water species relative to the tetramethylsilane trigger signal under the operating conditions of the instrument. In the evaluation of the relative peak areas due to H_2O and HOD particular attention was paid to the correct choice of base line and signal overlap. After detailed consideration of these limiting factors we deduce the value 3·94 ± 0·12 for K at 20°.

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