

Mass Spectrometric and IR Analysis of Deuterium Content of Water Using an Isocyanate Derivative

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A method was developed to analyze hydrogen isotopic compositions of heavy water samples in the deuterium fraction region of 0.1–0.9. A derivative of water, solid 1,3-diphenylurea, is formed by the reaction of a drop of a sample and phenyl isocyanate in diethyl ether. In its imino groups it has the same hydrogen isotopic composition as the sample. The analysis can be made by mass spectrometry or IR spectrometry or, with less accuracy, also by NMR.

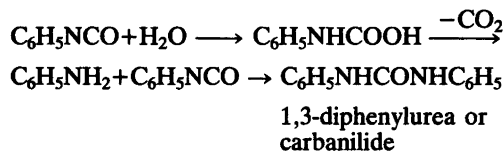
Deuterium content of heavy water can be determined by numerous methods.¹ Direct mass spectrometric analysis would seem to be a straightforward procedure, but great practical difficulties are then encountered, mainly due to the so-called memory effect. Although these difficulties can be reduced by using specially designed instruments,^{2,3} they are still present, if routine mass spectrometers are to be used for heavy water analyses. One way to circumvent these problems is to reduce water to hydrogen gas which is then analyzed.^{4,5} Some derivatives of water, *e.g.* ethane,⁶ have also been employed in analyses. Recently another approach has been introduced:⁷ 1-propanol is added into the samples when suitable metastable ions are formed in mass spectrometer.

The author made preliminary experiments to analyze the deuterium content of heavy water by methanol and deuteriomethanol, which are formed when methyl orthoformate is added to the samples.⁸ The mass spectrometric determination of these compounds with low molecular weights was, however, disturbed by the background peaks. Thus a heavier derivative of water

was looked for. In the literature, a promising compound, 1,3-diphenylurea or carbanilide, was found. This compound is also used in quantitative determinations of water by HPLC.⁹

EXPERIMENTAL

The reaction of phenyl isocyanate C_6H_5NCO with water is rather complicated, but for this case, it can be represented by Scheme 1.^{10,11}



Scheme 1. Eqn. (1).

In milder reaction conditions the phenyl groups are not deuterated. Consequently, the hydrogens of the water molecule go into the imino groups, which then have the same hydrogen isotopic composition as the water molecule. What actually happens is that the oxygen of the water is substituted by a urea residue (denoted hereafter with Ur) with a molecular weight of about 210.

Phenyl isocyanate is not miscible with water. Thus the above reaction can only occur at the phase edges, and it is difficult to constrain. It is more practical to accomplish the reaction in one liquid phase where both reagents dissolve. After preliminary experiments, diethyl ether and ethyl acetate were found to be suitable solvents. At

25 °C they dissolve water to form 1.22 and 3.27 % solutions,¹² respectively. As diethyl ether is easy to dry with sodium, it was used in the final experiments. The solvent, in 10 ml portions, and phenyl isocyanate, in amounts somewhat larger than needed for the reaction, were pipetted into test tubes with ground glass stoppers. Then one drop of the sample was added into the mixture. The test tubes were closed, but an escape for the formed CO₂ was provided by inserting a thin metal wire between the stopper and the tube. The test tubes were kept in a desiccator overnight to allow the reaction to be completed and the resulting carbanilide to precipitate. The crystal suspension was then mixed thoroughly in order to homogenize the composition after the possible kinetic isotope effect. The test tubes were centrifuged and the liquid decanted. The rest of the solvent and the unreacted phenyl isocyanate (b.p. 162–163 °C, from Ref. 13) were removed by heating the tubes at 170 °C for 1 h. Recrystallizing is possible, of course, but it was not considered necessary. All the procedures where isocyanate was present were carefully conducted under a hood, as this reagent irritates eyes and respiratory tracts.¹⁴

Mass spectra were determined with an MX 1320 mass spectrometer (U.S.S.R.) using direct inlet. The ionization chamber was thermostated at 110 °C, and the ionization energy was 60 eV. In the preliminary experiments the mass region around the molecular peaks was found the most suitable for analysis. The spectra were produced by repeated slow scanning (about 30 s) over the mass region of m/z : 211–218 with low resolution. The peak intensities were registered with a potentiometric recorder. The reproducibility of the relative intensities was 1–3 %. The averages of several scans (standard error of the mean about 1 %) were used in the calculations. The IR spectra were determined with a Perkin-Elmer type 283 IR spectrophotometer using the conventional KBr disc technique. In the NMR measurements, a Perkin-Elmer type R 12B (60 MHz) proton resonance instrument was used. The carbanilide samples were dissolved in DMSO dried by distillation *in vacuo*.

RESULTS AND DISCUSSION

Carbanilide proved to be a practical derivative of water. It can be prepared easily and as a solid organic compound it is convenient for handling and preserving. Its adsorption on the inner walls of the mass spectrometer is slight, and consequently, the pumping times are short. Around

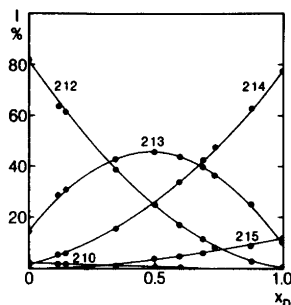


Fig. 1. The relative intensities of the mass peaks of the deuterated carbanilides in the molecular peak region plotted against the deuterium fractions of the heavy water samples. The curves were computed using the model explained in the text.

the molecular peaks the background is negligible. In this region there are eight mass peaks (m/z : 211–218, the two last ones very faint) due to the carbanilides deuterated in different degrees. Their relative intensities vary with the deuterium fractions of the water samples as presented in Fig. 1. The intensities most dependent on the deuterium contents are $I(212)$ and $I(214)$. The quotient $I(214)/(I(212)+I(214))$ is a sensitive indicator of the deuterium fraction (Fig. 2). This curve is sigmoidal in its form, but in the region of $x_D=0.1-0.9$ it is sufficiently steep for analysis. At low or high deuterium fractions the method becomes insensitive. As the relative peak intensities seem to depend on the constancy of the temperature of the ionization chamber, it is wise to check the calibration curve for every analysis using one or two standard samples with about the same isotopic composition as the unknown sam-

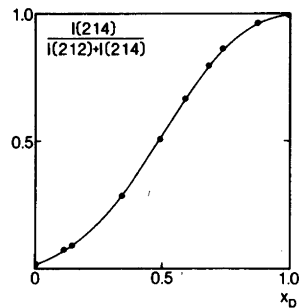


Fig. 2. The experimental calibration curve obtained from the results of Fig. 1.

ple. With this procedure, it was possible to achieve accuracies of 1–2 %.

The observed peak intensities can be formally explained with isotopic compositions of different carbanilides and their fragmentation routes in the mass spectrometer. The intensity of each mass peak is the sum of contributions from different molecules, and each contribution is the product of three different factors:

$$I = \sum A \cdot B \cdot C \quad (2)$$

Factor *A* is connected with the natural isotopic variations of the undeuterated molecules, *B* with the deuteration of the imino groups, and *C* with the fragmentation of the molecules.

The proportions of different “normal” carbanilides UrHH can be calculated from the known isotopic abundances of the elements with binomial distribution.^{15,16} By this means it is found that the relative abundances of carbanilide species with masses 212, 213, 214 and 215, or their *A* factors, are 0.856, 0.132, 0.011 and 0.001, respectively. On the basis of the reaction scheme (1) it can be assumed (neglecting a possible small kinetic isotope effect) that the relative portions of the molecular species UrHH, UrHD and UrDD are the same as the portions of H₂O, HDO and D₂O in the original water sample. A quantitative deuteration was actually verified in the case of a water sample with $x_D = 0.997$; the proton resonance peak of N–H was absent in the NMR spectrum of the corresponding carbanilide. To

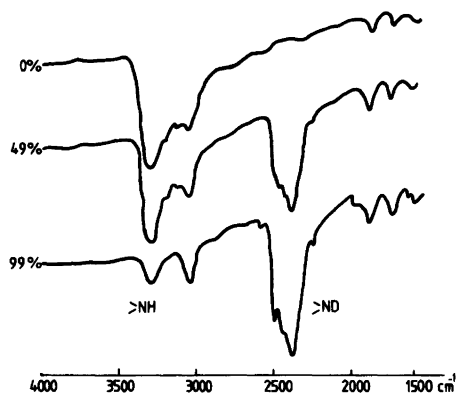


Fig. 3. IR spectra of deuterated carbanilides. The deuterium content of the original water sample is given for each curve.

the first approximation the proportions of different species can be calculated by taking a value of 4 for the equilibrium constant $K(\text{HDO})^2$ of the isotopic disproportionation reaction of heavy water.¹⁷ Thus the relative amounts of UrHH, UrHD and UrDD, or their *B* factors, are $(1-x)^2$, $2x(1-x)$, and x^2 , where *x* is the deuterium fraction of the water sample. The values of factor *C* heavily depend on the parameters and circumstances of the mass spectrometer, and they can be determined only experimentally. Inspection of the mass spectra revealed that near the molecular peak *M*, three other peaks can be distinguished. The *M*+1 and *M*–1 peaks are due to capture or loss of a protium. The latter peak is more intense with the deuterated carbanilides, which may be explained by a gas phase exchange of protium to the deuterated imino groups in the mass spectrometer. The *M*–2 peak corresponds to the loss of a deuterium. The fragmentation processes have different probabilities. They were determined with a personal computer by searching for a set of *C* factors, which resulted in close agreement between the experimental peak intensities and calculated ones. These values are given in Table 1, and the corresponding curves are shown in Fig. 1 together with the experimental points. To summarize the computing procedure of the peak intensities: e.g. a “normal” carbanilide molecule UrHH formed from a water sample with deuterium fraction *x* gives its contribution of $0.856(1-x)^2s(1)$ to the mass peak *m/z*: 212. Consequently, the relative intensity of each mass peak around the molecular peaks is the sum of 1–10 pieces of terms of this kind.

IR spectrometry can also be employed for the analysis of the imino groups of the carbanilides, as the stretching vibrations of N–H and N–D occur at different wave numbers, about 3000 cm⁻¹ and about 2400 cm⁻¹, respectively¹⁸ (Fig. 3).

Table 1. Probabilities for some mass peaks of different carbanilide molecules.

Peak	Probability	Actual relative probabilities C for		
		UrHH	UrHD	UrDD
<i>M</i> +1	$r(i)$	2	1	0
<i>M</i>	$s(i)$	95	92	89
<i>M</i> –1	$t(i)$	3	7	10
<i>M</i> –2	$u(i)$	0	0	1

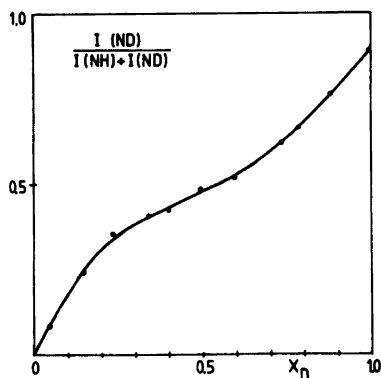


Fig. 4. The calibration curve derived from the peak areas of the IR spectra.

Unfortunately, the stretching vibrations of the aromatic C–H bonds at 3050 cm^{-1} disturb the analysis. The calibration curve $I(\text{ND}) / (I(\text{NH}) + I(\text{ND}))$ against the deuterium fractions of the water samples shown in Fig. 4 was obtained by using the peak areas measured by manual peak resolving. An essentially similar curve was also arrived at by using the peak heights, which are easier to measure. According to the calibration curve, the accuracy of this IR method may be a few per cent, like that of some other IR methods described in the literature.^{8,19}

Experiments were also made to analyze the deuterium contents of the imino groups of the carbanilides with proton nuclear magnetic resonance. The relative intensities of N–H peaks were measured using the aromatic hydrogens as an internal reference. With the old NMR instrument employed, the results were, however, poorly reproducible, and the accuracy was only about 5%.

CONCLUSIONS

Reaction with phenyl isocyanate presents a convenient way to make a derivative of water for isotopic analysis. The reaction product, carbanilide, saving the hydrogen isotopic composition of water in its imino groups, is an organic solid. It is readily obtained in a fairly pure form, and it is easy to handle and preserve. The isotopic analysis can be made by usual mass spectrometers without any sophisticated gas handling systems, which is a remarkable advantage in casual analy-

ses. Very small samples are needed, and the accuracy is sufficient for many purposes. The analysis can also be carried out with IR spectrophotometry, or, with less accuracy, by NMR.

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