[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NATIONAL TSING HUA UNIVERSITY]

Distribution of Iodine between Heavy Water and Carbon Tetrachloride

BY TSING-LIEN CHANG

Substitution of heavy water for ordinary water as a solvent usually changes considerably the physico-chemical properties of any solute. While a number of measurements on the solubility of single salts in heavy water have been described, little is known about ternary systems in which heavy water is one component. This has led the writer to investigate the distribution of iodine between heavy water and carbon tetrachloride, since the distribution of iodine between ordinary water and carbon tetrachloride, which is 1:85 in molarity ratio at 25°, is often taken as a classical example of the Nernst law of distribution. Judging from the fact that the solubility of salts in heavy water is mostly 10–20% lower than that in ordinary water,[1] one would expect a partition coefficient of iodine between heavy water and carbon tetrachloride of about 1:103.

Materials.—The heavy water used in the experiment was freshly distilled in an all-glass apparatus from a product of Norsk Hydro-Elektrisk Kvaelstof A/S, Oslo, and then had a density of 1.10391 at 25° corresponding to 99.54 mole per cent. heavy water. The iodine was repeatedly sublimed from a commercial product after mixing it with some potassium iodide in the first sublimation. The well-formed crystals were finally collected and dried over calcium chloride. The carbon tetrachloride was Schering-Kahlbaum Purest Reagent, free from sulfur. Its density was 1.58434 at 25°.

Procedure.—Five ml. of a carbon tetrachloride solution of iodine and 25 ml. of heavy water were pipetted into a 35-ml. tube made of neutral glass, bearing a stem to which the tube was sealed after the filling. The tube was mounted in a rocking device, in a thermostat at 25 ± 0.02°. Equilibrium was practically attained after two hours. Then the tube was put in the vertical position in the thermostat for a few minutes so as to allow the droplets of carbon tetrachloride to settle down. It was then cut open and its contents analyzed.

Two samples of the aqueous layer were taken out by a calibrated pipet of 9.8683-ml. capacity. The pipet was provided with a cotton plug near its top in order to exclude any moisture from the breath. Each sample was emptied into a small separatory funnel and shaken successively five times with 1 ml. of carbon tetrachloride. The fifth extraction was almost colorless. This process enabled the heavy water to be recovered and directly used for the next determination. The stopcock of the funnel was lubricated with Schering-Kahlbaum high-vacuum grease.

Two other samples were withdrawn from the carbon tetrachloride layer with a pipet of 1.0094-ml. capacity, previously calibrated to within 0.2% with carbon tetrachloride itself. Each of these samples was emptied into 10 ml. of conductivity water in a small conical flask, the water serving to cover the carbon tetrachloride solution, thus to reduce the possible loss of iodine through volatilization. After the addition of 5 ml. of 1% starch solution, the sample was titrated with 5.120 millimolar sodium thiosulfate solution. The titration was carried out by means of a 10-ml. buret, which allowed a volume of 0.01 ml. to be accurately estimated. The end-point was observed on both iodo-starch and carbon tetrachloride. Such double indicators render the end-point more conveniently fixed. In the titration of the aqueous layer, whose iodine content was very low, the starch solution did not develop immediately a blue color, but it appeared on the introduction of a few drops of the end-point solution from the titration of the carbon tetrachloride layer. The possible error so introduced was negligible.

Test with Ordinary Water.—The above described method of analysis was first tested with conductivity water, including the extraction process. The following results were obtained: two 1.0094-ml. samples of the carbon tetrachloride layer required, respectively, 21.57 and 21.59 ml. of 5.120 millimolar sodium thiosulfate solution, while two 9.8683-samples of the water layer required 2.45 and 2.45 ml. So the concentrations of iodine in carbon tetrachloride and water were respectively 54.73 and 0.636 millimolar and the partition coefficient was therefore 1/86.1. This agrees with the "I. C. T." value, 1/85.4 ± 0.5, for the same concentration,[2] our experimental error being less than ±2%. In view of the fact that the volume of water used in this experiment was only 1/400 of that employed by Washburn and Strachan,[3] this result may be considered satisfactory.

Results with Heavy Water.—Measurements with the 99.54 mole per cent. heavy water yielded the following results.

CCl_4 layer, ml.	5.120 milli-molar $Na_2S_2O_3$, ml.	D_2O layer, ml.	5.120 milli-molar $Na_2S_2O_3$, ml.	cI_2 in CCl_4, milli-molar	cI_2 in D_2O, milli-molar	Distribution ratio
1.0094	13.99	9.8683	1.33	35.38	0.342	103
	13.91		1.31			
1.0094	17.09	9.8683	1.62	43.33	.419	103
	17.08		1.61			
1.0094	22.08	9.8683	2.03	55.87	.531	105
	21.98		2.06			

The limiting error of the measurement was in the titration of the aqueous layer, an error of a half drop causing an error of about 1% in the coefficient. But it seemed inadvisable to use more dilute thiosulfate solution. The recovered heavy water, after purification, had a density of 1.1040 at 25° as determined by an 0.8 ml. pycnometer with an error of 0.0002 g./ml.

The correction for 100% heavy water amounts to only −0.08 in the value of the ratio. The distribution ratio in the case of ordinary water for the concentration range investigated is higher than that for infinite dilution[2] by the amount of 0.1–0.3. The corresponding difference in the case of heavy water may be of similar magnitude, which is also small in comparison with the experimental error. With these considerations, it is concluded that the molar distribution ratio of iodine between heavy water and carbon tetrachloride at infinite dilution is 1:103.2 at 25°. The writer has not attempted, however, to determine the so-called true distribution coefficient.[4]

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(1) O. Reitz, *Z. Elektrochem.*, **44**, 73 (1938).

(2) "Int. Crit. Tables," Vol. III, 1928, p. 420.

(3) E. W. Washburn and E. K. Strachan, THIS JOURNAL, **35**, 688 (1913).

(4) C. Winther, *Z. physik. Chem.*, **B3**, 301 (1929).

Summary

Iodine has been found to distribute itself between heavy water and carbon tetrachloride in the molarity ratio 1:103 at infinite dilution at 25°, as compared with a corresponding ratio of 1:85 for ordinary water.

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The Molecular Structures of Phosphoryltribromide, Thiophosphoryltribromide, Thiophosphorylmonofluorodibromide, and Thiophosphoryldifluoromonobromide

BY J. H. SECRIST AND L. O. BROCKWAY

Interesting deviations from predicted single covalent bond radii have been observed in the molecular structures of halogen derivatives of non-metals, especially those of silicon and phosphorus.[1,2] Phosphoryl and thiophosphoryl fluorides and chlorides having been previously studied,[3,4,5] it seemed desirable to extend this type of investigation to the phosphoryl and thiophosphoryl bromides and to two mixed thiophosphoryl halides, $PSFBr_2$ and PSF_2Br, which had been prepared and furnished us by Professor H. S. Booth of Western Reserve University. The unusual shortening effect on bond lengths of fluorine atoms in both organic and inorganic compounds has been a subject of investigation for some time.

In this study, the usual electron diffraction method was employed on the vapor of the compound. A constant wave length of 0.0592 Å. for the electron beam was used, the camera distance varying between 99.0 and 101.5 mm. Temperatures were maintained on the samples sufficient to furnish vapor pressures of 50–100 mm. at the time of photographing. To reach this vapor pressure in the case of the solids $POBr_3$ and $PSBr_3$, a special electrical heating coil was used around the sample holder to maintain temperatures at 50–60°. Room temperature was satisfactory for the compound $PSFBr_2$, and -35 to $-27°$ for the compound PSF_2Br.

Radial distribution curves for each compound were calculated from the distribution function of Pauling and Brockway, $D = \Sigma\, c_k(\sin s_k r)/(s_k r)$, where C_k is given by I_k, the visually estimated relative intensity, multiplied by the factor s_k^2 exp. $(-as_k^2)$. The exponential factor is set equal to 0.1 for the largest ring. These curves are shown in Fig. 1.

Phosphoryl Tribromide.—Phosphoryl tribromide was prepared from phosphorus tribromide by addition of bromine and subsequent treatment with phosphorus pentoxide.[6] The product boiling between 188 and 190° was recrystallized from anhydrous ether (m. p. 55–56°).

Theoretical intensity curves for the eight most favorable models are shown in Fig. 2. In calculating these models, trigonal symmetry through the P-O axis was assumed in each case. The models vary in decreasing order of BrPBr angle from 112° in model A to 103° in model H. The main difference in the curves appears at minima 3 and 4 and beyond peak 8. The photographs showed minimum 3 to be less deep than 4; and peaks 3 and 5 heavier than peak 4. This makes curve A inferior, as peaks 3 and 4 here are of about the same height. Regular gradations in the depth of minima 3 and 4 occur from top to bottom in Fig. 2. Curves F, G and H are, therefore, increasingly inferior in this respect to curves B, C, D and E. In curve H, the order is actually reversed for these two minima; moreover, peaks 6 and 7 show the wrong relative intensity in H. The conclusion is that curves C, D and E fit the observed features most closely, with B and F on the border line.

TABLE I

PHOSPHORYL TRIBROMIDE

Max.	Min.	s_0	c_k	s_C/s_0	s_D/s_0	s_E/s_0
	2	5.23	−44	0.922	0.924	0.893
3		6.27	44	.918	.928	.901
	3	7.11	−34	.918	.933	.913
4		8.00	32	.892	.905	.884
	4	8.93	−44	.899	.906	.879
5		9.87	47	.915	.920	.891
	5	10.86	−24	.919	.927	.897
6		11.85	24	.911	.919	.894
	6	12.62	−14	.915	.921	.896
7		13.54	14	.918	.923	.895
	7	14.64	− 8	.916	.922	.890
8		15.58	8	.921	.928	.895
	8	16.42	− 4	.930	.936	.907
9		17.41	3	.916	.926	.902
	Average			.915	.923	.896
	Average deviation			.006	.006	.006
	P-O, Å.			1.427	1.440	1.398
	P-Br			2.040	2.058	2.088
	O-Br			2.855	2.898	2.930
	Br-Br			3.331	3.332	3.333

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