tems containing polar materials such as methanol. The very good agreement in the set of systems containing benzene, cyclohexane and carbon tetrachloride makes it appear that the theory is sound for non-polar materials.

The validity of equations 11a and 11b as proposed by Spinner may find some justification in the expression derived from equations 12a and 12b

and

$$r_1 = \frac{S_{11}}{S_{12}} e(-L_{11} + L_{12})/RT$$

$$r_2 = \frac{S_{22}}{S_{21}} e(-L_{22} + L_{21})/RT$$

but any such justification involves a number of unwarranted assumptions.

TEXAS CITY, TEXAS

[A CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

The Distribution of Iodine between Carbon Tetrachloride and Water and a Proposed Mechanism for Dilute, Aqueous Iodine Reactions[1]

By RAYMOND G. WILLE AND MARY L. GOOD

The distribution of iodine between carbon tetrachloride and water at 25° has been studied as a function of the total iodine concentration (10^{-1} to 10^{-5} M); the pH of the aqueous phase (1.0 to 7.0); and the time of mixing. Both tracer techniques and spectrophotometric methods were used. Discrepancies between calculated and experimental distribution coefficients for low iodine concentrations are reported. Some information on the chemical behavior of the iodine species in the water phase is presented along with a mechanism to explain the anomalous behavior of dilute aqueous iodine solutions.

In a previous paper[2] an extensive study of the distribution of iodine between carbon disulfide and aqueous solutions was reported. In this study it was found that more iodine (in various chemical forms) appeared in the water phase than could be accounted for by considering the well-known iodine equilibrium reactions. The discrepancies became more pronounced as the total iodine concentration in the system was decreased. Attention was called to the fact that similar results were obtained by Kahn[3] in a study of the distribution of iodine between benzene and water. Also other investigators have found anomalous behavior in dilute iodine solutions. Examples are (1) the studies made by Reid and Mulliken[4] on dilute solutions of iodine in pyridine where excess triiodide appeared as the iodine concentration was decreased; and (2) the investigation of the ionization constant of iodine by Katzin[5] where the value obtained for the constant increased as the iodine concentration decreased. No definite conclusions were made to account for results reported in these cases. However, it was generally agreed that either impurities were playing an important role in these studies or there was some unknown reaction occurring at low iodine concentrations between iodine and the solvent in its "brown" solutions. The results of the carbon disulfide–water distribution study[2] indicated that the anomalous behavior was quite reproducible. This is not generally a characteristic of impurity reactions. Thus it seems the most likely explanation is that some iodine reaction, heretofore not taken into account, becomes important at low iodine concentrations.

To further study this interesting iodine behavior, a distribution study of iodine between carbon tetrachloride and aqueous solutions was carried out. Tracer techniques were employed to follow the distribution so that the lowest possible iodine concentrations could be used.

Experimental

The experimental procedure described previously[2] for the distribution study of iodine in the carbon disulfide–water system was essentially repeated. Reagent grade carbon tetrachloride was purified further by a method described by Edwards and Davies.[6] Buffers at pH 6.98, 5.01 and 2.98 were prepared using 0.1 M citric acid and 0.2 M disodium phosphate. A dilute solution of sulfuric acid was used for pH 1.02. All buffer systems were made up with conductivity water. A Beckman Model G pH meter was used to determine the pH of the buffer solutions. U. S. P. iodine (resublimed) was used to prepare carrier solutions of iodine in carbon tetrachloride. All carrier solutions were diluted from a 0.1 M stock solution. Eight day I^{131} obtained from the Oak Ridge National Laboratory in a "carrier-free" state, in a sodium sulfite solution, was used as a tracer. The radioactive solutions to be used in the distributions were obtained by shaking the carbon tetrachloride solutions of carrier iodine with diluted solutions of the Oak Ridge I^{131}. The two phases were separated leaving the iodine in the carbon tetrachloride phase tagged with I^{131} due to the exchange between the active iodide ions and the I_2 molecules. Radioactivity measurements were made on liquid samples using a well type NaI (thallium activated) scintillation counter. A Dumont 6292 photomultiplier tube; a Nuclear Corporation Power supply, Model 1090A; a Radiation Counter Laboratories linear amplifier, Model 2206; and a Nuclear Corporation scaling unit, Model 161, were used.

The distributions were made by adding 20 ml. of carbon tetrachloride containing radioactive iodine to an equal volume of buffered water in a 100-ml. glass-stoppered flask. The flask was immersed in a water-bath controlled at 25 ± 1°. The flask was mechanically shaken at a constant rate. The solutions were shaken for varying lengths of time from two minutes to several hours. After each period of mixing the layers were allowed to separate and equal volumes of solution were removed from each phase and counted. To obtain the reproducibility a second series of distributions were made. Results of the two separate runs agreed within experimental error (approximately 10%).

(1) This work was supported in part by a Frederick Gardner Cottrell Grant from the Research Corporation. Abstracted from a portion of the thesis submitted by Raymond G. Wille to the Graduate School of the Louisiana State University, Baton Rouge, in partial fulfillment of the requirements for the degree of Master of Science.

(2) M. L. Good and R. R. Edwards, J. Inorg. Nucl. Chem., 2, 196 (1956).

(3) M. Kahn, Thesis submitted for degree of Doctor of Philosophy, Washington University, St. Louis, Mo., 1950.

(4) C. Reid and R. S. Mulliken, THIS JOURNAL, 76, 3869 (1954).
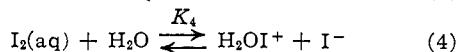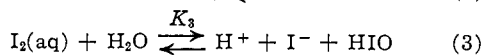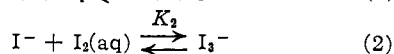
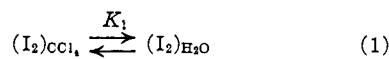(5) L. I. Katzin, J. Chem. Phys., 21, 490 (1953).

(6) R. R. Edwards and T. H. Davies, "National Nuclear Energy Series, Book 1, Radiochemical Studies; The Fission Products," Paper 23, McGraw-Hill Book Co., Inc., New York, N. Y., 1951.

To check the results of the radioactivity distribution, a spectrophotometric study was undertaken. Solutions of $10^{-1} M$, $5 \times 10^{-2} M$, $10^{-2} M$, $5 \times 10^{-3} M$ and $10^{-3} M$ iodine in purified carbon tetrachloride were prepared. Aliquots of these solutions were mixed with equal volumes of the buffer solutions. The two phases were mixed intimately for various periods of time. After each period, the phases were allowed to separate and equal volumes of both phases were removed. A portion of the water sample was placed in a 1-cm. quartz cell and analyzed spectrophotometrically using a Beckman Model DK-1 recording spectrophotometer. Scanning time was set at three minutes with a sensitivity of ten. A matching quartz cell filled with the corresponding buffer solution was used as a blank. Only the aqueous phase was analyzed.

Some experiments were carried out in an attempt to identify the chemical species of the iodine present in the aqueous phase. These will be reported in the discussion section.

Results

Tracer Distribution Study.—Plots of activity in the aqueous phase *vs.* time were made for each distribution run. It was found that the activity in the water layer increased with time. However, all of the well known iodine reactions which would contribute significantly to this distribution are quite rapid. These reactions

$$(I_2)_{CCl_4} \overset{K_1}{\rightleftharpoons} (I_2)_{H_2O} \qquad (1)$$

$$I^- + I_2(aq) \overset{K_2}{\rightleftharpoons} I_3^- \qquad (2)$$

$$I_2(aq) + H_2O \overset{K_3}{\rightleftharpoons} H^+ + I^- + HIO \qquad (3)$$

$$I_2(aq) + H_2O \overset{K_4}{\rightleftharpoons} H_2OI^+ + I^- \qquad (4)$$

all have well known equilibrium constants with the exception of (4). This ionization constant has been evaluated by several different investigators[5,7,8] and values ranging from 1.2×10^{-11} to 1×10^{-8} have been reported. However, Allen and Keefer[9] in a recent spectrophotometric study have set an upper limit on this constant of 1×10^{-10}. Thus to be able to obtain the distribution of·iodine between the two phases which is caused by the rapid reactions, we have extrapolated the aqueous activity curves back to zero time. Figure 1 shows a typical curve and the extrapolation which has been done.

Using these extrapolated activity data, an experimental distribution coefficient was calculated.

$$D_{expt} = \frac{(cts./min./ml.)_{CCl_4}}{(cts./min./ml.)_{H_2O}}$$

From the equilibrium constants for reactions 1, 2, 3 and 4 and the concentration of the iodine in the carbon tetrachloride it was possible to derive an expression for the expected distribution coefficient.[10]

$$D_{Calcd} = \frac{(I_2)_{CCl_4}}{\left[\dfrac{(I_2)_{CCl_4}}{K_1} + \left[1 + \dfrac{2K_2(I_2)_{CCl_4}}{K_1}\right]\left[\dfrac{K_3 + (H^+)K_4}{(H^+)\left[K_2 + \dfrac{K_1}{(I_2)_{CCl_4}}\right]}\right]^{1/2}\right]}$$

D_{expt} and D_{calcd} were obtained for all of the various distribution runs in which I^{131} was used as a tracer. The results are given in Table I.

(7) R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951).

(8) H. D. Murray, *ibid.*, **127**, 882 (1925).

(9) T. L. Allen and R. M. Keefer, THIS JOURNAL, **77**, 2957 (1955).

(10) A similar derivation for the calculated distribution of iodine between benzene and water was given by Kahn.[3]
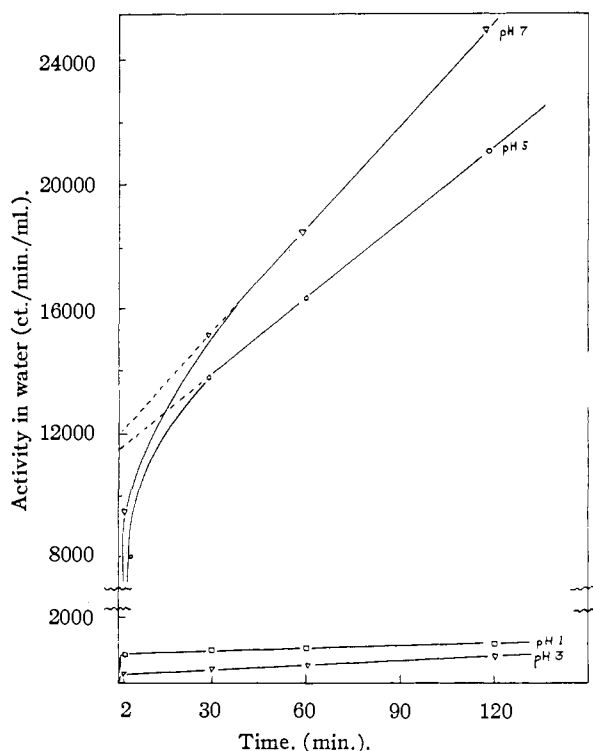
Fig. 1.—Variation of I^{131} activity in the water phase as a function of pH; total I_2 concn. in CCl_4, $10^{-5} M$.

Spectrophotometric Distribution.—The absorption spectra of the various aqueous solutions of iodine were obtained. A typical run is illustrated by Fig. 2. It is seen from these curves that the I_2

TABLE I

THE I^{131} ACTIVITY DISTRIBUTION BETWEEN CCl_4 AND H_2O

pH of aqueous phase	Concn. of carrier I_2 in CCl_4, M	D_{expt}	D_{calcd}
6.98	10^{-1}	59	81
	10^{-2}	55	72
	10^{-3}	18	56
	10^{-4}	2.1	30
	10^{-5}	0.26	5
5.01	10^{-1}	84	87
	10^{-2}	70	83
	10^{-3}	46	80
	10^{-4}	17	73
	10^{-5}	0.87	44
2.98	10^{-1}	90	87
	10^{-2}	85	85
	10^{-3}	75	84
	10^{-4}	58	83
	10^{-5}	15	79
1.02	10^{-1}	95	87
	10^{-2}	83	85
	10^{-3}	76	85
	10^{-4}	38	84
	10^{-5}	18	83

peak (461 mμ) remains constant with time but the I_3^- peaks (350 and 288 mμ) increase with time of mixing. This behavior corresponds to that seen in the tracer distribution. It should be pointed out that the I_2 concentration was 50 to 100 times greater
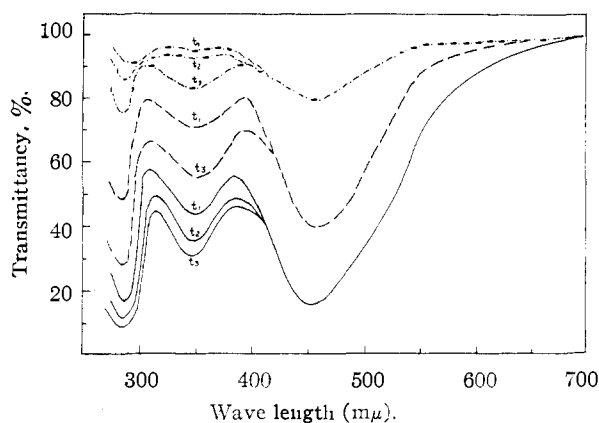
Fig. 2.—Aqueous iodine absorption spectra as a function of time and total I_2 concn.; water, pH 5.11. Concn. I_2 in CCl_4: 0.10 M (—); 0.05 M (— —); 0.01 M (—·—·). t_1 mixed, 2 min.; t_2 mixed, 30 min.; t_3 mixed, 2 hr.

than the I_3^- concentration even though the peaks were approximately equal in height. This is caused by the small I_2 molar extinction coefficient (742 at 461 mμ) as compared to the I_3^- molar extinction coefficient (40,000 at 288 mμ and 26,400 at 350 mμ).[9] By using these molar extinction coefficients, the intensity of the peaks, the total I_2 concentration originally present in the carbon tetrachloride, the I_2 partition coefficient between carbon tetrachloride and water (K_1), the triiodide formation constant (K_2) and the hydrolysis constant for iodine (K_3) it was possible to calculate a distribution coefficient corresponding to that obtained in the tracer experiment. However, no large deviations between the spectrophotometric value so calculated and D_{calcd} were obtained because of the limited concentration range of the spectrophotometer.

Discussion

It has been shown in both the tracer and the spectrophotometric distribution studies that more iodine is found in the aqueous phase than can be accounted for by the known fast equilibrium reactions of iodine in water. Also it has been shown that the amount of iodine in the water phase increases with time. So to explain these results one must postulate some rapid reaction followed by a slower reaction occurring in the aqueous solution.

It was thought that the slower reaction might be the formation of iodate

$$3I_2(aq) + 3H_2O \rightleftharpoons IO_3^- + 5I^- + 6H^+.$$
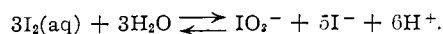
This reaction is known to reach equilibrium slowly.[11] However, no appreciable amount of iodate could be found in the aqueous solutions, even at high pH values and after the two phases were allowed to mix for several days.

Since IO_3^- exchanges very slowly with I_2 it was possible to obtain the upper limit of the IO_3^- content in the following manner. After shaking the two phases intimately for 24 hours (water buffered to a pH of 7.0 and the carbon tetrachloride containing 10^{-4} M carrier iodine tagged with I^{131}) the layers were separated. The water layer was counted (10,654 ct./min./ml.) and extracted with a 0.1 M iodine in

(11) W. O. Lundberg, C. S. Vestling and J. E. Ahlberg, THIS JOURNAL, 59, 264 (1937).

carbon tetrachloride solution. After one extraction the water contained only 195 ct./min./ml. After a second extraction the water contained only 53 ct./min./ml. Thus the maximum amount of iodate that could have been present was less than 0.5%. Also these exchange results indicate that the excess iodine in the water layer must be in some chemical form exchangeable with I_2 such as I^-, I_3^- or HOI.

It has been suggested in earlier studies that perhaps the anomalous behavior of dilute iodine solutions was caused by impurities in the solvents used. Since in the case at hand excess activity in the water layer appears to be in a reduced state, then it seems reasonable to assume that the impurity, if present, is a reducing agent. Thus if an oxidizing agent is added to the system to oxidize I^- to I_2, then we should be able to observe the calculated distribution coefficient experimentally.

It is known that in acid solution Fe^{+++} will selectively oxidize macro amounts of I^- to I_2 without further oxidation. Ferric sulfate was added to an aqueous solution containing sulfuric acid at pH less than 1. This was shaken with an equal volume of 10^{-4} M iodine (tagged with I^{131}) in carbon tetrachloride. The same distribution coefficient was observed with the Fe^{+++} that had been obtained previously. The procedure was repeated using ferric nitrate but no difference was observed.

From this observation we must conclude one of three things, namely (1) a reducing impurity is not the cause of the excess activity in the water phase; or (2) I^- at these concentrations cannot be oxidized by Fe^{+++}[12]; or (3) the excess activity in the water layer is not I^- but some other chemical form readily exchangeable with I^- and I_2.

To prove conclusively the reproducibility of the activity distributions a final experiment was performed.

A 10^{-4} M solution of iodine in carbon tetrachloride was exchanged with 5 ml. of radioactive iodine. The tagged I_2-carbon tetrachloride solution was washed with three separate but equal portions of conductivity water. After each washing the layers were separated and the distribution ratio determined. The D values were found to decrease slightly with each washing due to the decrease in total iodine concentration. A second solution of 10^{-4} M iodine in carbon tetrachloride was washed twice with an equal volume of conductivity water. This washed solution was then exchanged with 5 ml. of active iodine, the layers separated, and the carbon tetrachloride phase added to an equal portion of conductivity water. The distribution was determined. The D value agreed (within experimental error) with the one previously determined.

One may conclude from this experiment that if impurities are causing the low D values, they do not originate exclusively in the Oak Ridge I^{131} solutions. Furthermore it seems unlikely that an impurity reaction would give rise to such reproducible results.

The best explanation for the observed phenomena seems to be that some heretofore unknown reaction between water and iodine becomes increasingly important at low iodine concentrations. Also there is an unexplained slow reaction occurring in the aqueous phase which is important even at so-called macro concentrations (10^{-3} M and higher). From our observations both of these reactions must produce a chemical form of iodine which is readily exchangeable with I_2. The slow reaction must give rise to excess I^- or at least have I_3^- as the ultimate end product as is shown by our spectrophotometric data. Our data also indicate
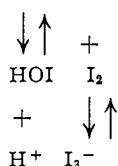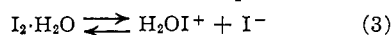
(12) M. Kahn and A. C. Wahl, J. Chem. Phys., 21, 1185 (1953).

that although these reactions are more prominent at high pH values, they are important over the entire pH range studied.

To account for the observed phenomena the following mechanism is proposed. Let us consider that the first initial activity in the water layer is due to the partition of iodine and to reactions between iodine and water.

$$I_{2(CCl_4)} \rightleftharpoons I_{2(H_2O)} \qquad (1)$$

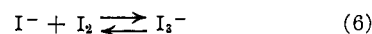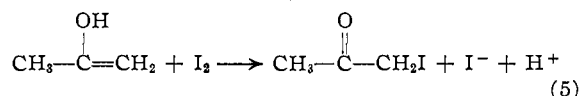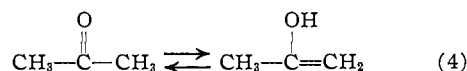$$I_2 + H_2O \rightleftharpoons I_2 \cdot H_2O \qquad (2)$$
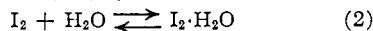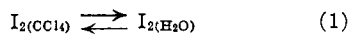
At low concentrations reaction 2 would lie far to the right. To calculate the exact effect of this reaction on the distribution coefficient, the equilibrium constant would have to be known. However, the effect of this reaction would be seen at all pH values, which corresponds to the data obtained. Secondly, the slow rise in activity of the aqueous phase with time could be caused by the following dissociation of the water–iodine complex.

$$I_2 \cdot H_2O \rightleftharpoons H_2OI^+ + I^-\qquad (3)$$

$$\begin{array}{ccc} & \downarrow\uparrow & + \\ & HOI & I_2 \\ & + & \downarrow\uparrow \\ & H^+ & I_3^- \end{array}$$

This equilibrium would be pH dependent due to the decomposition of H_2OI^+. Thus the equilibrium concentrations of HOI and I_3^- should decrease with a decrease in pH. This also is consistent with the data shown in Fig. 1.

The end products of the above reactions would be HOI and I_3^-. Since no iodate is found in the solutions, even after standing, apparently HOI is stable at these concentrations. The above mechanism would explain the gradual appearance of I_3^- and the increase in conductance with time in freshly prepared aqueous iodine solutions. A similar explanation has been given for the rise in conductance of iodine–pyridine solutions with time.[13],[14]

This mechanism is also consistent with the results obtained by Benesi and Hildebrand[15] in a study of iodine–acetone solutions. They found that I_3^- was formed immediately when iodine was added to acetone. After observing the behavior and characteristics of these solutions they concluded that the following reactions were occurring

$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \rightleftharpoons CH_3{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}CH_2 \qquad (4)$$

$$CH_3{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}CH_2 + I_2 \longrightarrow CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2I + I^- + H^+ \qquad (5)$$

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (6)$$

Equation 5 may be written stepwise to show complete analogy to eq. 3.

(13) L. F. Audrieth and E. J. Birr, THIS JOURNAL, **55**, 668 (1933).

(14) G. Kortüm and H. Wilski, Z. physik. Chem., **202**, 35 (1953).

(15) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **72**, 2273 (1950).

BATON ROUGE 3, LA.

Nuclear Magnetic Resonance Spectra of Some Perfluoroalkyl Derivatives of Sulfur Hexafluoride

BY NORBERT MULLER,[1] PAUL C. LAUTERBUR AND GEORGE F. SVATOS

High-resolution F^{19} NMR spectra have been obtained for several perfluoroalkyl derivatives of sulfur hexafluoride of the types R_FSF_5 and $(R_F)_2SF_4$. Indirect spin–spin coupling leads to an unusually complex resonance multiplet for the F^{19} nuclei of the $-SF_5$ group. Calculations show that the observed fine structure is consistent with the assumption that these fluorines form a square pyramid. The resonance of the $-SF_4-$ group is a single line if the C–S–C angle is near 180°, and a characteristic pair of triplets if the C–S–C angle is near 90°.

Introduction

Compounds of the types R_FSF_5 and $(R_F)_2SF_4$ give F^{19} NMR signals in two, well-separated regions. One of these contains the resonances of the fluorine nuclei in the perfluoroalkyl (R_F) radical, which may be used to identify this radical. The other contains the resonances of fluorine bonded to the sulfur atom. A study of the multiplet patterns in this S–F region constitutes an interesting application of the theory of indirect spin–spin coupling.[2-4] We made a detailed analysis of the multi-

(1) Department of Chemistry, Purdue University, Lafayette, Ind.

(2) E. L. Hahn and D. E. Maxwell, Phys. Rev., **88**, 1070 (1952).

(3) M. K. Banerjee, T. P. Das and A. K. Saha, Proc. Roy. Soc. (London), **226A**, 490 (1954).

(4) H. M. McConnell, A. D. McLean and C. A. Reilly, J. Chem. Phys., **23** 1152 (1955).

plet of the SF_5 group, using the method of reference 4; this required more precise calculations than the customary first-order approximation. The results are compatible with the supposition that the five fluorine atoms form a square pyramid. The pattern obtained for $-SF_4-$ groups was found to depend characteristically on whether the C–S–C angle is near 90° or near 180°.

Experimental

All materials used in these studies were prepared in these laboratories; methods of synthesis and purification are. being published elsewhere.[5] The absence of NMR signals other than those which can be accounted for on the basis of the structures assumed for the materials indicates that no more than a few per cent. of fluorine-containing impurities can have been present in any of the samples.

(5) F. W. Hoffmann, T. C. Simmons, et al., to be published.