The question of whether or not these peaks may be assigned to N–H–N bonding between the secondary pyrrole nitrogens and the tertiary nitrogens in these compounds arises from a consideration of the structures involved. It must be stated at once that infrared spectroscopy can only give evidence for *intra*molecular bonding when a set of absorption frequencies can be compared with those exhibited by like acceptors and donors in different molecules. On the other hand, *inter*molecular bonding between molecules of like or unlike species may be demonstrated conclusively by observing the effect of concentration changes in solution upon "bonded" or "unbonded" peaks. This criterion of course becomes inapplicable in testing for intramolecular bonding.

Since the absorption peaks in question differ markedly from the pyrrole N–H peak at 2.85 μ,[12] one is inclined to suggest that N–H–N bonding exists in these molecules. However, this is unproved as yet, since the character of the substituted pyrrole rings may have been changed in the formation of these compounds. This seems possible in light of the recent work on unbonded N–H frequencies.[18] Hence we can only state at present that the absorption peaks occur at frequencies which might be expected[12] if N–H–N bonding were existent in the porphin and dipyrrylmethene nuclei.

The authors wish to express their gratitude to Professors A. M. Buswell and W. H. Rodebush for use of the infrared apparatus and for timely suggestions.

Summary

1. The infrared absorption of two dipyrrylmethenes, the copper complex of one of them, etioporphyrin I, and etiohemin I chloride has been measured. Replacement of acidic hydrogens with metal atoms eliminated nitrogen–hydrogen absorption in the dipyrrylmethenes and in etioporphyrin I.

2. The possibility of N–H–N bonding in these compounds is discussed.

(12) A. M. Buswell, J. R. Downing and W. H. Rodebush, THIS JOURNAL, 61, 3252 (1939).

(13) A. M. Buswell, G. W. McMillan, W. H. Rodebush and F. T. Wall, *ibid.*, 61, 2809 (1939).

The Hydrolysis of Bromine. The Hydration of the Halogens. The Mechanism of Certain Halogen Reactions

BY HERMAN A. LIEBHAFSKY

Corrections.—Jones and Baeckstrom[1] and Liebhafsky[2] have independently established 5.8 (10^{-9}) as the value of K_1, the equilibrium constant of the bromine hydrolysis, at 25°. The temperature coefficients of this reaction (*cf.* Ref. 2, Table II, last column) are probably more accurately known than is K_1 at any temperature except 25°. For these reasons, it is especially desirable to correct a computational error that Professors R. H. Gillette and H. A. Young of the Division of Chemistry, University of California at Davis, have kindly called to my attention. Through some mischance, $11.9(10^{-9})$ at 35°, the result for Series 5, instead of $11.3(10^{-9})$, the result for Series 7 (*cf.* Ref. 2, Table II), was used in deriving an incorrect equation for K_1 as a function of temperature. A table and a conclusion in Ref. 2 consequently should be changed to read as follows.

(1) Jones and Baeckstrom, THIS JOURNAL, **56**, 1517 (1934).

(2) Liebhafsky, *ibid.*, **56**, 1500 (1934).

TABLE IV (Ref. 2)

SUMMARY OF BEST VALUES FOR $K_1 \times 10^{-9}$ AT DIFFERENT TEMPERATURES

	0°	10°	25°	30°	35°
Liebhafsky	0.69	1.76	5.8	8.2	11.3
Computed	.88	1.95	(5.8)[a]	8.14	(11.3)[a]
Selected[b]	.70	1.78	5.8	8.3	11.3

[a] Value assumed in deriving the equation log $K_1 = 0.6876 - 2660.3/T$ from which computed values were obtained. [b] Only these finally selected values for K_1 are expressed in activities. (Similar changes are to be made in Ref. 3, p. 95, Table I.)

Summary (Ref. 2)

4. The temperature variation of the K_1 for bromine is anomalous in the neighborhood of 10°; but the departure of $d(\log K_1)/d(1/T)$ from constancy is less pronounced than that observed by Jakowkin in the case of chlorine.

Also, the line "a. Measurements at 0° by Jones and Hartmann" has been omitted above the first row of data in Table III.

Hydration of the Halogens.—The temperature coefficients of halogen equilibria involving aqueous solutions are generally anomalous.[3]

Type of measurement	Chlorine	Bromine	Iodine
Equilibrium (distribution between air and H_2O)	$-$ 9,700 cal.	$-13,100$ cal.	$-11,800$ cal.
Equilibrium (hydrolysis of the halogen)	$-$ 9,900 cal.	$-14,300$ cal.	
Equilibrium (distribution between CCl_4 and H_2O)	$-10,700$ cal.		
Kinetic (see text below)		$-25,000$ cal.	$-22,800$ cal.

The calculated values[3] of the heats of hydration (Equilibrium 1) now are:

The new value for bromine is in good agreement with the other value derived from equilibrium data.

When the corresponding equilibrium constants are calculated in the usual manner—that is, by using (X_2), the concentration of free halogen in the aqueous solution—the log K_{X_2} vs. $1/T$ plot approaches a limiting straight line at higher temperatures but bends more and more sharply to the $1/T$ axis as $0°$ is approached. Figure 1 illustrates this behavior. While D', the distribution ratio of iodine between air and carbon tetrachloride, shows the orthodox temperature dependence, D, the distribution ratio between air and water, behaves anomalously.[4] This anomaly has found a reasonably satisfactory quantitative explanation in the assumption that the degree of hydration of the halogen is changing in the temperature region where the anomaly occurs; as $0°$ is approached, the equilibrium

$$U + (h - u) H_2O \rightleftarrows H \qquad (1)$$
$$(H) + (U) = (X_2)$$
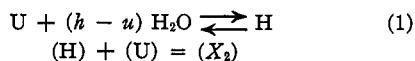
shifts so as to increase (H), the concentration of the more hydrated form. (The formula of U is $I_2 \cdot u H_2O$; that of H, $I_2 \cdot h H_2O$.) The correction of the above error tends to strengthen this explanation and has a bearing on the important problem of correlating kinetic and equilibrium data (cf. Ref. 3, p. 111). The data in Table 2d, Ref. 3, for the bromine hydrolysis should be:

d. For bromine from reaction 12 (cf. Table I)

T, °C.	35.0	25.0	10.0	0.0
$10^9 \times K_{Br_2}$ (measd.)	11.3	5.8	1.76	.69
d	($d = 0$ assumed)		0.045	.106
(H)/(U)			.109	.276

$d = \log K_{Br_2}$ (calcd.) $- \log K_{Br_2}$ (measd.)
$\log K_{Br_2}$ (calcd.) $= 0.6876 - 2660.3/T$
$\Delta H_{II_n} = -14300$ cal.

The difference between d for $0°$ from kinetic (0.21) and equilibrium data (new value, 0.11) is now cut virtually in half (cf. Ref. 3, p. 95, last paragraph).

(3) Liebhafsky, Chem. Rev., 17, 89 (1935).

(4) The data for aqueous solutions have been reproduced from Ref. 3, where the original sources are cited. D' has been obtained for each temperature by dividing the vapor pressure of iodine in mm. of mercury [Baxter and Grose, This Journal, 37, 1061 (1915)] by the solubility in mole fractions of iodine for that solvent [Hildebrand and Jenks, ibid., 42, 2180 (1920)].
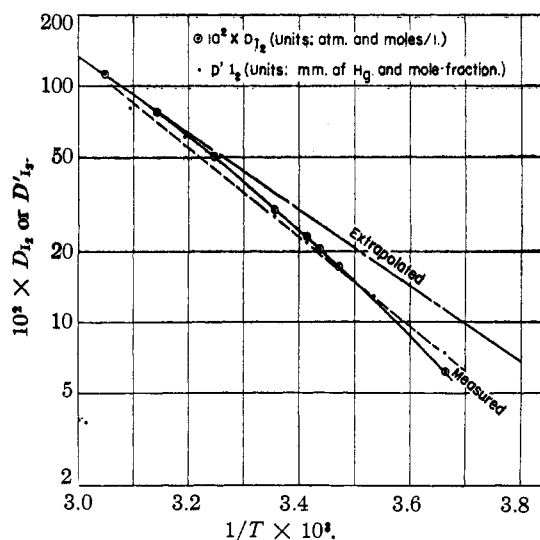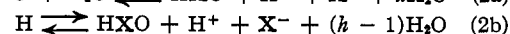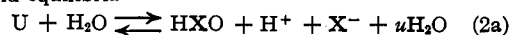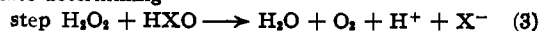
Fig. 1.—Distribution ratios for iodine between air and water (D, anomalous temperature coefficient), and between air and carbon tetrachloride (D', normal temperature coefficient). The plot is semi-logarithmic.

The specific rates at which hydrogen peroxide is oxidized by each of the three halogens, X_2, are the kinetic data from which heats of hydration were deduced. For bromine and iodine, these large (and, perhaps, unreasonably large) heats are obtained because the downward curvatures in the $1/T$ plots are more pronounced for the kinetic than for the equilibrium measurements. These unexplained minor inconsistencies should not be permitted to obscure the more important fact that for bromine and iodine both types of measurements reveal the existence of similar temperature coefficient anomalies. This fact indicates that the assumed mechanisms, which are of the type

Rapid equilibria
$$U + H_2O \rightleftarrows HXO + H^+ + X^- + uH_2O \quad (2a)$$
$$H \rightleftarrows HXO + H^+ + X^- + (h - 1)H_2O \quad (2b)$$
Rate-determining
step $$H_2O_2 + HXO \longrightarrow H_2O + O_2 + H^+ + X^- \quad (3)$$
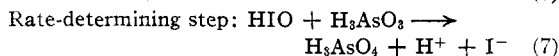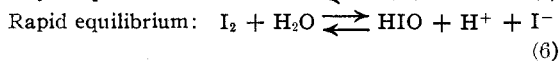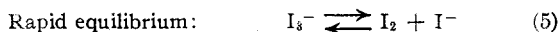are in the main correct, for mechanisms of this

type will reflect a change in the ratio (H)/(U) because such a change necessarily causes a change in the ratio (HXO)/(X₂).

The reaction between chlorine and hydrogen peroxide,[5] however, does not appear to proceed mainly by such a mechanism; for the kinetic data give a linear log k vs. $1/T$ plot from 0 to 25°. (The temperature coefficient of the chlorine hydrolysis equilibrium is nearly twice as great at 0° as at the higher temperature.[6]) This conclusion is strengthened greatly by the experimental fact that hypochlorous acid when mixed directly with hydrogen peroxide reacted at approximately one-millionth the rate to be expected from kinetic measurements on the chlorine–hydrogen peroxide reaction.[7] The difficulty has been thoroughly discussed by Makower, who presented this conclusion as a third alternative explanation; the evidence from other reactions[8] seems convincing enough to warrant rejection of the other two. To summarize: The rate of the chlorine–hydrogen peroxide reaction, unlike the rates of the corresponding bromine and iodine reactions, is unaffected by the shift from U to H which occurs when the temperature of an aqueous X₂ solution is lowered. The mechanism of this reaction must therefore differ from the mechanisms of the other two.

The Reaction between Arsenious Acid and Iodine.

—Roebuck's classical investigation[8a,b] of the reaction

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^- \quad (4)$$
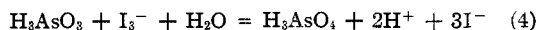
was the first complete experimental demonstration of the relation obtaining between chemical kinetics and chemical equilibrium. The mechanism for the forward reaction

Rapid equilibrium: $I_3^- \rightleftharpoons I_2 + I^-$ (5)

Rapid equilibrium: $I_2 + H_2O \rightleftharpoons HIO + H^+ + I^-$ (6)

Rate-determining step: $HIO + H_3AsO_3 \longrightarrow$
$$H_3AsO_4 + H^+ + I^- \quad (7)$$

does not appear to have been questioned seriously although the work of Makower and Liebhafsky[9] left little doubt that further verification was desirable. Since hypoiodous acid is so unstable that it can scarcely be treated directly with ar-

(5) Makower, THIS JOURNAL, **56**, 1315 (1934).

(6) Jakowkin, Z. physik. Chem., **29**, 613 (1899).

(7) Bray, Chem. Rev., **10**, 175 (1932).

(8) (a) Roebuck, J. Phys. Chem., **6**, 365 (1902), and (b) **9**, 727 (1905); (c) Liebhafsky, ibid., **35**, 1648 (1931); references to other work will be found in Ref. 8c.

(9) Makower and Liebhafsky, Trans. Faraday Soc., **29**, 597 (1933).

senious acid in the absence of iodine, this verification was sought in a study of the temperature coefficient of the forward reaction.

The following measurements were made in 1932 in the Chemical Laboratory of the University of California at Berkeley. Since the rate law of the forward reaction has been established, it sufficed to perform the experiments under conditions such that no concentration except that of total iodine changed greatly during the course of an experiment. Sodium iodide, sodium meta-arsenite and perchloric acid solutions were mixed, diluted and placed in a thermostat; the reaction was begun by adding sodium triiodide solution that was also at thermostat temperature. The rate was measured by rapidly titrating samples of the reaction mixture withdrawn from time to time, with 0.02 N sodium thiosulfate. The detailed data for Experiment 5 are given in Fig. 2, where the thiosulfate titer is plotted on semi-logarithmic paper against the time. The initial
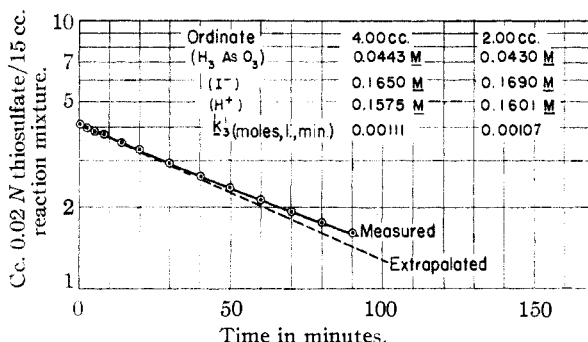

Fig. 2.—Detailed results for expt. 5 on the rate of reaction 4. The plot is semi-logarithmic.

concentrations for all experiments were nearly identical, except that the concentration of arsenious acid was cut in half for the experiments at the two highest temperatures. Under the concentration conditions chosen, the reaction is approximately first order; the deviations from straight lines in the log $\Sigma(I_2)$ vs. t plots were satisfactorily removed by correcting for the changes in (H^+), (I^-) and (H_3AsO_3) that occurred as the reaction proceeded. (The change in (H^+) caused by mixing meta-arsenite and perchloric acid was of course allowed for.) In other words, the rate law

$$-d(I_3^-)/dt = k_3' \frac{(I_3^-)}{(H^+)(I^-)^2} (H_3AsO_3) \quad (8)$$

was obeyed satisfactorily. The temperatures and results are summarized in Table I.

Comparison of the last two columns in Table I shows that here, as in the chlorine–hydrogen peroxide reaction, the logarithm of the specific rate is a linear function of $1/T$ to within the experimental error. Roebuck's[8c] value for k_3' at $0°$ in sulfuric acid solution is $9.4(10^{-4})$ (units: moles, liters, minutes); this result, when corrected for the decreased acid concentration due to the presence of HSO_4^-, is in good agreement with the Table I value.[10] Roebuck gives several values for the temperature coefficient of k_3' between 0 and $10°$; his highest value, 3.5,[8a] corresponds to a heat of activation $Q = +19,200$ cal.; his lowest, 3.17,[8b] to $+17,710$ cal., which is in fair agreement with $+16,970$ cal., the value from Table I.

TABLE I

TEMPERATURE COEFFICIENT DATA FOR THE ARSENIOUS
ACID–IODINE REACTION

Experiment	T, °K.	$10^4 \times k_3'$ (meas.)	$10^4 \times k_3'$ (calcd.)[a]
3	273.1	6.7	6.6
4	273.1	6.5	6.6
5	277.7	10.9	11.2
6	283.5	21.6	21.1
7	288.1	36	34
8	293.1	58	57

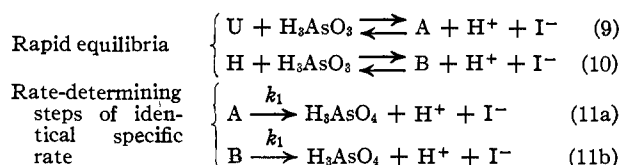[a] Calculated values from the equation $\log k_3' = 10.411 - (3710.0/T)$.

The magnitude of Q and its constancy (or near constancy) both suggest the necessity of revising the mechanism of the arsenious acid–iodine reaction. The heat of dissociation of triiodide ion $(+4320$ cal.)[8c] and the heat of hydrolysis of iodine $(+22,700$ cal.)[8c] must both be included in Q if the accepted mechanism is correct; on this basis the heat of activation for the rate-determining step between hypoiodous and arsenious acids would have a *negative* heat of activation of 10,000 cal. When Roebuck's work was reexamined some years ago,[8c] it was not known that a constant Q was in conflict with most of the data for aqueous halogen solutions[3]; as it now appears, the previous conclusion[11] that the rate-determining step has a negative temperature coefficient must be rejected, and the mechanism for the arsenious acid–iodine reaction revised.

The revised mechanism must meet the requirement that the rate at all temperatures be inde-

pendent of the ratio (H)/(U). Perhaps the simplest mechanism that can be devised to meet this requirement is

Rapid equilibria
$$\begin{cases} U + H_3AsO_3 \rightleftarrows A + H^+ + I^- & (9) \\ H + H_3AsO_3 \rightleftarrows B + H^+ + I^- & (10) \end{cases}$$

Rate-determining steps of identical specific rate
$$\begin{cases} A \xrightarrow{k_1} H_3AsO_4 + H^+ + I^- & (11a) \\ B \xrightarrow{k_1} H_3AsO_4 + H^+ + I^- & (11b) \end{cases}$$

The device of having A and B decompose at the same (or nearly the same) specific rate is saved from being an obvious artifice by the fact that these two intermediate products differ only in the degree of hydration. An analogous mechanism would eliminate the conflict between equilibrium and kinetic data for the chlorine–hydrogen peroxide reaction.

A detailed discussion of the arguments for and against this mechanism is scarcely warranted. Accurate measurements of the equilibrium constant for the iodine hydrolysis over the temperature range in question would be more valuable than such a discussion; but these data, especially for the lower temperatures, will be difficult to obtain. The existence of accurate hydrolysis equilibrium measurements for the analogous chlorine–hydrogen peroxide reaction to some extent compensates this difficulty.

It may be pointed out, finally, that the equilibrium constant of a halogen reaction could, if heat capacity terms are ignored, be a linear function of $1/T$. This linearity will result if the forward (reverse) reaction has a mechanism like that outlined for the arsenious acid, while the reverse (forward) reaction proceeds by a mechanism whose temperature coefficient is normal. The triiodide equilibrium (Reaction 5) appears to be one case of this kind, and Equilibrium 4 another. Further experimental work to test these ideas is highly desirable.

Light Absorption by Iodine Solutions.—The General Electric recording spectrophotometer[12] was used to establish whether a characteristic change in the absorption of visible light accompanied the change in the hydration of iodine between 0 and $75°$. For purposes of comparison, carbon tetrachloride solutions were also investigated at different temperatures. The ease with which iodine volatilizes from aqueous solutions is well known; this difficulty was minimized by filling the cell (5.15 cm. long) with the warm or

(10) (a) The dissociation constant at 25° of HSO_4^- in concentration units for the above reaction mixtures is near 0.03: Noyes and Sherrill, THIS JOURNAL, **48**, 186 (1926). (b) The corresponding heat of dissociation is small; Hamer, *ibid.*, **56**, 860 (1934).

(11) (a) Ref. 8c; (b) *cf.* also, Moelwyn-Hughes, "Kinetics of Reactions in Solution," Clarendon Press, Oxford, 1933, p. 207.

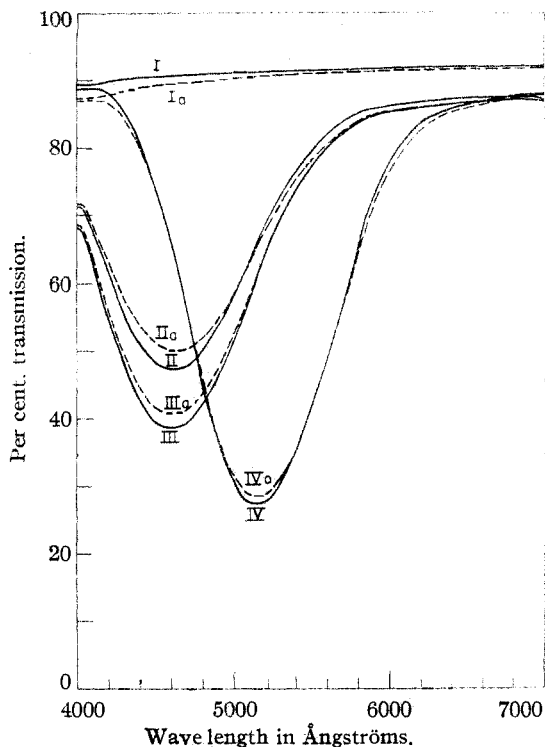(12) Michaelson and Liebhafsky, *Gen. Elec. Rev.*, **39**, 445 (1936).

Fig. 3.—Effect of temperature change on the absorption of visible light by iodine solutions:

Curve	Solvent	Moles I_2/l.	T, °C.
I	CCl_4	None	25
Ia	CCl_4	None	50
II	H_2O	6×10^{-5}	24
IIa	H_2O	6×10^{-5}	76
III	H_2O	9×10^{-5}	0.3
IIIa	H_2O	9×10^{-5}	24
IV	CCl_4	9.5×10^{-5}	25
IVa	CCl_4	9.5×10^{-5}	51

cold solution, tracing its transmission curve (less than three minutes is required), and permitting the covered cell to stand until its contents reached room temperature, when the transmission was again measured. Some of the curves obtained are shown in Fig. 3; that the effect of changing temperature on the water-filled cell is very small is obvious from the uppermost curves in Fig. 4.

Figure 1 shows clearly that aqueous iodine solutions show anomalous temperature coefficients while carbon tetrachloride solutions do not; Fig. 3 shows that changing temperature affects light absorption by both solutions almost identically when the change in the absorption by carbon tetrachloride itself is allowed for. It follows, therefore, that the change in hydration presumably responsible for the curvature in Fig. 1 cannot be detected on the spectrophotometer, and that U is itself hydrated. The noticeable displace-

ment toward longer wave lengths of Curve IIa, Fig. 3, indicates that the complete dehydration of iodine is beginning at 76°.
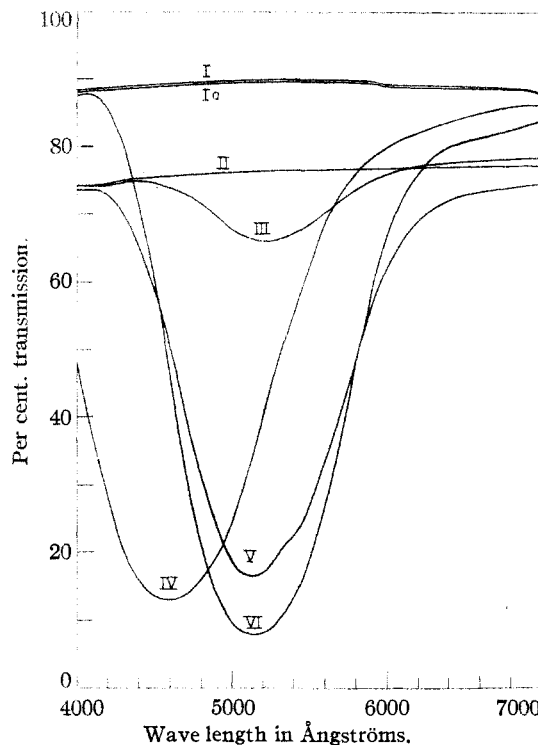

Fig. 4.—Absorption of visible light by gaseous and dissolved iodine:

Curve	Solvent	Moles I_2/l.	T, °C.
I	H_2O	None	25
Ia	H_2O	None	50
II	Air	None	25
III	Air	1.6×10^{-5}	25
IV	H_2O	2.36×10^{-4}	25
V	Air	Unknown	25
VI	CCl_4	2.39×10^{-4}	25

The small decrease in absorption with increasing temperature shown in Fig. 3 doubtless results from the concomitant increase in the number of iodine molecules in the first vibrational level, an explanation that Gibson, Rice and Bayliss[13] have shown to be quantitatively satisfactory in the case of gaseous chlorine. The fact that this decrease occurs to about the same extent for aqueous as for carbon tetrachloride solutions indicates that light absorption leads to comparable processes in both kinds of solutions, even though water probably forms definite solvates with iodine and carbon tetrachloride does not.

The failure of the spectrophotometer to detect the shift from U to H (which, according to results

(13) (a) Gibson and Bayliss, *Phys. Rev.*, **44**, 188 (1933); (b) Gibson, Rice and Bayliss, *ibid.*, p. 193.

given above, involves some 10,000 cal. at least) suggested that transmission curves be obtained for iodine vapor.[14] The vapor was generated by heating the quartz cell, into which a crystal of iodine had been placed, so that the ends remained hotter than the other portions. The room temperature curve was obtained after the cell had cooled; the corresponding concentration of iodine was calculated from its vapor pressure.[4] The data derived from the various curves in Fig. 4 are $(\log I_0/I = \epsilon \times 1 \times \text{moles/liter})$:

Source	Solvent	$\lambda_{max.}$, Å.	$\epsilon_{max.}$	Width, W, at $\epsilon = \frac{1}{2}\epsilon_{max.}$, Å.	Product $W \times \epsilon_{max.}$, Å.
Curve V	Air	5120	..	860	..
Curve III	Air	5200	810	850	69(10⁴)
Curve VI	CCl₄	5140	870	860	75(10⁴)
Curve IV	H₂O	4600	690	1010	70(10⁴)
Ref 14	Inert gases	5200	830	880	73(10⁴)

Although the work was done with reasonable care, extreme accuracy is not claimed for the $\epsilon_{max.}$ values; relative ϵ values and the positions of the absorption maxima are more reliable. A detailed comparison with the large amount of earlier work is not feasible—among other things, because the effects of differences in cell thickness and in concentration would have to be known. The parameters in the last two columns are given in an effort to describe the curves without listing the individual ϵ values. The product in the last column should be approximately proportional to the area under the curve, and its departure from constancy may be a partial measure of solvent influence.

The data from Curve III are obviously in good agreement with those derived from the "limiting" curve of Rabinowitsch and Wood.[14] In Curve V, the limiting conditions are probably not quite reached because of the higher pressure of iodine vapor; the slight "hump" near 5400 Å. results, as they have pointed out, from the superposition on the main band series of the series due to the first vibrational state. They state: "It is noteworthy that these humps appear in *solutions* of Br₂ and I₂ as well, showing that the vibrational quanta of these molecules are not strongly affected by dissolution in carbon tetrachloride and similar solvents." The spectrophotometric curves, published and unpublished, obtained in this Laboratory for iodine–carbon tetrachloride solutions do

not support this conclusion since they do not show the "hump" in question. A small spectroscope that resolved the bands of iodine vapor showed no structure whatever in the absorption by a carbon tetrachloride solution. This empirical evidence of how completely the interaction of solvent with solute molecules modifies quantum restrictions could not, of course, have been obtained with the spectrophotometer, which has a slit width of 100 Å.

Figure 1 shows that approximately 9000 cal./ mole is evolved when an infinitesimal amount of iodine vapor is dissolved in a saturated carbon tetrachloride solution. The spectrophotometric curves for vapor and solution are virtually identical, except that the solution shows a somewhat higher transition probability (higher value of $\epsilon_{max.}$ and of the product $W \times \epsilon_{max.}$).[15] The failure of the spectrophotometer to reflect the interaction of carbon tetrachloride with iodine makes its failure to detect the shift from U to H seem less serious.

The following differences in visible light absorption exist between solutions of iodine in carbon tetrachloride (in which there are no definite solvates) and solutions in water (in which definite hydrates are present): the absorption maximum in water 5–600 Å. further toward the violet; $\epsilon_{max.}$ is smaller; the absorption curve is broader (the product $W \times \epsilon_{max.}$, however, is approximately the same for both solutions). It is probable that these differences result from the formation of definite iodine–solvent compounds, but how and why is uncertain. Further work is necessary.

Summary

Certain corrections of earlier work on the bromine hydrolysis have strengthened the case for the hypothesis that the anomalous temperature coefficients associated with aqueous halogen solutions result from shifts in the hydration equilibria.

Temperature coefficient data for the arsenious acid–iodine reaction have been given.

Evidence against the conventional mechanisms

(14) Rabinowitsch and Wood, *Trans. Faraday Soc.*, **32**, 540 (1936). Professor H. Sponer kindly called this valuable paper to the author's attention after his own experimental work was completed.

(15) Rabinowitsch and Wood[14] hold a weakening of the selection rules by the electric fields of the solvent molecules responsible for the increase in transition probability. If this explanation and the work of Groh and Papp [*Z. physik. Chem.*, **A149**, 153 (1930)] are correct, the order of increasing influence by these electric fields for several solvents is carbon tetrachloride, hexane, carbon bisulfide, with only small differences among the three. Moreover, if water has a similar effect, this effect must be masked by others as the table above shows. The data for chlorine, which should show the effect most strongly, are worth consulting in this connection (*cf.* Fergusson, Slotin and Style, *Trans. Faraday Soc.*, **32**, 956 (1936), Fig. 2).

for this and the chlorine–hydrogen peroxide reaction seems strong enough to warrant their revision. One such revision has been carried out.

Anomalies in the temperature coefficients of processes in aqueous iodine solutions find no counterpart in the absorption of visible light by these solutions. Gaseous iodine in air and iodine dissolved in carbon tetrachloride are virtually indistinguishable with a spectrophotometer. Aqueous iodine solutions differ from them in three spectrophotometrically measurable ways.

SCHENECTADY, N. Y.   RECEIVED AUGUST 19, 1939

Thermal and Photochemical Exchange Reactions of Bromine

BY J. NORTON WILSON AND ROSCOE G. DICKINSON

Several reactions involving exchange of bromine atoms between elementary bromine and bromine compounds in carbon tetrachloride solutions have been investigated in this Laboratory with the use of radioactive bromine. The results obtained from the study of the thermal reactions between bromine and arsenious bromide, stannic bromide, ethylene bromide, and trichlorobromomethane and the photochemical reaction between bromine and trichlorobromomethane are here described.

Experimental Method.—The thermal exchanges were investigated in general as follows. A solution of radioactive bromine in carbon tetrachloride was divided into two portions: the bromine was extracted from one of these portions and converted to silver bromide for electroscopic measurements; the other portion of the solution was mixed with a solution of the bromine compound to be investigated, and the mixture, hereafter referred to as the reaction mixture, was kept at a definite temperature for a convenient time; a precipitate of silver bromide was then prepared from either the bromine or the bromine compound in the mixture. The extent of exchange was then calculated from the known composition of the reaction mixture and the relative electroscopic activities of the two silver bromide precipitates, and is reported here as percentage of complete exchange. The electroscopic measurements were made by a method described elsewhere.[1]

The method used to prepare the dilute highly radioactive solutions of bromine used in the photochemical experiments may be of interest: a small amount of highly radioactive sodium bromide was prepared by the method of Erbacher and Philipp[2] from a large amount of ethylene bromide which had been exposed to slow neutrons from a radon–beryllium source. The sodium bromide, dissolved in a small amount of water, was shaken with a dilute solution of bromine in carbon tetrachloride. As was expected from the known rapidity of the exchange between bromine and bromide ion in aqueous solution,[3] exchange was rapid; the resulting solution of radioactive bromine was dried with phosphorus pentoxide, distilled and diluted to the desired concentration with carbon tetrachloride.

Experiments with Stannic and Arsenious Bromides.—The reaction mixtures were subjected immediately after mixing to vacuum distillation at 25° to remove bromine. The residue of metallic bromide was then hydrolyzed and the resulting bromide ion was precipitated as silver bromide for radioactivity measurements. Exchange was apparently complete with solutions containing 4 mole per cent. of bromine and 2 mole per cent. of either metallic bromide. Since the extent of exchange was calculated on the basis of the initial composition of the solution, exchange was probably completed before an appreciable fraction of the bromine had distilled away, i. e., within about ten minutes. The time elapsing between the initial mixing of the solutions and the conclusion of the distillation was about thirty minutes.

Experiments with Ethylene Bromide.—The reaction mixtures were sealed in glass ampoules and kept in the dark at the desired temperature for a convenient time; the bromine was then extracted with sodium nitrite solution and converted to silver bromide. No exchange beyond the limits of experimental error was detected in a solution of the composition 24 mole per cent. Br_2, 28 mole per cent. $C_2H_4Br_2$, which was kept at 100° for sixty-five minutes. Experiments using lower concentrations and temperatures similarly indicated no exchange. In no experiment was the apparent extent of exchange greater than 3%; this value is less than the estimated experimental error.

Experiments with Trichlorobromomethane.—The thermal reactions were carried out similarly to those involving ethylene bromide. At concentrations of approximately 0.3 moles of bromine and 1 mole of CCl_3Br per liter, the apparent extents of exchange observed in solutions kept for four minutes at 25°, forty minutes at 95° and fifty minutes at 115° were, respectively, −5, 7 and 9%. These measurements are obviously uncertain by at least 5% of

(1) Wilson and Dickinson, THIS JOURNAL, **59**, 1358 (1937).
(2) Erbacher and Philipp, Z. physik. Chem., **A176**, 169 (1936).
(3) Roginskii and Gopshtein, Physik. Z. Sowjetunion, **7**, 672 (1935).