ferences between the constants for the six- and seven-membered rings may not be significant. We have examined our results *in* terms of the variations of bond order in five-, six- and seven-membered aromatic rings but have been unable to find any definite correlation.

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Rhodamine B Equilibria

BY R. W. RAMETTE[1] AND E. B. SANDELL

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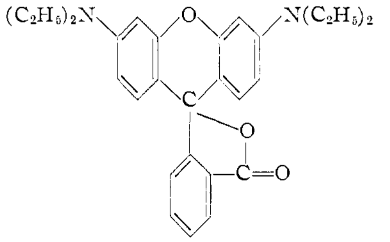
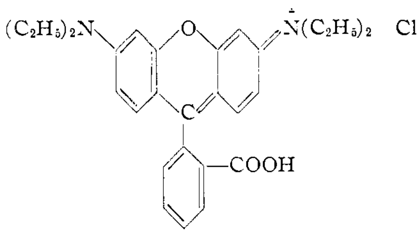
An investigation of rhodamine B (R) equilibria included a benzene extraction study, measurement of solubility of R salts and a spectrophotometric study in aqueous solution. The colorless lactone form (R°) undergoes a separation of charges in polar solvents to form an intensely colored violet zwitterion (R^{+-}). R^{+-} can add a proton to the carboxyl group formed by the opening of the lactone ring, giving RH^+ which has nearly the same absorption spectrum as R^{+-}. Addition of a second proton, probably to one of the nitrogen atoms, yields an orange species RH_2^{++}. A third proton gives RH_3^{+++}, which is yellow. The color changes are explained in terms of canonical structures. The cations are capable of interaction with anions such as chloride, bromide and perchlorate in solution to form ion pairs having the same absorption spectra as the free cations. In addition, R^{+-} and ion pairs containing RH^+ or RH_2^{++} undergo dimerization as the concentration is increased, causing an apparent deviation from Beer's law. Most of the equilibrium constants were determined.

The preparation, purification and chemical structure of rhodamine B (C.I. 749) were reported by Noelting and Dziewonski.[2] They concluded that the two principal forms of the dye were the lactone (R°)



and a salt form (RHCl)



The present work shows that several other forms exist in solution in equilibrium.

Apparatus.—Qualitative studies of absorption spectra were made with a Cary Model 11 Recording Spectrophotometer. Special adapters were machined to permit the use of rectangular cells. Quantitative measurements of absorbance were made with a Beckman Model B spectrophotometer. The 10 cm. cells were cylindrical with silica windows. The 1 cm. cells were Pyrex. Also used were Beckman cell-spacers, which are 9 mm. blocks of quartz designed to reduce the light path of 1 cm. cells to 1 mm. They are supplied with two polished sides, the other sides and bottom being ground. It was found that the ground sides strongly adsorbed rhodamine B from solution, causing erratic results. To eliminate this difficulty the rough sides were polished. A mechanical shaker was used to establish equilibrium in the two-phase systems. A Beckman Model H *p*H meter was used for *p*H measurements.

Reagents.—Rhodamine B chloride was purified by adding slowly, with stirring, about ten volumes of anhydrous ether to a saturated solution of the dye in absolute ethanol. The salt precipitated in the form of golden-green flakes. The process was repeated and the filtered solid was washed with ether and air-dried. The absorptivity of the purified dye in an ammonia–ammonium chloride buffer, the procedure proposed by Dolinski[3] for analysis of commercial preparations of the dye, was about 5% greater than that of the original. Amperometric titration of chloride with silver nitrate, using a rotated platinum electrode, indicated a purity of 99%.

Rhodamine B bromide was prepared by addition of 2 *M* potassium bromide to a saturated solution of the chloride in water. It was purified in the same manner as the chloride.

Rhodamine B perchlorate was prepared analogously. All three salts were of similar appearance except that the particles of the perchlorate tended to be much smaller because of its very low solubility.

All other chemicals were reagent grade.

Qualitative Spectrophotometric Study.—Figure 1 shows the absorption spectra of very dilute solutions of the dye as a function of acidity. It is seen that there are four distinct species in aqueous solution. Curve 1 is the spectrum of the violet form used by Dolinski and is representative of solutions having *p*H values from 13 to 4. Curve 2 is virtually identical to curve 1, except that there has been a 3 mμ shift toward longer wave lengths. This slight change is not observable visually. The species responsible for this spectrum is the principal one in the *p*H range from 3 to 1. Curve 3 is the spectrum of an orange form which is the main constituent in solutions of *p*H 0 to −1. Curve 4 is characteristic of a yellow form fully present only in concentrated sulfuric or perchloric acid, and virtually absent in aqueous solutions of less than 6 *M* acidity. Curve 5 is the spectrum of a colorless benzene solution of the dye, prepared by extraction of a neutral water solution.

Curves 1–3 change shape when the concentration of the dye is increased. Figure 2 shows this concentration effect for solutions of *p*H 8 and −0.6 corresponding to curves 1 and 3 of Fig. 1. The effect on curve 2 of Fig. 1 is very similar to that shown in Fig. 2 for *p*H 8.

Discussion

The qualitative observations, coupled with the quantitative results to be described, lead to the fol-

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[1] Carleton College, Northfield, Minnesota. From the Ph.D. thesis of R. W. Ramette, 1954.

[2] E. Noelting and K. Dziewonski, *Ber.*, **38**, 3516 (1905).

[3] M. Dolinski, *J. Assoc. Offic. Agr. Chem.*, **32**, 130 (1949).

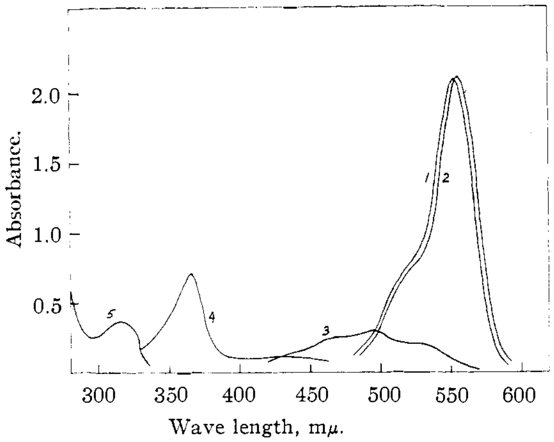
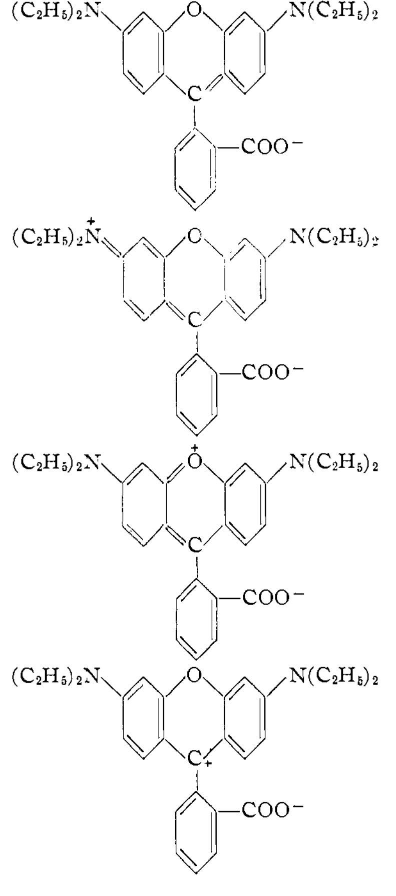


Fig. 1.—Absorption spectra of dilute solutions of rhodamine B, $C = 1.0 \times 10^{-5}$ M; cell path = 2.00 cm. Curve 1, 1.0 M KCl, 0.03 M NH_3; curve 2, 1.0 M KCl, 4×10^{-3} M HCl; curve 3, 5.0 M HCl; curve 4, concd. H_2SO_4; curve 5, benzene.

lowing interpretation. The colorless benzene and ether solutions of the dye in equilibrium with aqueous phases contain the lactone form R°. Little or no color would be expected since only benzenoid rings are present. In a polar solvent such as alcohol, acetone or water the R° molecule has an overwhelming tendency to open the lactone ring with a resulting separation of charges, forming a zwitterion R^{+-}. The structure is a resonance hybrid with properties of the following extreme structures



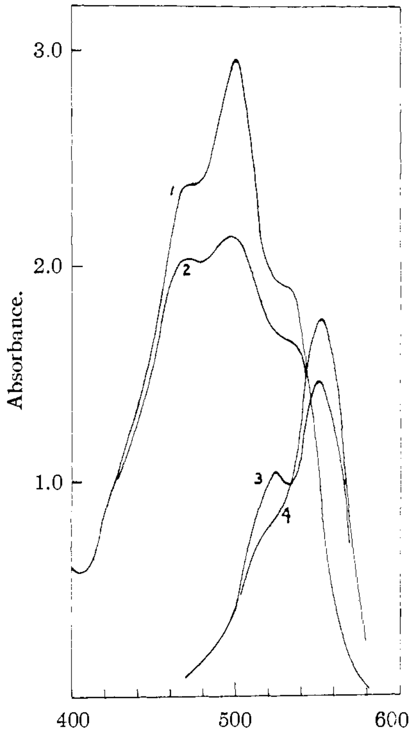
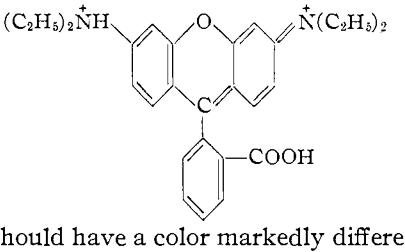


Fig. 2.—Absorption spectra of rhodamine B as a function of concentration: curve 1, 4 M HCl, $C = 2 \cdot 10^{-5}$ M, cell path = 10.0 cm.; curve 2, 4 M HCl, $C = 2 \cdot 10^{-3}$ M, cell path = 0.1 cm.; curve 3, pH 8, NH_3-NH_4Cl buffer, $C = 2.0 \cdot 10^{-4}$ M, cell path = 0.1 cm.; curve 4, pH 8, NH_3-NH_4Cl buffer, $C = 2.0 \cdot 10^{-5}$ M, cell path = 1.00 cm.

This is the violet form which yields curve 1 of Fig. 1. In view of the resonance possibilities, an intense color would be expected, and indeed the molar absorptivity is found to be 1.1×10^5. The stability associated with resonance explains the absence of the lactone form in water.

The carboxyl anion of R^{+-} takes on a proton when the pH is lowered to about 3. The structure of the resulting RH^+ may be written in the same extreme forms as the zwitterion, except for the carboxyl group. It seems reasonable to assign the 3 mμ shift of the spectrum to the presence of the proton on this group.

As the acidity of the solution is increased another proton adds to the cation, probably on one of the amine nitrogens, resulting in the following structure (one extreme hybrid form)



RH_2^{++} should have a color markedly different from that of RH^+ since the second proton blocks resonance in one ring. Curve 3 of Fig. 1 is the spectrum of this orange form. The yellow color of concentrated sulfuric acid solutions is due to the addition of a third proton, probably to the second nitrogen, forming RH_3^{+++}.

The dye cations have a rather strong tendency to interact with whatever anions are present in solution, forming ion pairs and triplets such as RHCl, RH_2Cl^+ and RH_2Cl_2. The effect of concentration on the spectra is explained by the interaction of the ion pairs and ion triplets to form dimers, probably by electrostatic and van der Waals forces.

The various forms of rhodamine B and some of their properties are summarized in Table I.

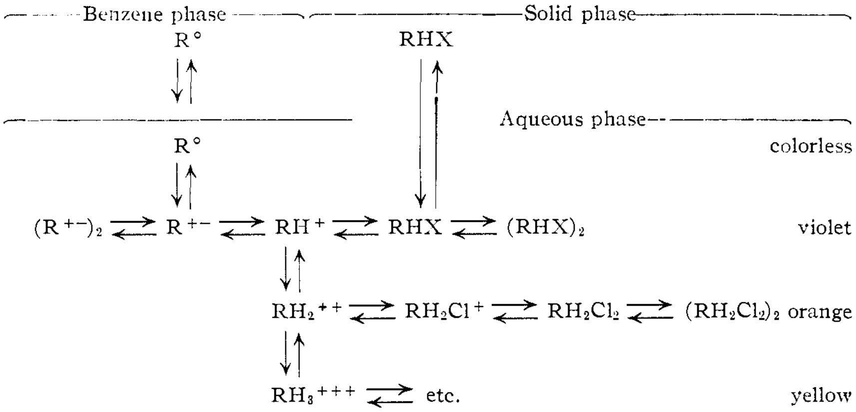
TABLE I

SPECIES OF RHODAMINE B

Symbol	Color	Absorption max. (mμ)	Absorptivity (max.)	pH range	Fluorescence (Hg lamp)
R^0	None	316	1.8×10^4	...	Weak blue
R^{+-}	Violet	553	1.1×10^5	>3	Strong yellow
RH^+	Violet	556	1.1×10^5	3-1	Strong yellow
RH_2^{++}	Orange	494	1.5×10^4	0 to −1	Weak yellow[a]
RH_3^{+++}	Yellow	366	3.6×10^4	<−1	None
$(R^{+-})_2$	Violet	520			
$(RHX)_2$	Violet	520			
$(RH_2X_2)_2$	Orange	..			

[a] Unless due to a very small amount of RH^+.

The equilibrium system may be represented by the diagram



The equilibrium constants are defined in terms of concentration since the ionic strength was held constant at 1.00 M except in one experiment reported in the spectrophotometric section. The constants are

$$\begin{aligned}
D &= [R^\circ]_{C_6H_6}/[R^\circ]_{H_2O} & K_5 &= [RH^+][H^+]/[RH_2^{++}] \\
Z &= [R^{+-}]/[R^\circ]_{H_2O} & K_6 &= [RH_2^{++}][X^-]/[RH_2X^+] \\
K_1 &= [R^{+-}]^2/[(R^{+-})_2] & K_7 &= [RH_2X^+][X^-]/[RH_2X_2] \\
K_2 &= [R^{+-}][H^+]/[RH^+] & K_8 &= [RH_2X_2]^2/[(RH_2X_2)_2] \\
K_3 &= [RH^+][X^-]/[RHX] & K_9 &= [RH_2^{++}][H^+]/[RH_3^{+++}] \\
K_4 &= [RHX]^2/[(RHX)_2] & &
\end{aligned}$$

Since the yellow form RH_3^{+++} is absent in solutions of acidity lower than 6 M, K_9 is large. No effort was made to evaluate this constant and from now on the yellow forms will not be considered as part of the equilibrium system.

Benzene Extraction Study.—A benzene phase in equilibrium with an aqueous solution of rhodamine B will contain only the lactone R°. The composition of the aqueous phase depends upon the pH, the dye concentration, and the concentration and nature of the anion present. The extraction coefficient is defined as the ratio of the molarity of the lactone in the benzene phase to the total molarity of all species present in the aqueous phase. In the experiment to be described, the concentration in the aqueous phase was so small (max. = 5×10^{-5} M) that the dimers may be considered absent. Also, the acidity was always less than 0.006 M so that the orange forms (RH_2^{++} and ion pairs) are not present to an appreciable extent. Thus, the aqueous phase contains only R^{+-}, RH^+ and RHCl. The extraction coefficient is accordingly written as

$$E = [R^\circ]_{C_6H_6}/\{[R^{+-}] + [RH^+] + [RHCl]\}$$

The various equilibrium constants are introduced into this expression, and the result is written in an inverted form

$$1/E = Z/D + \{Z[H^+](1 + [Cl^-]/K_3)\}/DK_2$$

Both Z and D are extremely large and cannot be determined. The extraction experiment gives a value for the quotient, and the symbol D' will be used to represent D/Z. Also, no method was devised to determine K_3 in 1 M chloride solutions. Therefore in such solutions it is necessary to define a mixed constant, K_2', equal to $K_2/(1 + [Cl^-]/K_3)$. Thus the above expression may be rewritten as

$$1/E = 1/D' + [H^+]/D'K_2'$$

A plot of $1/E$ *versus* $[H^+]$ should therefore be linear with an intercept of $1/D'$ and a slope of $1/D'K_2'$.

The extraction coefficient was determined as a function of acidity as follows: benzene solutions of the lactone (R°), prepared by extraction of a pure water solution of the dye chloride, were shaken mechanically for 30 minutes with solutions of hydrochloric acid and potassium chloride having a total chloride concentration of 1.00 M and acidities ranging from 1 to 6×10^{-3} M. The aqueous phase was analyzed by making it 5 M in hydrochloric acid and measuring the absorbance at 494 mμ. Beer's law is obeyed by the orange forms of the dye up to at least 1×10^{-3} M. The concentration of dye in the benzene was found similarly after evaporation. The ratio of the measured absorbances, corrected for dilution, is the extraction coefficient E. The determinations of E were made for two different concentrations of dye (5×10^{-3} and 1.0×10^{-2} M in the benzene phase).

The intercept gives an approximate value of 4×10^3 for D', and the slope of 0.83 allows calculation of the value 3×10^{-4} for K_2'. Since the intercept is not very precise, these values for D' and K_2' are only approximate. However, the slope gives a reliable value for the product $D'K_2'$, namely, 1.20 In the spectrophotometric study (*vide infra*) K_2' was determined directly and found to be 4.3×10^{-4}. Hence, a good value for D' can be calculated, and this is found to be 2.8×10^3.

Solubility Study.—Since aqueous solutions of relatively high acidity in equilibrium with solid rhodamine B salts do not contain an appreciable amount of R^{+-} and the tendency for ion pair formation is large, the assumption may be made that R^{+-}, RH^+, RH_2^{++} and RH_2Cl^+ are not present at

TABLE II

CONSTANTS OBTAINED FROM SOLUBILITY STUDY

Salt	a	b	c	a/b	$2b^2/c = K_8$
Chloride	2×10^{-4}	7.65×10^{-4}	1.47×10^{-3}	0.26	8.0×10^{-4}
Bromide	4×10^{-5}	1.5×10^{-4}	5.3×10^{-4}	.27	8.5×10^{-5}
Perchlorate	3.5×10^{-7}	3.3×10^{-6}	5.4×10^{-6}	.11	4.0×10^{-6}

an anion concentration of 1 *M*.[4] The solubility then is given by

$$S = [\mathrm{RHX}]_s + 2[(\mathrm{RHX})_2] + [\mathrm{RH_2X_2}] + 2[(\mathrm{RH_2X_2})_2]$$

The subscript s refers to the saturation value for the concentration of RHX. Introduction of the appropriate equilibrium constants gives (since $[\mathrm{X}^-] = 1$)

$$S = [\mathrm{RHX}]_s + 2[\mathrm{RHX}]_s^2/K_4 + [\mathrm{H}^+][\mathrm{RHX}]_s K_3/K_5K_6K_7 + \frac{2[\mathrm{H}^+]^2\{[\mathrm{RHX}]_s K_3/K_5K_6K_7\}^2}{K_8}$$

This equation is of the form: $S = a + b[\mathrm{H}^+] + c[\mathrm{H}^+]^2$. If the plot of S *versus* $[\mathrm{H}^+]$ is extrapolated to the point where $[\mathrm{H}^+]$ approaches zero, the intercept will be the constant a. Then a plot of the quantity $(S - a)/[\mathrm{H}^+]$ *versus* $[\mathrm{H}^+]$ can be made. This should be linear with the constant b as intercept and the constant c as slope. Once the constants are known, certain relationships can be found. One of these is given by the ratio of a to b

$$a/b = \frac{\{1 + 2[\mathrm{RHX}]_s/K_4\}K_5K_6K_7}{K_3}$$

Except for the term $2[\mathrm{RHX}]_5/K_4$, referring to the dimerization of RHX, this quantity is the same as that defined as K_5' in the spectrophotometric study. A second derived relationship is given by the quantity $2b^2/c$, which is numerically equal to K_8, the constant for the dissociation of the orange dimer $(\mathrm{RH_2X_2})_2$.

The solubility of rhodamine B chloride was determined in solutions of potassium chloride and hydrochloric acid having a total chloride concentration of 1.00 *M* and acid concentrations ranging from 0.100 to 1.00 *M*. An excess of the salt was shaken mechanically with the solution for one hour at 25°. The total dye concentration was found by making the centrifugate 5 *M* in hydrochloric acid and measuring the absorbance at 494 mμ. The solubility of the bromide salt was found similarly in solutions of potassium bromide and hydrobromic acid. The solubility of the perchlorate was so small that the more sensitive method of Dolinski[4] was used to determine the dissolved dye.

Figure 3 shows the variation of solubility with acidity for the three salts. Linear plots of $(S - a)/[\mathrm{H}^+]$ *versus* $[\mathrm{H}^+]$ were obtained for each case. Table II gives the values obtained for the various constants.

The calculation of the dimer dissociation constants, K_8, is of special interest because no direct method could be devised for this constant. It is especially noteworthy that K_8 is markedly dependent upon the particular anion, *e.g.*, there is a factor of 200 between the chloride and perchlorate values. If the dimerization were actually between ions, as proposed for thionine and methylene blue by Rabinowitch and Epstein,[5] *i.e.*

$$2\mathrm{RH_2}^{++} = (\mathrm{RH_2}^{++})_2$$

the constants K_8 should not differ so greatly because the ionic strength was the same in each case. Therefore it seems reasonable to assume that the dimerization takes place between the ion triplet forms, $\mathrm{RH_2X_2}$.

Quantitative Spectrophotometric Study.—Figure 4 shows the absorption spectra of very dilute solutions of rhodamine B as a function of acidity in 0.1 to 5.5 *M* hydrochloric acid. At these acidities essentially no zwitterion is present, and because of the low concentrations the dimers may also be considered absent. Thus, the equilibrium is between the violet monomers RH^+ and RHX, and the orange monomers $\mathrm{RH_2}^{++}$, $\mathrm{RH_2X}^+$ and $\mathrm{RH_2X_2}$. Since the anion concentration was maintained constant at 1 *M* in the determination of the equilibrium constants there was always a constant ratio between the cations and "neutral" forms. It is shown later that K_3 is small. If it is assumed that K_6 and K_7 are also small, *i.e.*, that there is a large tendency toward ion pair and triplet formation, then the equilibrium discussed here may be considered to exist between the violet ion pair RHX, and the orange ion triplet $\mathrm{RH_2X_2}$. The equilibrium constant will be called K_5'

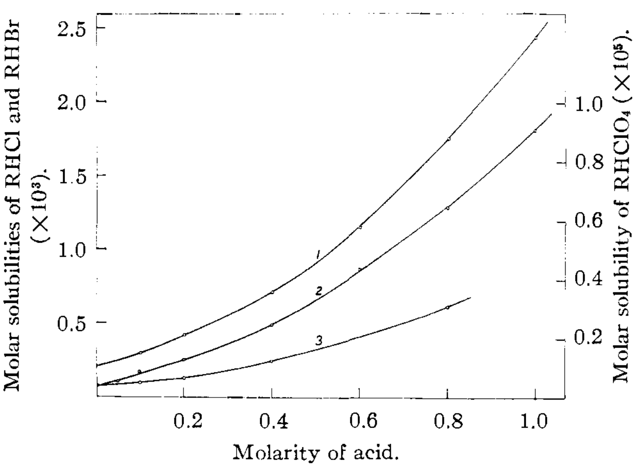


Fig. 3.—Solubility of rhodamine B salts as a function of acidity in solutions of the corresponding strong acid and alkali metal salt: curve 1, RHCl in HCl–KCl mixtures; curve 2, $\mathrm{RHClO_4}$ in $\mathrm{HClO_4}$–$\mathrm{NaClO_4}$ mixtures; curve 3, RHBr in HBr–KBr mixtures.

$$K_5' = [\mathrm{RHX}][\mathrm{H}^+][\mathrm{X}^-]/[\mathrm{RH_2X_2}] = K_5K_6K_7/K_3$$

It was assumed that the maximum absorptivity of the violet form RHX is equal to that of the zwitterion. The former could not be determined directly because the constants K_2' and K_5' are so close together that a pure solution of RHX cannot be prepared. From the curves of Fig. 4 the con-

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[4] A more complex treatment, taking these forms into account may be found in reference 1.

[5] E. Rabinowitch and L. F. Epstein, THIS JOURNAL, **63**, 69 (1941).

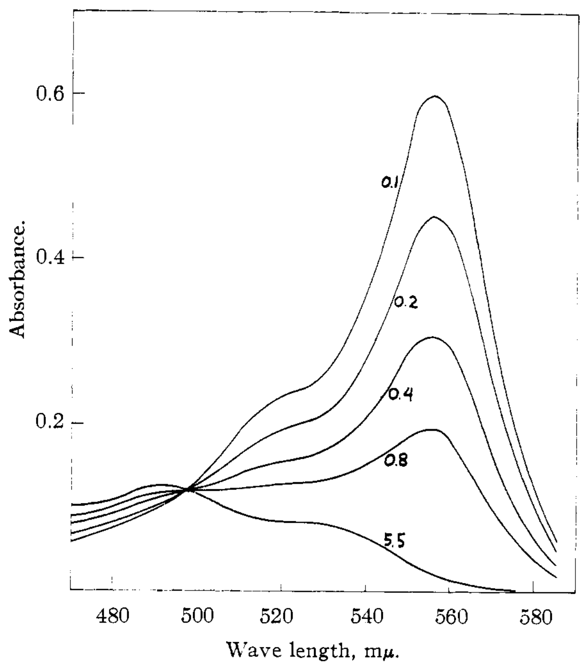

Fig. 4.—Absorption spectra of rhodamine B in HCl–KCl solutions as a function of acidity. Numbers refer to the molarity of HCl. $C = 8.32 \times 10^{-6}$ *M;* cell path = 1.00 cm.

stant K_5' was calculated in the classical manner for acidities of 0.1, 0.2, 0.4 and 0.8 *M* hydrochloric acid. The average value for eight determinations is 0.207 ± 0.004. For bromide and perchlorate as anions, the corresponding constants have the values 0.18 and 0.15, respectively. Since the ionic strength was unity in each experiment, this is evidence that ion pairs exist, for if the equilibrium were simply between the dye cations, the same constant (K_5) should be observed in each case.

The direct spectrophotometric determination of K_2' is more difficult because of the slight difference in the absorption spectra of the forms R^{+-} and RH^+ (or RHCl), as shown by Fig. 1. The greatest difference is on the steep slope on the long wave length side, for example at 565 mμ.

The following procedure was found to give fairly precise results. Fifteen ml. of 2×10^{-6} *M* rhodamine B chloride in 1 *M* potassium chloride were put into a 5-cm. cylindrical glass-stoppered Pyrex cell. The initial absorbance A_0 at 565 mμ was due entirely to the zwitterion, since at this concentration (with no hydrochloric acid present) the ion pair dissociates virtually completely into R^{+-}, H^+ and Cl^-. Then 0.200 *M* hydrochloric acid was added to the cell in 0.0100 ml. increments, the absorbance *A* being measured after each increment. When 0.1 ml. of acid had been added, the micro-buret was refilled with 2.00 *M* acid and another series of increments was added.

Figure 5 shows the plot of absorbance *versus* acidity, corrected for the slight dilution effect. The decrease at higher acidities is due to the formation of some of the orange form of the dye. Since K_5' is known, it was possible to correct the absorbance values for this effect, giving the dotted line of Fig. 5. In this way a limiting value of absorbance was found, designated A', which represents the value the absorbance would have if all the dye were converted to the RH^+ form. It can be derived that the constant K_2' is equal to $(A' - A)$ $H^+/(A - A_0)$. Thus a plot of $(A - A_0)/(A' - A)$ *versus* $[H^+]$ is linear with a slope of $1/K_2'$. K_2' is calculated to be 4.3×10^{-4}.

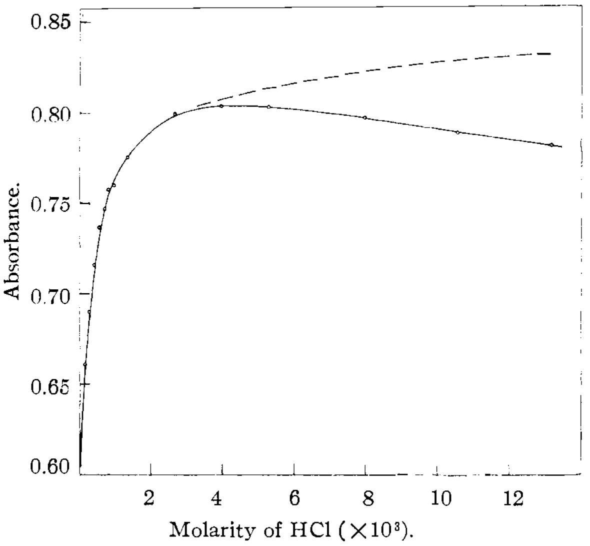

Fig. 5.—Absorbance at 565 mμ of a 2×10^{-6} *M* solution of rhodamine B as a function of acidity. Cell path = 5.0 cm. Dotted line shows values obtained by correction of data for presence of orange forms.

The expression for K_2' (*vide supra*) can be rearranged to: $1/K_2' = 1/K_2 + [Cl^-]/K_2K_3$. According to this equation, a plot of K_2' *versus* $[Cl^-]$ should be linear with an intercept of $1/K_2$ and a slope of $1/K_2K_3$.

To test this equation, values of K_2' were determined as a function of chloride concentration in the following manner. An aqueous solution of the zwitterion was prepared by evaporating a benzene solution of the lactone and taking up the residue in pure water. The concentration after dilution was 2.5×10^{-6} *M*. Fifteen ml. of this solution was put into a 5 cm. cell and the absorbance measured at 565 mμ, after which increments of 7.50 *M* hydrochloric acid were added.

The dilution effect was negligible. Thus, the acidity and chloride concentration varied simultaneously, and each could be calculated simply from the amount of acid added. For each point, using the absorbance relationship given above, K_2' was calculated. The plot of $1/K_2'$ as a function of chloride concentration has an intercept which gives a value of 6×10^{-4} for K_2 and the slope allows calculation of 3.4×10^{-3} for K_3. These are approximately the thermodynamic values, since the ionic strength was low. Since K_2 is a simple acid dissociation constant, supposedly independent of the particular anion present in the solution, the experiment was repeated with perchloric acid instead of hydrochloric acid. The intercept should be the same for both, but the slopes should differ unless the ion-pair dissociation constant K_3 is the same for RHCl as for $RHClO_4$, an unlikely condition. These predictions are fulfilled. This supports the reliability of the thermodynamic value of K_2 and also furnishes good evidence for the existence of ion pairs. The value of K_3 is calculated to be 1.3×10^{-3} when the anion is perchlorate. Thus, the perchlorate ion pair is somewhat more stable than the chloride ion pair.

As shown in Fig. 2, the absorption spectra of the violet forms of rhodamine B are dependent upon concentration. Holmes[6] also observed the effect for rhodamine B as well as for many other dyes. Similar results were obtained by Speas[7] who apparently did not control *p*H and probably dealt with mixtures of R^{+-} and RH^+. Speas also studied the effect of temperature on the shape of the spectrum. In very dilute solutions temperature change had no effect, but in relatively concentrated solutions rise in temperature changed the shape of the curve toward that of dilute solutions. He concluded that these effects confirmed Holmes' view of a dynamic equilibrium between single and associated molecules. Rabinowitch and Epstein[5] studied the polymerization of thionine and methylene blue in aqueous solution. Qualitatively the spectra of these compounds behave like that of rhodamine B.

The dimer dissociation constants for the reactions: $(R^{+-})_2 = 2R^{+-}$, and $(RHCl)_2 = 2RHCl$, *i.e.*, K_1 and K_4, can be obtained as follows: curve 4 of Fig. 2 is the spectrum of R^{+-}; curve 3 represents a mixture of monomer and dimer $(R^{+-})_2$. Figure 6 shows the apparent departure from Beer's law at 553 mμ. Since the deviation is in a negative direction the dimer has a lower absorptivity than the monomer at 553 mμ. The absorbance of a solution containing both monomer and dimer is given by

$$A = (a_m C_m + a_d C_d)b$$

where a_m and a_d are the absorptivities of the monomer and dimer, respectively, C_m and C_d refer to molar concentrations and b to the cell path. The quantity A' is defined by

$$A' = a_m b C = a_m b(C_m + 2C_d)$$

where C is the total dye concentration. A' is the value the absorbance would have at concentration C if no dimerization occurred, and is calculated using the absorptivity a_m obtained at very low concentrations. From these definitions the following quantity can be derived

$$A^2/(A' - A) = b(a_m C_m + a_d C_d)^2/C_d(2a_m - a_d)$$

The approximation that a_d is much smaller than a_m at 553 mμ simplifies the expression to

$$A^2/(A' - A) = (ba_m/2) \times C_m^2/C_d = (ba_m/2) \times K_1$$

Thus if A^2 is plotted *versus* $(A' - A)$ the slope of the straight line is $ba_mK_1/2$. Since the cell path and absorptivity (a_m) are known, K_1 can be calculated. By the use of a cell spacer the cell path was reduced to 1 mm., thus allowing the measurement of the absorbance of the concentrated solutions of dye in which dimerization is appreciable. For the determination of K_1 the measurements were made on rhodamine B solutions in *p*H 8 ammonia buffers which were 1 *M* in chloride. From the slope of the line and the value $a_m = 1.07 \times 10^5$, K_1 was calculated to be 1.0×10^{-3}. Using this value it is possible to show that the approximation that a_d is small is valid.

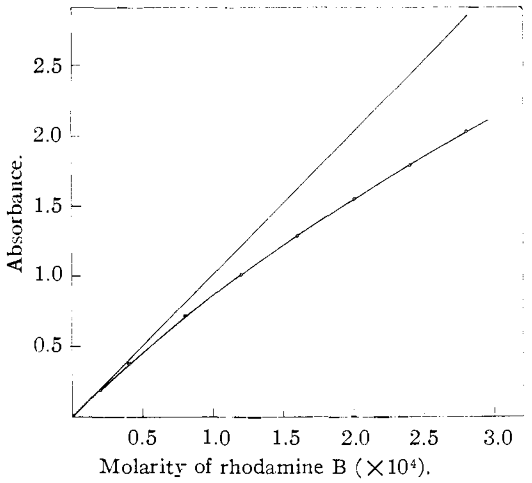

Fig. 6.—Apparent deviation from Beer's law for solutions of rhodamine B (R^{+-}) in *p*H 8 ammonia buffers. Straight line shows absorbance expected if the chemical state of the dye were not a function of concentration. Cell path = 0.1 cm.

The same procedure was used to obtain the constant K_4. The only difference was that the solutions were 0.05 *M* in hydrochloric acid and 0.95 *M* in potassium chloride. This was done to be sure that no R^{+-} was present in solution. From the known value of K_5' the concentrations of the orange species were calculated and subtracted from the total concentration to give the concentration of violet forms. It was found that K_4 is equal to 1.9×10^{-3}.

An application of this result is the calculation of the intrinsic solubility of RHCl in 1 *M* chloride. The intercept of Fig. 3 gives 2×10^{-4} *M* as the saturation concentration of RHCl plus its dimer. Using the dimer constant K_4, one can then calculate that the concentration of RHCl in the saturated solution is 1.7×10^{-4} *M*.

***p*H Measurements.**—The direct determination of K_2' by *p*H measurement of partially neutralized solutions of the dye chloride was considered. For good results the concentration of the conjugate acid–base pair should be fairly high, so that the buffer capacity of the solution has a reasonable value. However, the solubility in 1 *M* potassium chloride is only about 2×10^{-4} *M*. Even at this concentration there is the unfavorable condition of dimer formation, which will introduce an error. Higher concentrations of dye can be obtained in solutions of lower chloride concentration, but dimerization is then even more important. Woislawski[8,9] determined an apparent constant by potentiometric titration of the dye chloride with sodium hydroxide. He did not consider anion concentration or dimer formation, however, and since his concentrations were relatively high these effects are not negligible. In the present work the *p*H values of half-neutralized solutions of the chloride were determined with the following results

Electrolyte	C	*p*H	K_2' (apparent)
1 *M* KCl	4×10^{-4}	4.1	8×10^{-5}
0.05 *M* KCl	5×10^{-3}	3.5	3×10^{-4}
None	5×10^{-3}	3.4	4×10^{-4}
None	1×10^{-3}	3.7	2×10^{-4} (Woislawski)

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[8] S. Woislawski, *Proc. Soc. Exp. Biol. Med.*, **79**, 390 (1952).

[9] S. Woislawski, THIS JOURNAL, **75**, 5201 (1953).

TABLE III

EQUILIBRIUM CONSTANTS FOR RHODAMINE B; TEMP. = 25°

Constant	Chloride	Bromide	Perchlorate
$[\mathrm{RHCl}]_s$	1.7×10^{-4}		
D'	2.8×10^{3}		
K_1	1.0×10^{-3}		
K_2'	4.3×10^{-4}		
K_2	6×10^{-4}		6×10^{-4}
K_3	3.4×10^{-3}		1.3×10^{-3}
K_4	1.9×10^{-3}		
K_5'	2.1×10^{-1}	1.8×10^{-1}	1.5×10^{-1}
K_6 K_7	Probably small		
K_8	8.0×10^{-4}	8.5×10^{-5}	4.0×10^{-6}

Little significance is attached to these values; those determined spectrophotometrically are considered much more reliable.

Summary of Values of Equilibrium Constants.—Table III lists the values of the constants determined in this work. The values refer to solutions which are 1 *M* in the particular anion, with the exception of the values for K_2 and K_3 which are the thermodynamic values.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. X. π-Bonding in Dissociation Reactions of Octahedral Complexes[1,2]

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In order to account for the high rates of hydrolysis of chloroamido and chlorohydroxo complexes of cobalt(III) and other rate data, it is proposed that π-bonding stabilizes the transition state. This π-bonding consists of the sharing of an additional pair of electrons on the donor atom with the cobalt. The stereochemical requirements and consequences of such bonding are discussed. An explanation is given for the failure of the "*trans-effect*" rule in the case of octahedral complexes.

In previous papers[1] we have reported results strongly supporting an SN1CB[3] mechanism for the base hydrolysis of complex ions of cobalt(III). The steps in a typical example would be

$$\mathrm{Co(NH_3)_5Cl^{+2} + OH^- \underset{}{\overset{\text{fast}}{\rightleftarrows}} Co(NH_3)_4NH_2Cl^+ + H_2O} \quad (1)$$

$$\mathrm{Co(NH_3)_4NH_2Cl^+ \xrightarrow{k_{CB}} Co(NH_3)_4NH_2{}^{+2} + Cl^-} \quad (2)$$

$$\mathrm{Co(NH_3)_4NH_2{}^{+2} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_4NH_2H_2O^{+2}} \quad (3)$$

$$\mathrm{Co(NH_3)_4NH_2H_2O^{+2} \xrightarrow{\text{fast}} Co(NH_3)_5OH^{+2}} \quad (4)$$

The kinetics follow a second-order course if the complex ion is a weak enough acid so that 1 is very incomplete. The rate equation would then be

$$\text{rate} = k_{\mathrm{CB}}\, K_{\mathrm{a}}/K_{\mathrm{w}}\, [\mathrm{OH^-}][\text{Complex}] \quad (5)$$

and the observed second-order constant is the product of a first-order constant, k_{CB}, for reaction 2 and the equilibrium constant $K_{\mathrm{a}}/K_{\mathrm{w}}$ for reaction 1.

The values of K_{a} cannot be measured, in general, because of the rapid reaction of the complex ions with alkali. However, an estimate can be made of the magnitude of the acid ionization constants involved by considering some related compounds. The aquo complexes of cobalt(III) are acidic enough so that their K_{a} values can be measured and the values found are of the order of 10^{-5} for tripositive cations and 10^{-7} for dipositive cations.[4]

From a consideration of such data and by comparing the acidities of $\mathrm{Pt(NH_3)_6{}^{+4}}$ and $\mathrm{Pt(NH_3)_5H_2O^{+4}}$, which differ by a factor of 10^5, Anderson, Briscoe and Spoor[5] estimated that K_{a} for $\mathrm{Co(NH_3)_6{}^{+3}}$ would be approximately 10^{-11}. However, one might argue that the comparison should involve the acidities of $\mathrm{NH_4{}^+}$ and $\mathrm{H_3O^+}$ (factor of 10^{11}) which would lead to a K_{a} for $\mathrm{Co(NH_3)_6{}^{+3}}$ of 10^{-17}. An intermediate value of 10^{-13} seems reasonable based on the greater resemblance of $\mathrm{Co^{+3}}$ to $\mathrm{Pt^{+4}}$ than to $\mathrm{H^+}$.

We have tried to measure the K_{a} for several complex ions such as $\mathrm{Coen_3{}^{+3}}$ directly using a conventional titration procedure and a *p*H meter. A good "constant" was in fact obtained for such ions as shown in Table I. However, spectroscopic examination in the visible and near ultraviolet regions of alkaline solutions of $\mathrm{Coen_3{}^{+3}}$ showed no shifts to longer wave lengths as is expected for the loss of a proton.[6] Instead, a shift to longer wave lengths occurred in the far ultraviolet indicating ion pair formation.[7] Such ion pair formation should in fact occur between hydroxide ion and $\mathrm{Coen_3{}^{+3}}$ and the constants recorded in Table I are of the expected order of magnitude[7] if the data are reinterpreted in this way.

It thus appears that the ionization constant as

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[1] For previous papers in this series see F. Basolo, J. G. Bergmann, R. E. Meeker and R. G. Pearson, THIS JOURNAL, **78**, 2676 (1956).

[2] This investigation supported by the U. S. Atomic Energy Commission under Contract AT(11-1)89. Project No. 2.

[3] SN1CB refers to substitution, nucleophilic, unimolecular, conjugate base, in the convenient terminology of Hughes and Ingold, see D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

[4] (a) R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956); (b) F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, *ibid.*, **76**, 3079 (1954).

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