[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STATE UNIVERSITY OF IOWA]

Thermodynamic Constants and the Degree of Dissociation of Bromine Chloride in Carbon Tetrachloride Solution

BY ALEXANDER I. POPOV AND JAMES J. MANNION[1]

The absorption spectra of bromine, chlorine and bromine chloride solutions in carbon tetrachloride were measured with a Beckman DU spectrophotometer. The dissociation of bromine chloride at 25° was found to be 43.2 ± 1%. The equilibrium constant for the reaction $2BrCl \rightleftarrows Br_2 + Cl_2$ in carbon tetrachloride was calculated to be 0.145 ± 0.006. Approximately the same values were obtained at 15° and at 10°. The true absorption curve of bromine chloride is given as well as its molar absorbancy index at the maximum. New values for ΔH^0_{298}, ΔF^0_{298} and ΔS^0_{298} are given for the formation of bromine chloride.

Introduction

The existence of bromine chloride in bromine and chlorine mixtures was first clearly proven by Gillam and Morton.[2] Spectrophotometric study of the bromine–chlorine mixtures in carbon tetrachloride showed that the mixture absorption curve was quite different from the summation of bromine and chlorine absorption curves. The authors stated that the compound was probably highly dissociated, but gave no numerical values.

The only previous attempt to determine the degree of dissociation of bromine chloride in carbon tetrachloride solution was made by Barratt and Stein.[3] The work was based on the absorption curves obtained with a Hilger photographic spectrophotometer. They reported a dissociation constant of 0.28. However, as it was pointed out by Vesper and Rollefson,[4] Barratt and Stein made a wrong assumption that bromine chloride does not absorb at the wave lengths at which they measured the absorption and their results were erroneous. Recalculation of their data by Vesper and Rollefson indicated that the dissociation constant was not above 0.18.

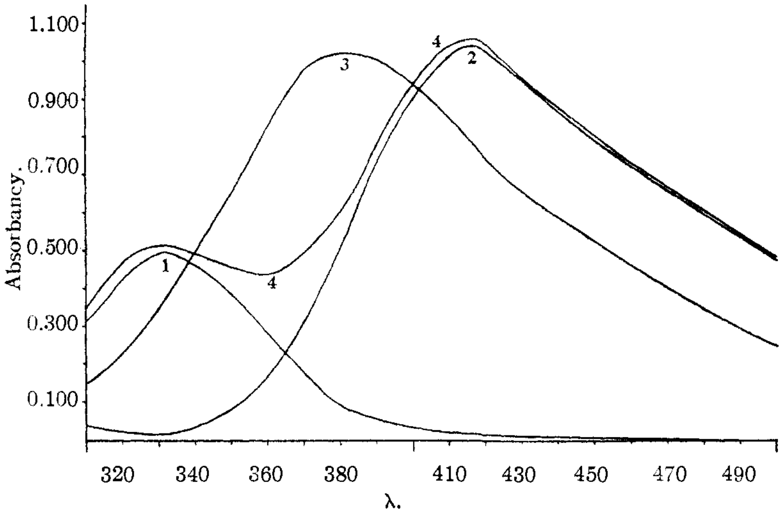

Fig. 1.—Absorption of bromine, chlorine and bromine chloride in carbon tetrachloride solution: curve 1, chlorine 5 × 10^{-3} *M*; curve 2, bromine 5 × 10^{-3} *M*; curve 3, bromine chloride 1 × 10^{-2} *M*; curve 4, addition of chlorine and bromine curves.

Blair and Yost,[5] in 1933, studied the thermodynamic properties of iodine chloride, iodine bromide and bromine chloride. In their calculation of the thermodynamic constants of bromine chloride, they took the Barratt and Stein value for the degree of dissociation of bromine chloride which led to inaccurate values of derived thermodynamic constants.

Many investigators[6-9] have determined the dissociation of bromine chloride in vapor phase, by various methods. The values obtained for K vary between 0.10 and 0.14 at room temperature.

Experimental

Carbon tetrachloride and bromine used in this investigation were carefully purified by the usual methods. Chlorine was obtained from commercial cylinders and was dehydrated by passing it through sulfuric acid. Stock solutions were prepared by addition of the halogens to carbon tetrachloride. The concentration was then determined by iodometric titration and the solutions were diluted to the desired concentration. Both chlorine and bromine solutions were found to be stable in carbon tetrachloride for a period of several days provided that the solvent was free from traces of moisture and that the halogen concentration did not exceed 0.01 *M*. However, to avoid any possible source of error, fresh solutions were prepared for each set of experiments.

Since the establishment of equilibrium in bromine–chlorine solutions is facilitated by ultraviolet light,[4] the solutions were irradiated by a mercury lamp for five minutes before the absorption measurements were made.

A Beckman DU model spectrophotometer was used for absorption measurements. It was equipped with thermospacers which allowed temperature control to ±0.1°. Most of the measurements were made at 25°. An attempt was made to determine dissociation constant also at 15° and at 10°. Corex-stoppered cells of path length 1.000 ± 0.001 cm. were used.

Results and Discussion

Preliminary measurements showed good agreement with the results of Gillam and Morton,[2] with the exception that the molar absorbancy index[10] of

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[1] Abstracted from a thesis presented by James J. Mannion to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Master of Science, August, 1951.

[2] A. E. Gillam and R. A. Morton, *Proc. Roy. Soc.* (*London*), **A124**, 604 (1929).

[3] S. Barratt and C. P. Stein, *ibid.*, **A122**, 582 (1929).

[4] H. G. Vesper and G. K. Rollefson, THIS JOURNAL, **56**, 620 (1934).

[5] C. M. Blair and D. M. Yost, *ibid.*, **55**, 4489 (1933).

[6] L. M. T. Grey and D. W. G. Style, *Proc. Roy. Soc.* (*London*), **A126**, 603 (1930).

[7] W. Jost, *Z. physik. Chem.*, **153A**, 143 (1931).

[8] G. Brauer and E. Victor, *Z. Electrochem.*, **41**, 508 (1935).

[9] C. M. Beeson and D. M. Yost, THIS JOURNAL, **61**, 1432 (1939).

[10] The nomenclature and the symbols used in this paper follow the recommendation of the National Bureau of Standards Letter Circular LC-857 (1947).

TABLE I

ABSORBANCY VALUES FOR CHLORINE, BROMINE AND BROMINE CHLORIDE

λ, mμ	Solution, *M*	A_s	Solution, *M*	A_s	Solution, *M*	A_s	$A_{s(\mathrm{BrCl})}$	a_{BrCl}
332	BrCl, 4.9×10^{-3}	0.181	BrCl, 4.9×10^{-3} Br_2, 9.8×10^{-3}	0.190	Br_2, 9.8×10^{-3}	0.029	0.161	32.85
332	BrCl, 4.9×10^{-3}	.181	BrCl, 4.9×10^{-3} Br_2, 1.95×10^{-2}	.208	Br_2, 1.95×10^{-2}	.058	.158	30.6
332	BrCl, 4.9×10^{-3}	.181	BrCl, 4.9×10^{-3} Br_2, 3.98×10^{-2}	.251	Br_2, 3.98×10^{-2}	.119	.132	26.94
332	BrCl, 5.0×10^{-3}	.189	BrCl, 5.0×10^{-3} Br_2, 5.04×10^{-2}	.286	Br_2, 5.04×10^{-2}	.151	.135	26.78
440	BrCl, 5.01×10^{-3}	.310	BrCl, 5.01×10^{-3} Cl_2, 1×10^{-2}	.250	Cl_2, 1×10^{-2}	.019	.231	46.10
450	BrCl, 5.01×10^{-3}	.275		.212	Cl_2, 1×10^{-2}	.015	.197	39.32
460	BrCl, 5.01×10^{-3}	.245		.185	Cl_2, 1×10^{-2}	.011	.174	34.73
440	BrCl, 5.01×10^{-3}	.310	BrCl, 5.01×10^{-3} Cl_2, 2×10^{-2}	.265	Cl_2, 2×10^{-2}	.038	.227	45.39
450	BrCl, 5.01×10^{-3}	.275		.223	Cl_2, 2×10^{-2}	.030	.193	38.52
460	BrCl, 5.01×10^{-3}	.245		.187	Cl_2, 2×10^{-2}	.022	.165	32.93
440	BrCl, 5.01×10^{-3}	.310	BrCl, 5.01×10^{-3} Cl_2, 4×10^{-2}	.270	Cl_2, 4×10^{-2}	.076	.194	38.72
450	BrCl, 5.01×10^{-3}	.275		.228	Cl_2, 4×10^{-2}	.060	.168	33.53
460	BrCl, 5.01×10^{-3}	.245		.183	Cl_2, 4×10^{-2}	.044	.139	27.74
440	BrCl, 5.01×10^{-3}	.310	BrCl, 5.01×10^{-3} Cl_2, 5×10^{-2}	.288	Cl_2, 5×10^{-2}	.095	.194	38.52
450	BrCl, 5.01×10^{-3}	.275		.242	Cl_2, 5×10^{-2}	.075	.167	33.33
460	BrCl, 5.01×10^{-3}	.245		.190	Cl_2, 5×10^{-2}	.055	.135	26.94

the bromine chloride peak was found to be 102 instead of 97 as claimed by the above authors.

In order to determine the molar absorbancy indices for pure bromine chloride, excess amounts of one or the other halogen had to be added to the bromine chloride solution in order to repress the dissociation. The wave lengths at which measurements were made were so chosen that the excess of a halogen would not mask the absorption due to bromine chloride. As seen from Fig. 1, the optimum wave length to use with an excess of bromine is 332 mμ where the absorption of this halogen is very small but still can be measured accurately. Also, at this wave length the ratio of bromine absorption to bromine chloride absorption is at a minimum. Likewise, optimum wave lengths for excess chlorine lie in the region 440–460 mμ.

Varying amounts of excess halogen were added to the bromine chloride solutions and the absorbancy of the mixture was measured. Assuming complete suppression of dissociation, the absorbancy obtained was the sum of the absorbancies of the bromine chloride and the excess halogen

$$A_s = a_{\mathrm{BrCl}}\, bc_{\mathrm{BrCl}} + a_{\mathrm{hal}}\, bc_{\mathrm{hal}} \qquad (1)$$

where:

a_{BrCl} and a_{hal} are the molar absorbancy indices of bromine chloride and the excess halogen, respectively.

b is the optical path length.

c_{BrCl} and c_{hal} are the concentration of bromine chloride and excess halogen, respectively.

From the above equation, knowing the molar absorbancy index of the excess halogen from previous measurements, the molar absorbancy index of bromine chloride was calculated. As seen from Table I, the molar absorbancy index thus determined varied with excess halogen added and reached a constant value only on addition of 8–10-fold excess. This shows that at least 8-fold excess of a halogen is needed in order to suppress the dissociation of bromine chloride.

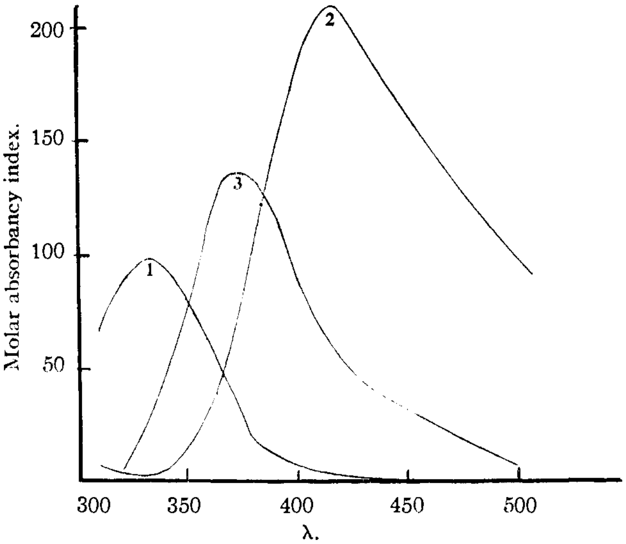

Fig. 2.—Molar absorption of chlorine, bromine and bromine chloride: curve 1, chlorine; curve 2, bromine; curve 3, bromine chloride.

The concentrations of chlorine, bromine and bromine chloride present in an equimolar mixture of chlorine and bromine can now be calculated by the method given in a previous paper,[11] from data given in Table I.

In a series of 16 experiments, the degree of dissociation was found to be equal to 43.2% with an average deviation of 1%. The dissociation constant for the reaction

$$2\mathrm{BrCl}_{(\mathrm{CCl_4})} \rightleftharpoons \mathrm{Br}_{2(\mathrm{CCl_4})} + \mathrm{Cl}_{2(\mathrm{CCl_4})} \qquad (2)$$

was then calculated to be equal to 0.145 with an average deviation of ±0.006. These values are con-

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[11] A. I. Popov, K. C. Brinker, L. Campanaro and R. W. Rinehart, THIS JOURNAL, 73, 514 (1951).

siderably different from the values obtained by Barratt and Stein,[3] but they agree well with the values obtained for the dissociation in vapor phase.

A true absorption curve for the bromine chloride molecule can now be drawn by subtracting the known amounts of bromine and chlorine absorption from the absorption curve of the equimolar mixture of the two halogens. This absorption curve is given in Fig. 2. The position of the maximum is now at 370 mμ instead of 380 and the value of the molar absorbancy index is 135 instead of 102.

Measurements were also made at temperatures of 15 and 10°. The results were essentially the same as those obtained at 25°, variation being only slightly higher than the experimental error. This agrees well with the small heat of formation of bromine chloride.

Blair and Yost[5] have determined experimentally the heat of formation of bromine chloride in carbon tetrachloride solution. However, since they have taken the dissociation of bromine chloride to be 52.4% the value of ΔH°_{298} they obtained was too high. Recalculation of heat of formation on the basis of 43.2% dissociation gives $\Delta H^\circ_{298} = -317$ cal. Likewise, ΔF°_{298} and ΔS°_{298} can be recalculated as shown by Table II.

TABLE II

THERMODYNAMIC CONSTANTS FOR THE REACTION $^1/_2\mathrm{Br}_{2(\mathrm{CCl}_4)} + {}^1/_2\mathrm{Cl}_{2(\mathrm{CCl}_4)} \longrightarrow \mathrm{BrCl}_{(\mathrm{CCl}_4)}$

	Blair and Yost	This paper
ΔH°_{298}, cal.	−378	−312
ΔF°_{298}, cal.	−357	−572
ΔS°_{298}, cal./deg.	− 0.0705	+ 0.872

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

A Spectrophotometric Study of Chromate–Phosphate Complexes in Solution

BY FRANK HOLLOWAY[1]

The spectrum of chromic acid is reported. Spectrophotometric investigation of chromic acid–phosphoric acid solutions indicate that two chromate-phosphate complex ions are formed. The equilibrium constants for the formation of the two complexes were determined at 25° and ionic strength equal to 0.25.

In the course of the study of the chromic acid oxidation of isopropyl alcohol[2] in buffered systems, it became necessary to consider the possibility of the interaction of chromic acid and buffer components, giving rise to complex molecules or ions. A preliminary spectrophotometric study of the systems employed indicated that the chromic acid–phosphoric acid system exhibited the largest spectral changes from the spectrum of chromic acid alone. Subsequent studies of this system, reported here, led to the determination of the number of complexes formed and the equilibrium constants for their formation at 25° and an ionic strength of 0.25.

These data led to an internally consistent analysis of the rate data for the dihydrogenphosphate–phosphoric acid buffer catalyzed chromic acid oxidation of isopropyl alcohol. However, the resulting kinetic equations, because of alternative mathematical formulations, did not permit a unique interpretation of the observed catalysis.

Viterbi and Krausz[3] have reported the spectrum of chromic acid. Their work is in qualitative agreement with the work here reported, in the wave length range of 230 to 390 mμ, and in quantitative agreement in the wave length range of 400 to 480 mμ. The observations of Brownell[4] and of Lingane and Collat[5] substantiate the positions of the near ultraviolet maxima here reported for the chromic acid or chromic acid–phosphoric acid systems. The spectra for these systems were determined from 220 to 480 mμ.

Figure 1 describes the essential differences in the absorption spectra of chromic acid and chromic acid–phosphoric acid systems. In all cases the concentration of the buffer was in excess of the concentration of chromic acid. The absorption due to the buffers was small and was compensated by employing a solvent blank containing the same buffer.

Increasing concentrations of the buffer lowered and shifted the peak in the 250 mμ region, lowered the peak at 350 mμ, and decreased the apparent specific extinction coefficient between 300 and 450 mμ. Studies were made which indicated that these observed changes were not due to any appreciable degree to *p*H, ionic strength or asymmetrical ion effects. The 250 mμ region was selected for detailed analysis because of the presence there of two separate absorption bands.

Determination of the Number of Complexes.—The very close correspondence between the experimental data and a mathematical model (see appendix) which assumes two complexes, confirms the existence of two complexes. The reactions which give rise to the complexes may be represented as

$$\mathrm{HCrO_4^-} + \mathrm{H_2PO_4^-} \rightleftharpoons \mathrm{HCrPO_7^{=}} + \mathrm{H_2O} \quad (1)$$

$$\mathrm{HCrO_4^-} + \mathrm{H_3PO_4} \rightleftharpoons \mathrm{H_2CrPO_7^-} + \mathrm{H_2O} \quad (2)$$

Determination of Formation Equilibrium Constants and Specific Extinction Coefficients for the Complexes.—It is shown in the appendix that the

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(1) University of Illinois, Division of Physical Sciences, Chicago 11, Illinois.

(2) F. Holloway, M. Cohen and F. H. Westheimer, THIS JOURNAL, **73**, 65 (1951).

(3) E. Viterbi and G. Krausz, *Gazz. chim. ital.*, **57**, 690 (1927).

(4) R. M. Brownell, Doctorate Dissertation, University of Chicago, 1947.

(5) J. J. Lingane and J. W. Collat, *Anal. Chem.*, **22**, 166 (1950).