

The simple Hückel molecular orbital calculations obtained for the aliphatic Schiff bases indicate that the system is polar with an appreciable negative charge on oxygen and with a partially delocalized positive charge.<sup>4</sup> The same situation probably occurs in the aromatic Schiff bases IV and V with the possibility of delocalizing the charge into the aromatic system. In the enol-imine form, the charge distri-

bution calculated for the aliphatic system suggests the system is less polar than the keto-amine form, primarily owing to the removal of the highly dipolar carbonyl group. The carbonyl oxygen would be a logical site for association with a hydrogen bonding solvent such as chloroform.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HEBREW UNIVERSITY, JERUSALEM, ISRAEL]

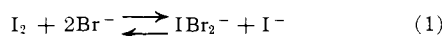
## A Spectrophotometric Study of the System I<sub>2</sub> + Br<sup>-</sup>

BY EHUD EYAL AND AVNER TREININ

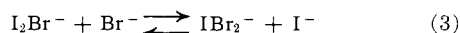
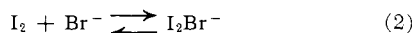
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The ultraviolet spectrum of the system I<sub>2</sub> + Br<sup>-</sup> was thoroughly investigated. The shift of the main absorption band to shorter wave lengths on raising the concentration of Br<sup>-</sup> is ascribed to the equilibrium: I<sub>2</sub>Br<sup>-</sup> + Br<sup>-</sup> ⇌ IBr<sub>2</sub><sup>-</sup> + I<sup>-</sup>. The spectroscopic and thermodynamic properties of the two complexes involved were determined. The origin of the electronic transitions is discussed.

Solutions containing I<sub>2</sub> and Br<sup>-</sup> exhibit an intense absorption band, the location of which depends markedly on the concentration of Br<sup>-</sup>.<sup>1,2</sup> Thus on raising the concentration of Br<sup>-</sup> from 2 × 10<sup>-3</sup> to 3 M, the peak of the band is shifted from 270 to 256 mμ.<sup>1</sup> The spectrum at low Br<sup>-</sup> concentration was assigned to I<sub>2</sub>Br<sup>-</sup>, this assignment being in agreement with the proposed origin of the band,<sup>1</sup> but the nature of the spectral shift on raising the bromide concentration remained unclear. The spectrum of IBr<sub>2</sub><sup>-</sup> in aqueous solution displays an intense band at about 254 mμ.<sup>3</sup> Therefore, Daniele<sup>2</sup> proposed that the spectral shift is due to IBr<sub>2</sub><sup>-</sup>, which he considered to be photochemically produced in concentrated bromide solutions. However, we found the same spectral shifts irrespective of room and spectrophotometric illumination, so this cannot be the correct answer. But IBr<sub>2</sub><sup>-</sup> is normally produced in I<sub>2</sub> + Br<sup>-</sup> solutions as expressed by the equilibrium



or



From the available thermodynamic data,<sup>4</sup> we obtain at 25°

$$K_3 = \frac{(IBr_2^-)(I^-)}{(I_2Br^-)(Br^-)} = 1.4 \times 10^{-4} \quad (4)$$

which shows that when (Br<sup>-</sup>)/(I<sup>-</sup>) is ~10<sup>6</sup>, practically no complex but IBr<sub>2</sub><sup>-</sup> is present in solution.

In this work we present the results of a detailed spectrophotometric study of the system I<sub>2</sub> + Br<sup>-</sup>, from which we derive the spectra and some thermodynamic properties of I<sub>2</sub>Br<sup>-</sup> and IBr<sub>2</sub><sup>-</sup>.

### Experimental

The absorption spectra were measured for (a) iodine in solutions of NaBr at various concentrations; (b) the same, but

(1) P. Meyerstein and A. Treinin, *Trans. Faraday Soc.*, **59**, 1114 (1963).

(2) G. Daniele, *Gazz. chim. ital.*, **90**, 1082 (1960).

(3) A. E. Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933).

(4) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

with addition of a relatively small concentration of NaI; (c) IBr in solutions of 0.02 M HClO<sub>4</sub> and various concentrations of NaBr; (d) IBr in 10 M HClO<sub>4</sub> and a small concentration of NaCl. The spectrophotometric measurements were carried out with a Hilger Uvispek spectrophotometer in a thermostated cell compartment (±0.5°); 1-cm. silica cells were used.

**Materials.**—NaBr, NaI, and HClO<sub>4</sub> of A.R. grade were used without further purification. Resublimed I<sub>2</sub> was further sublimed. To prepare IBr we added excess of Br<sub>2</sub> (A.R.) to I<sub>2</sub> and kept the mixture at 50° for several hours. The IBr was sublimed from this mixture and its purity checked by determining its melting point (41°). Solutions of freshly sublimed IBr were used, but nevertheless they always appeared to contain excess I<sub>2</sub> (see Results). Water was redistilled from alkaline permanganate and from dilute phosphoric acid in an all-glass still.

**Solutions.**—The solutions of sets a and b were prepared from a saturated stock solution of I<sub>2</sub> and solutions of NaBr and NaI. At the end of each measurement, the total concentration of the iodine was determined by adding few crystals of KI to the solution and measuring the absorbance of I<sub>3</sub><sup>-</sup> at 352 mμ.<sup>1</sup> We confirmed that this absorbance was independent of further addition of KI. The solutions of set c were prepared by dissolving about 50 mg. of IBr in 1 M NaBr solutions and then diluting by a factor of 1/500. This procedure was used in order to rapidly dissolve the IBr. The dilute solution of IBr was used as a stock solution for preparing the mixtures, which contained HClO<sub>4</sub> to prevent hydrolysis. The exact concentration of IBr was determined in the same way as done for I<sub>2</sub>, but now the excess of KI was added to a blank solution containing the same concentrations of IBr and NaBr but with no HClO<sub>4</sub> present. This was done to prevent autoxidation of I<sup>-</sup>. The solutions of set d were prepared by adding few crystals of NaCl to solutions of IBr in 10 M HClO<sub>4</sub>.

### Results

On raising the Br<sup>-</sup> concentration at constant I<sub>2</sub> concentration (~10<sup>-5</sup> M), the peak of the absorption band is gradually shifted from 270 to 254 mμ. The apparent extinction coefficient,  $\bar{\epsilon}_{\max} = D_{\max}/(I_2)_0$  [(I<sub>2</sub>)<sub>0</sub> is the total concentration of iodine] increases thereby till it reaches a constant value of 5.4 × 10<sup>4</sup> (Fig. 1). The following preliminary experiments seem to prove that the 270-mμ band is due to I<sub>2</sub>Br<sup>-</sup>, which is converted to IBr<sub>2</sub><sup>-</sup> on raising the Br<sup>-</sup> concentration.

a. Job's method of continuous variations<sup>5</sup> tested on 10<sup>-3</sup> M solutions of I<sub>2</sub> and NaBr indicate the formation of a 1:1 complex (Fig. 2).

(5) P. Job, *Ann. chim. (Paris)*, **9**, 113, 135 (1928). It should be realized that the use of equal concentrations of reactants is not essential provided only a little of both reactants enters into the complex.

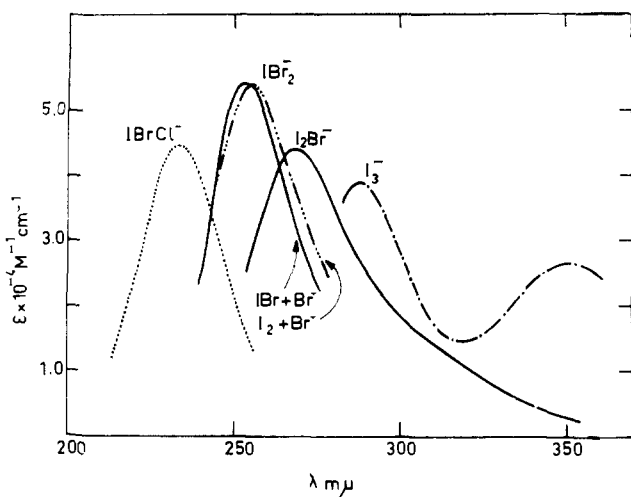


Fig. 1.—The absorption spectra of some polyhalides (the spectrum of  $\text{IBrCl}^-$  on an arbitrary scale).

b. In presence of a large concentration of  $\text{Br}^-$ ,  $\text{I}_2$  and  $\text{IBr}$  display nearly the same spectra (Fig. 1). The small difference between the two spectra may be due to some  $\text{I}_2\text{Br}^-$  present in the  $\text{I}_2\text{-Br}^-$  system.

c. The iodide ion, even at very low concentrations, has a pronounced antagonistic effect to that of  $\text{Br}^-$  in shifting the spectrum back to longer wave lengths. For example, a solution of  $3.5 \times 10^{-5} M$   $\text{I}_2$  and  $0.06 M$   $\text{NaBr}$  displays a band with  $\lambda_{\text{max}}$  at  $263 m\mu$ , which is shifted to  $267 m\mu$  by adding  $10^{-4} M$   $\text{NaI}$  (the absorption of  $\text{I}_3^-$  was subtracted as explained later). This result is readily understood by considering eq. 4.

In order to suppress the formation of  $\text{IBr}_2^-$  in determining the spectroscopic and thermodynamic properties of  $\text{I}_2\text{Br}^-$ , we thus turned to study the system  $\text{I}_2 + \text{NaBr} + \text{NaI}$ . The iodide ion also acts to suppress the hydrolysis of  $\text{I}_2$ ; addition of  $\text{HClO}_4$  had hardly any effect on the spectrum of this system.

**The System  $\text{I}_2 + \text{NaBr} + \text{NaI}$ .**—Two sets of experiments were carried out with this system:

a. All the iodine was practically kept complexed by employing a relative large concentration of  $\text{NaI}$ . The ratio  $(\text{Br}^-)/(\text{I}^-)$  was such as to nearly eliminate the formation of  $\text{IBr}_2^-$ . The iodine was thus present as both  $\text{I}_3^-$  and  $\text{I}_2\text{Br}^-$ , their concentrations obeying the relation

$$\frac{(\text{I}_3^-)(\text{Br}^-)}{(\text{I}_2\text{Br}^-)(\text{I}^-)} = F \frac{K_{\text{I}_3^-}}{K_{\text{I}_2\text{Br}^-}} \quad (5)$$

where  $K_{\text{I}_2\text{Br}^-}$  and  $K_{\text{I}_3^-}$  are the stability constants of the corresponding complexes and  $F$  is the activity coefficient ratio. The absorbance of the system, at wave lengths where  $\text{I}_2\text{Br}^-$  hardly absorbs, was compared to that of another solution containing the same concentration of  $\text{I}_2$  and  $\text{NaI}$  but with no  $\text{NaBr}$  present. Denoting the absorbance of the system by  $D$  and that of the  $\text{I}_3^-$  solution by  $D + \Delta D$  it follows that

$$\frac{(\text{I}_2\text{Br}^-)}{(\text{I}_3^-)} = \frac{\Delta D}{D} \quad (6)$$

Table I contains the experimental results at two wave lengths and the calculated value of  $FK_{\text{I}_3^-}/K_{\text{I}_2\text{Br}^-}$ . The approximate constancy of this ratio (with apparent accidental errors), despite the large

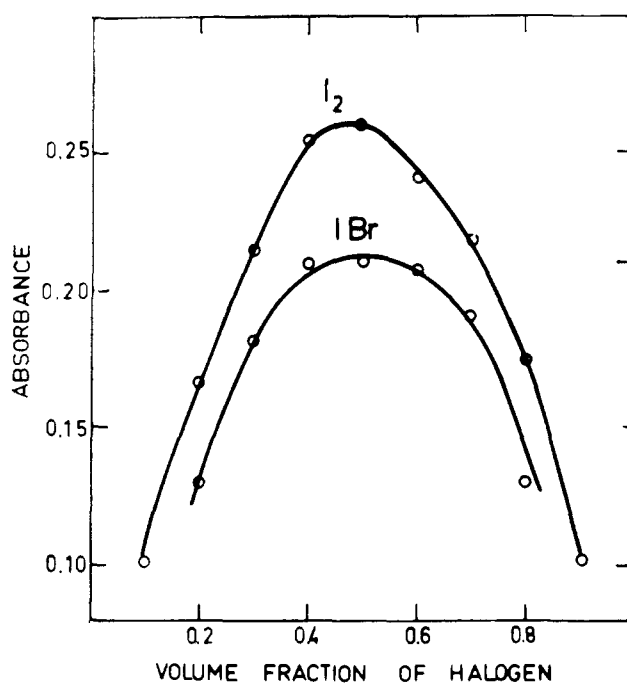


Fig. 2.—Job's method applied to the systems:  $\text{I}_2 + \text{Br}^-$  ( $\sim 10^{-3} M$ ) and  $\text{IBr} + \text{Br}^-$  ( $\sim 10^{-4} M$ ).

variation in ionic strength, is easily explained by eq. 5. The activity coefficient products in the numerator and the denominator should be nearly the same and should vary in the same way with the ionic strength. Thus we can put  $F = 1$ . Using the value  $K_{\text{I}_3^-} = 824$ ,<sup>6</sup> we obtain  $K_{\text{I}_2\text{Br}^-} = 10.5 \pm 0.4 M^{-1}$  at  $20^\circ$ .

TABLE I  
RESULTS NECESSARY FOR EVALUATING  $FK_{\text{I}_3^-}/K_{\text{I}_2\text{Br}^-}$ <sup>a</sup>

(NaBr), M	(NaI), M	$\Delta D/D$ at 352 $m\mu$	$\Delta D/D$ at 370 $m\mu$	$FK_{\text{I}_3^-}/K_{\text{I}_2\text{Br}^-}$ (average)
1.0	0.06	0.228	0.234	72
1.5	0.06	0.324	0.343	75
2.0	0.06	0.450	0.440	75
2.0	0.09	0.280	0.277	80
2.0	0.12	0.216	0.208	79
2.0	0.15	0.163	0.154	84
2.5	0.06	0.520	0.520	80
3.0	0.06	0.672	0.680	74
3.5	0.06	0.755	0.746	78

<sup>a</sup> According to eq. 5 and 6;  $(\text{I}_2)_0 = 3 \times 10^{-5} M$ ,  $20^\circ$ .

b. In this set the concentration of  $\text{I}^-$  was small ( $4 \times 10^{-4} M$ ), the concentration of  $\text{I}_2$  was about  $10^{-5} M$ , and that of  $\text{Br}^-$  was varied between 0.04 and 0.14  $M$ . Under these conditions the iodine was only partly complexed and  $(\text{IBr}_2^-)/(\text{I}_2\text{Br}^-)$  did not exceed 5%. The contribution of  $\text{I}_3^-$  to the absorption was evaluated as follows: the absorbance was measured at 302 and 344  $m\mu$ , where  $\text{I}_3^-$  has the same extinction coefficient (Fig. 1). Denoting the contribution of  $\text{I}_2\text{Br}^-$  and  $\text{I}_3^-$  to the absorbance at 344  $m\mu$  by  $D_{\text{I}_2\text{Br}^-}$  and  $D_{\text{I}_3^-}$ , respectively, we obtain  $D_{344} = D_{\text{I}_2\text{Br}^-} + D_{\text{I}_3^-}$  and  $D_{302} = \beta D_{\text{I}_2\text{Br}^-} + D_{\text{I}_3^-}$ . The constant  $\beta$  was determined from the spectrum of  $\text{I}_2\text{Br}^-$  at an unknown concentration. For this purpose a solution was prepared which contained about  $10^{-3} M$   $\text{I}_2$ ,  $10^{-3} M$   $\text{Br}^-$ , and  $10^{-5} M$   $\text{I}^-$ , and its absorption was measured against a solution of the same concentration of  $\text{I}_2$  and  $\text{I}^-$ . Under these conditions only a little of the

(6) G. Daniele, *Gazz. chim. ital.*, **90**, 1068 (1960).

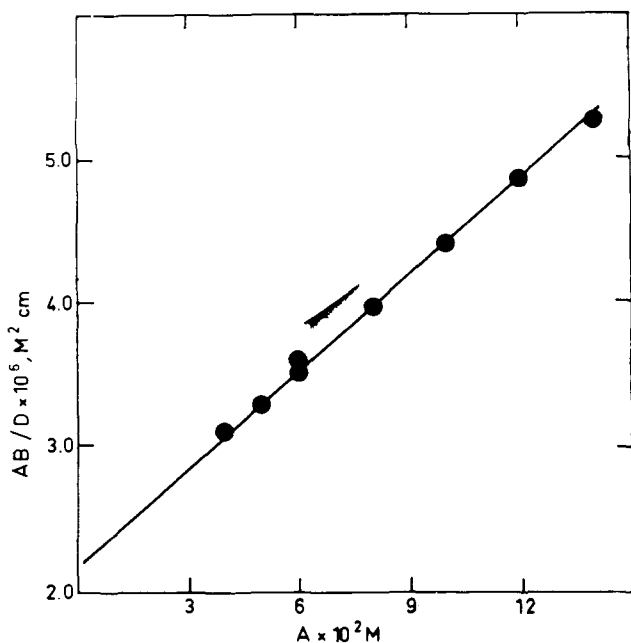


Fig. 3.—Scott's method applied to the system  $I_2 + Br^-$ , in the presence of a little  $I^-$  to suppress the formation of  $IBr_2^-$  at  $20^\circ$ .

$I_2$  was complexed, so that the sample and reference solutions contained nearly identical concentrations of  $I_3^-$ . The value of  $\beta$  thus determined is 7. In this way  $D_{I_3^-}$  and hence the contribution of  $I_3^-$  to the absorption at any other wave length could be determined. Moreover, the total iodine concentration, apart from that of  $I_3^-$ , could also be determined. Denoting the latter by  $B$ , Scott's equation<sup>7</sup> takes the form

$$\frac{AB}{D} = \frac{A}{\epsilon} + \frac{1}{K\epsilon} \quad (7)$$

where  $A$  is the  $Br^-$  concentration,  $K$  is the stability constant of  $I_2Br^-$ ,  $D$  is the contribution of  $I_2Br^-$  to the total absorbance, and  $\epsilon$  is its extinction coefficient at the corresponding wave length ( $\epsilon$  of  $I_2$  is relatively very small at the wave length region studied). Figure 3 shows a plot of the results at  $270 \text{ m}\mu$  ( $\lambda_{\max}$ ) according to Scott's equation. By the method of least squares, the following parameters were derived at  $20^\circ$ :  $K_{I_2Br^-} = 10.5 \text{ M}^{-1}$ ,  $\epsilon_{\max} = 4.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . The values of  $K_{I_2Br^-}$  derived by the two methods are thus in excellent agreement though the range of ionic strength is very wide. This indicates that the salt effect on  $K_{I_2Br^-}$  is smaller than what was previously assumed.<sup>8</sup> The spectrum of  $I_2Br^-$ , based on the derived value of  $\epsilon_{\max}$ , is recorded in Fig. 1. To determine  $\Delta H_f$  of the complex, a simple method was employed. The same type of measurement which was used for determining the spectrum of  $I_2Br^-$  was conducted at several temperatures. When the concentrations of  $I_2$  and  $Br^-$  are both small (about  $10^{-3} \text{ M}$ ), we can put

$$K \epsilon_{I_2Br^-} = \frac{D_{I_2Br^-}}{(I_2)_0 (Br^-)_0} \quad (8)$$

where  $(I_2)_0$  and  $(Br^-)_0$  are the total concentrations of iodine and bromide. Assuming that the extinction coefficient does not vary with temperature, the variation of  $K$  with temperature should be proportional to

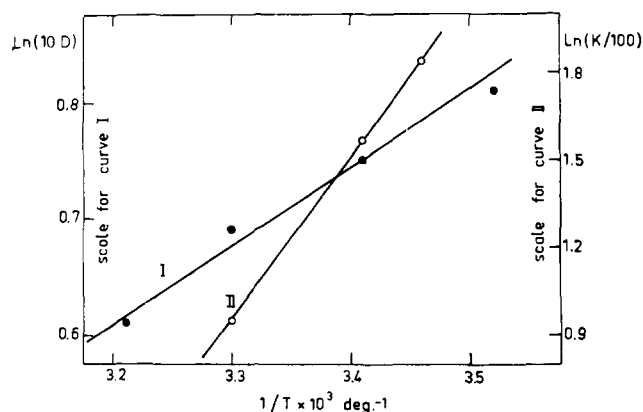


Fig. 4.—The plot of the van't Hoff equation for the systems:  $I_2 + Br^-$  (curve I) and  $IBr + Br^-$  (curve II).

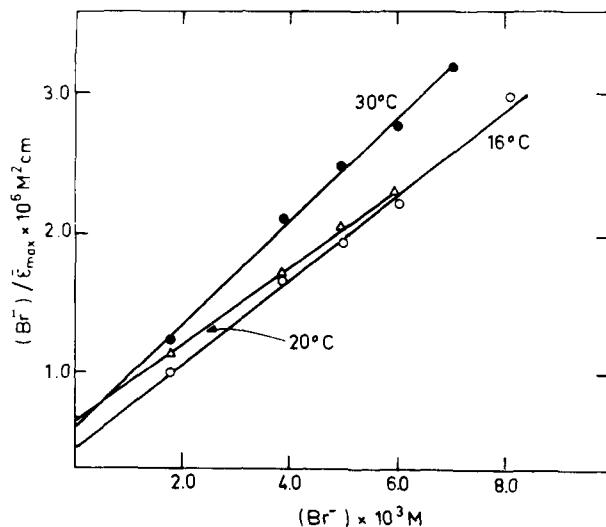


Fig. 5.—Scott's method applied to the system  $IBr + Br^-$  at various temperatures.

that of  $D$ . Figure 4 shows the van't Hoff plot at  $270 \text{ m}\mu$ . From the slope of the line we obtain  $\Delta H = -1.37 \text{ kcal./mole}$ .

**The System  $IBr + NaBr + HClO_4$ .**—This system was investigated in order to determine the spectrum and thermodynamic properties of  $IBr_2^-$ .  $HClO_4$  ( $0.02 \text{ M}$ ) was introduced to suppress the hydrolysis of  $IBr$ . Job's method<sup>5</sup> applied to this system (Fig. 2) indicates the formation of a 1:1 complex.

Scott's method was applied to this system at  $\lambda_{\max}$  ( $253.5 \text{ m}\mu$ ). In the range of concentrations studied (including that of  $HClO_4$ ), the salt effect on  $K_{IBr_2^-}$  is very small,<sup>8</sup> and so no effort was taken to keep the ionic strength constant.

The apparent extinction coefficient  $\epsilon_{\max}$  is defined as the ratio between the observed absorbance and the total halogen concentration, as determined by its final conversion to  $I_3^-$  (see Experimental).  $IBr$  decomposes to  $I_2 + BrI_2$ ; furthermore, it appears that the  $IBr$  used was mixed with excess of  $I_2$ . At low  $Br^-$  concentration only the  $IBr$  is complexed, while at high concentrations the  $I_2$  is also converted to  $IBr_2^-$ , and indeed, a relatively high concentration of  $Br^-$  ( $>0.1 \text{ M}$ ) was required for  $\epsilon_{\max}$  to reach its saturation value though the stability constant of  $IBr_2^-$  is quite large. This explains the behavior of the system as displayed in Fig. 5: the extinction coefficient derived from the slope of the line ( $\sim 3.5 \times 10^4$ ) is much smaller than that

(7) R. L. Scott, *Rec. trav. chim.*, **76**, 787 (1956).

(8) A. E. H. Appelman, *J. Phys. Chem.*, **65**, 324 (1961).

TABLE II  
 SPECTROSCOPIC AND THERMODYNAMIC DATA FOR SOME POLYHALIDES IN SOLUTIONS<sup>a</sup>

Complex	$h\nu_{\max}$ , kcal.	$\epsilon_{\max}$ , $10^4 M^{-1} \text{ cm.}^{-1}$	$K$ , $M^{-1}$	$\Delta H_f$ , kcal.
$I_2Br^-$	106, <sup>b</sup> 108, <sup>c</sup> 102 <sup>d</sup>	4.4, <sup>b</sup> 3.54, <sup>c</sup> 4.06 <sup>d</sup>	10.5, <sup>b</sup> 14.9 <sup>e</sup>	-1.37, <sup>b</sup> -1.48 <sup>e</sup>
$IBr_2^-$	113, <sup>b,e</sup> 112 <sup>d</sup>	5.5, <sup>b</sup> 5.04, <sup>c</sup> 5.4 <sup>d</sup>	480, <sup>b</sup> 444 <sup>f</sup>	-10.8 <sup>b</sup>
$IBrCl^-$	122.5, <sup>b</sup> 121 <sup>d</sup>	3.87 <sup>e</sup>	43.5 <sup>g</sup>	
$I_2Cl^-$ <sup>h</sup>	115	1.0	5	+1.0

<sup>a</sup> For some early data see "Stability Constants," Part 2, Chemical Society, London, 1958. <sup>b</sup> Present work (20°). <sup>c</sup> See ref. 2, 25°. <sup>d</sup> A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, **77**, 3724 (1955) (in acetonitrile). <sup>e</sup> See ref. 3. <sup>f</sup> See ref. 8 (21°). <sup>g</sup> J. H. Faull, *J. Am. Chem. Soc.*, **56**, 522 (1934) (25°). <sup>h</sup> See ref. 1.

obtained at high concentration of  $Br^-$  ( $5.5 \times 10^4$ ) and it varies with temperature. However, the derived value of  $K_{IBr_2^-}$  (determined from the ratio between the slope and intercept of the line) does not depend on the concentration of  $IBr$ . At 20°  $K_{IBr_2^-} = 480 M^{-1}$ . Figure 4 includes the van't Hoff plot for  $IBr_2^-$ , from which we derived  $\Delta H_f = -10.8$  kcal.

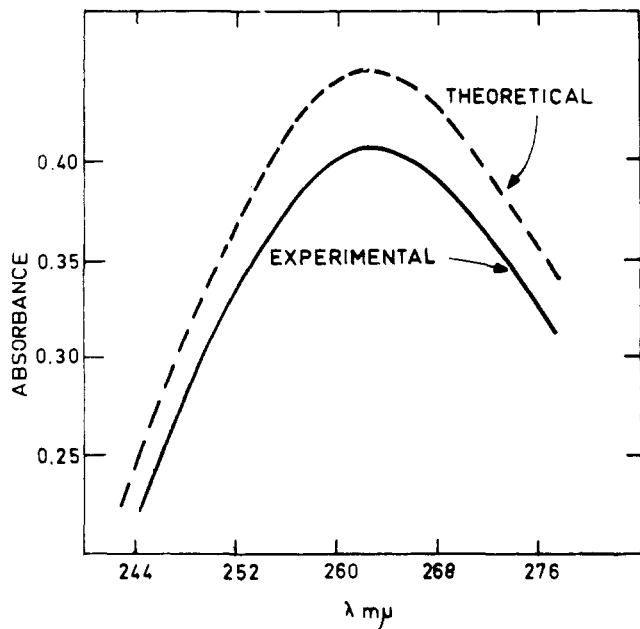


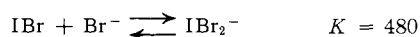
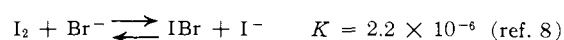
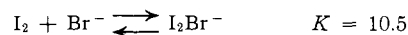
Fig. 6.—The theoretical and experimental spectra of a solution containing  $3 \times 10^{-2} M$  NaBr,  $3.03 \times 10^{-5} M$   $I_2$ , and  $2 \times 10^{-2} M$   $HClO_4$  at 20°.

**The System  $IBr + NaCl + HClO_4$ .**—This system was studied for obtaining the spectrum of  $IBrCl^-$  and its comparison with that of  $IBr_2^-$ . The spectrum was measured against a reference solution containing the same concentrations of  $HClO_4$  (10  $M$ ) and  $IBr$ . It is recorded in Fig. 1 on an arbitrary scale.

### Discussion

Table II summarizes the present and some previous results. Our result for  $K_{IBr_2^-}$  is in good agreement with some previous results, which were derived by a distribution-between-two-phases method. On the other hand, our result for  $I_2Br^-$  is appreciably lower than those derived before by a few methods, including spectrophotometric. This is probably because all early works ignored the presence of  $IBr_2^-$  in the  $I_2 + Br^-$  system.

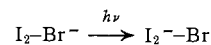
As a check for the validity of our results and interpretation, we constructed the theoretical absorption band for an arbitrary mixture of  $I_2$  and  $Br^-$  at 20°. The following equations were used



$$(I_2)_0 = (I_2) + (I_2Br^-) + (IBr_2^-) + (IBr)$$

(since  $(I^-) = (IBr_2^-) + (IBr)$ ). Assuming that  $(IBr) = 0$ , the equations can be easily solved to give the concentrations of the light absorbing species,  $I_2Br^-$  and  $IBr_2^-$ . The absorbance at any wave length is then simply  $D = \epsilon_{I_2Br^-} \cdot (I_2Br^-) + \epsilon_{IBr_2^-} \cdot (IBr_2^-)$ . Figure 6 presents the theoretical and experimental spectra for a mixture of 0.03  $M$  NaBr,  $3.03 \times 10^{-5} M$   $I_2$ , and 0.02  $M$   $HClO_4$  (to prevent hydrolysis). The theoretical band is more intense by about 10% than the experimental one, but both display nearly the same  $\lambda_{\max}$  (263  $m\mu$ ). This seems to us a rather satisfactory agreement.

It was already shown<sup>1</sup> that  $I_2Br^-$  may be considered as a charge-transfer complex and its spectrum to originate from an internal electronic transition of the donor-acceptor type



A similar interpretation may be given to the structure and spectra of  $IBr_2^-$  and  $IBrCl^-$ , where the acceptor is probably  $IBr$ , and indeed the difference between the transition energies of these two complexes ( $\sim 9$  kcal.) is the same as between that of  $I_2Cl^-$  and  $I_2Br^-$  (see Table II). Considering the transition energies of the two pairs  $I_2Br^- - IBr_2^-$  and  $I_2Cl^- - IBrCl^-$ , it appears that the vertical electron affinity of  $I_2$  is *ca.* 7 kcal. larger than that of  $IBr$ . [A somewhat larger difference ( $\sim 10$  kcal.) results from the spectra of the complexes of  $I_2$  and  $IBr$  with pyridine, 2-picoline, and 2,6-lutidine.<sup>9</sup>] Thus, in both  $IBr_2^-$  and  $IBrCl^-$ , the halide ions ( $Br^-$  and  $Cl^-$ ) are attached to the same atom, probably the iodine atom of  $IBr$  which acts as its positive pole. This was already suggested before from a free energy consideration.<sup>10</sup> X-Ray study of solid  $IBrCl^-$  salt has already shown that the  $Cl^-$  ion is attached to the iodine atom.<sup>11</sup>

(9) A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957).

(10) R. L. Scott, *ibid.*, **75**, 1550 (1953).

(11) R. C. L. Mooney, *Z. Krist.*, **98**, 324 (1937). We are indebted to the referee for drawing our attention to the X-ray work.