

under these conditions to approach a state of equilibrium in which approximately 20% conversion to the unstable benzalacetophenone diiodide has occurred. There is evidently also a very slow permanent consumption of iodine, but a mixture similar to that described above did not yield any detectable quantity of an iodinated benzalacetophenone after it had been allowed to stand for one week.

**(B) Attempted Preparation of  $\alpha$ -Iodobenzalacetophenone.**—To a solution of 10 g. (0.048 mole) of benzalacetophenone and 25 g. (0.1 mole) of iodine in 100 ml. of methanol, 18.0 g. (0.178 mole) of triethylamine was added. The reaction mixture was allowed to stand for more than two days, then diluted with water to precipitate an oil. Following extraction with sodium thiosulfate solution to remove unchanged iodine, a portion of the oil was treated with excess morpholine. The formation of  $\alpha,\beta$ -dimorpholinobenzylacetophe-

none could not be detected. From another portion of the oil a quantity of unchanged benzalacetophenone was easily separated, but no other pure product could be found.

A solution was then prepared containing 10 g. (0.048 mole) of benzalacetophenone, 12.2 g. (0.048 mole) of iodine and 8 g. (0.059 mole) of sodium acetate trihydrate in 80 ml. of 95% ethanol. The iodine color did not fade from the solution during an 18-hour period of heating under reflux. The mixture was cooled and diluted with an aqueous sodium thiosulfate solution to remove iodine and precipitate the ketone, which separated as an oil, then solidified. Recrystallization of this solid yielded 9.8 g. of pure, unchanged benzalacetophenone.

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## The Interaction of Iodine and Bromine with Organic Halides

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Solutions of iodine or bromine in organic iodides or bromides display pronounced light absorption in the 300–350  $m\mu$  region. This intense absorption, which is lacking in the spectra of halogens in solvents such as carbon tetrachloride or heptane, is regarded as characteristic of a 1:1 molecular complex. Equilibrium constants for the formation of a number of these organic halide–halogen complexes have been calculated from spectrophotometric data.

In recent publications<sup>1</sup> experimental evidence for the formation of 1:1 complexes between silver ion and certain organic iodides and bromides has been presented. Both iodine and silver ion show a pronounced tendency to form addition complexes with electron donor type reagents. It has therefore seemed desirable to investigate the possibility that iodine and also bromine, as well as silver ion, might form coordination complexes with organic halides. The results of a study of the ultraviolet absorption spectra of solutions of these halogens and various organic halides indicate that such complexes are formed. The spectrophotometric data have been used to evaluate equilibrium constants for the coordination reactions.

### Experimental

**The Organic Halides.**—Samples of the various halides used in this work were prepared by drying and fractionating available Eastman Kodak Co. white label products. The iodides were washed with sodium thiosulfate solution before fractionation to remove traces of iodine. Isopropyl iodide (b.p. 88.2–89.0°) was prepared from isopropyl alcohol and hydriodic acid.<sup>3</sup>

**Solvents.**—Eastman Kodak Co. white label carbon tetrachloride was used without purification. The "heptane" was Skellysolve C which had been rendered optically pure by two washings with fuming sulfuric acid followed by washings with water and dilute sodium hydroxide solution. The dried product distilled from 92–97°.

**The Absorption Spectrum Measurements.**—Solutions (about 0.05 *M*) of the halogens in carbon tetrachloride or heptane were prepared and equilibrated to 25° before standardization. The more dilute halogen solutions used in the spectrum measurements were prepared from these solutions by volumetric procedures. Weighed samples of the organic halides were diluted to known volumes at 25° with either carbon tetrachloride or heptane. Known volumes of the

halogen and the organic halide solutions were mixed for measurement on the Beckman spectrophotometer. In each case the blank cell contained a carbon tetrachloride or heptane solution of organic halide of the same concentration as that of the solution being measured. Glass stoppered absorption cells were used, and the cell housing was maintained at 25°. All extinction coefficients,  $\epsilon$ , which are reported in Figs. 1 and 2 are related to the measured optical densities by the expression  $d = \epsilon lc$  where  $l$  is the light path length in cm. and  $c$  is the concentration of halogen in moles/liter.

### Results

In heptane or carbon tetrachloride, so called "normal" solvents, iodine gives a violet colored solution. Alkyl iodide solutions of iodine display the brown color which is generally regarded as indicative of halogen–solvent interaction.<sup>2b</sup> Alkyl bromide–iodine solutions are less brown than the iodide solutions, and in a solvent such as *t*-butyl chloride iodine is pinkish violet. These color gradations are qualitatively indicative of the relative tendencies for organic halide–iodine interaction. Such color gradations are not markedly apparent for bromine solutions of these halides.

The ultraviolet absorption spectra of iodine or bromine solutions of organic halides, Figs. 1 and 2, can be used to determine the extent to which these interactions occur. Curve IV of Fig. 1 gives the spectrum of a solution of iodine in heptane. A solution of iodine in carbon tetrachloride shows a spectrum almost identical with that of the heptane solution. The spectrum of iodine in *t*-butyl chloride is also very similar to that of iodine in the normal solvents except for a slight shift of the visible maximum toward the ultraviolet (525 to 498  $m\mu$ ). However, solutions of iodine in *n*-butyl bromide (curve II) and *t*-butyl iodide (curve I) show, in addition to the slight shift of the visible maximum, marked absorption in the region of 280–360  $m\mu$ . In normal solvents iodine shows very little absorption at these wave lengths.

Bromine in methyl iodide (Fig. 2, curve II) shows a pronounced increase in the intensity of ab-

(1) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **73**, 3113 (1950); **73**, 5733 (1951).

(2) (a) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938); (b) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); (c) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); (d) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 458 (1952).

(3) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 283.

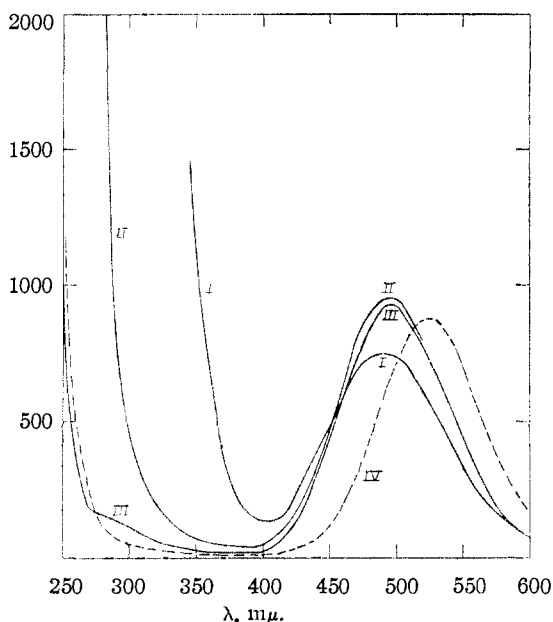


Fig. 1.—The absorption spectrum of iodine in various solvents: curve I, in heptane and *t*-butyl iodide, ( $I_2$ ) =  $1.78 \times 10^{-4} M$ , (BuI) =  $0.819 M$ ; curve II, in carbon tetrachloride and *n*-butyl bromide, ( $I_2$ ) =  $1.63 \times 10^{-4} M$ , (BuBr) =  $7.71 M$ ; curve III, in heptane and *t*-butyl chloride, ( $I_2$ ) =  $1.48 \times 10^{-3} M$ , (BuCl) =  $7.53 M$ ; curve IV, in heptane, ( $I_2$ ) =  $1.31 \times 10^{-3} M$ .

sorption in the  $350 m\mu$  region which is lacking in the spectrum of bromine in carbon tetrachloride (curve I). In *n*-butyl bromide solutions (curve III) the enhanced ultraviolet absorption of bromine becomes noticeable at about  $290 m\mu$ . The position of the visible bromine absorption peak is not markedly different for these different solvents.

Since the organic halides, particularly the iodides, absorb strongly in the ultraviolet region it was necessary to work with dilute solutions of the alkyl halides (0.1 to 1 *M*) and at wave lengths much higher than those of the ultraviolet absorption maxima for the complexes. The equilibrium constants reported in Table I were calculated from the optical densities, measured at several different wave lengths (in the region  $330$ – $370 m\mu$ ), of 0.1 to 1 *M* organic halide solutions containing iodine or bromine. Carbon tetrachloride and heptane were used as solvents. The results of studies on toluene-iodine solutions are also recorded in Table I for comparative purposes.

In calculating the equilibrium constants for the formation of the 1:1 complex,  $X_2 \cdot RX$ , it was assumed that the optical densities,  $d$ , measured at any given wave length were related to the complex and free halogen concentrations by the expression

$$\log_{10} I_0/I = d = (X_2 \cdot RX)\epsilon_c l + (X_2)\epsilon_{X_2} l$$

or

$$d_c = d - (X_2)\epsilon_{X_2} l = (X_2 \cdot RX)\epsilon_c l \quad (1)$$

where  $\epsilon_c$  and  $\epsilon_{X_2}$  represent the extinction coefficients, respectively, of the complex and of free halogen and  $l$  is the light path length in cm.

Using equation (1) and the equilibrium constant for formation of the complex according to equation (2)

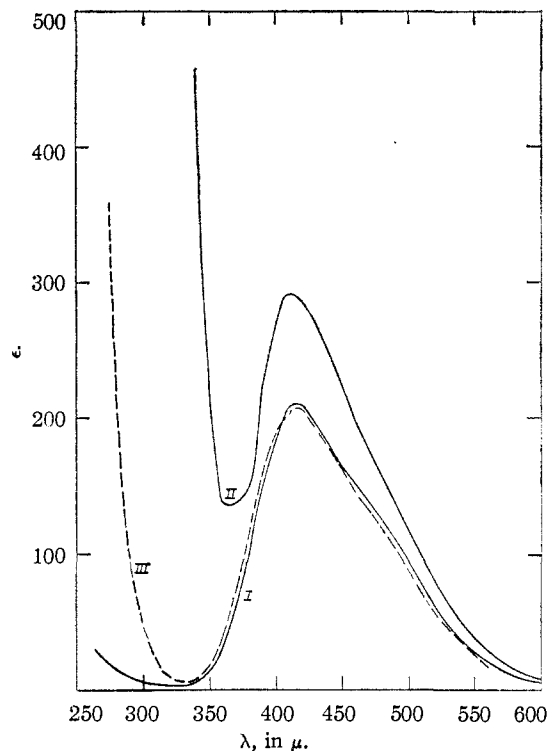
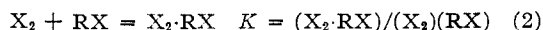


Fig. 2.—The absorption spectrum of bromine in various solvents: Curve I, in carbon tetrachloride, ( $Br_2$ ) =  $0.0126 M$ ; Curve II, in carbon tetrachloride and methyl iodide, ( $Br_2$ ) =  $7.57 \times 10^{-4} M$ , (MeI) =  $1.05 M$ ; Curve III, in carbon tetrachloride and *n*-butyl bromide, ( $Br_2$ ) =  $7.57 \times 10^{-4} M$ , (BuBr) =  $0.945 M$ .

it may be shown that

$$\frac{A}{d_c} = \frac{1}{K\epsilon_c} \times B + \frac{1}{\epsilon_c} \quad (3)$$

where  $A$  and  $B$  represent, respectively,  $(X_2)_i \cdot (RX)_i l / ((X_2)_i + (RX)_i - (X_2 \cdot RX))$  and  $1 / ((X_2)_i + (RX)_i - (X_2 \cdot RX))$  and where  $(X_2)_i$  and

TABLE I

EQUILIBRIUM CONSTANTS (25°) FOR THE FORMATION OF ALKYL HALIDE-HALOGEN COMPLEXES

Methyl iodide- $I_2$ in heptane			Ethyl iodide- $I_2$ in heptane		
$\lambda$	$K$	$\epsilon_c$	$\lambda$	$K$	$\epsilon_c$
330	0.22	6750	335	0.37	6150
335	.23	4600	340	.37	4400
345	.23	2300	345	.34	3350
Isopropyl iodide- $I_2$ in heptane			<i>t</i> -Butyl iodide- $I_2$ in heptane		
345	0.44	4400	355	1.33	1850
350	.43	3150	360	1.32	1350
360	.43	1600	370	1.34	720
<i>n</i> -Butyl bromide- $I_2$ in heptane			Ethyl iodide- $I_2$ in $CCl_4$		
261	0.25	12000	340	0.29	6350
265	.20	10500	345	.28	4700
270	.18	6200	350	.29	3200
Toluene- $I_2$ in $CCl_4$			Methyl iodide- $Br_2$ in $CCl_4$		
340	0.16	5250	330	0.07	13000
350	.15	3000	335	.07	9500
360	.15	1600	340	.06	7700

$(RX)_i$  represent molar concentrations of halogen and of organic halide both in the free and complexed state. Then if equation (4) fits the data, plots of  $A/d_c$  values for any given wave length against the corresponding values of  $B$  should give straight lines.

In treating the experimental data by this procedure it was found for all cases reported that values of  $(X_2 \cdot RX)$  were negligible compared to  $(X_2)_i + (RX)_i$ . Values of  $d_c^A$  were calculated from equation (1) by assuming as a first approximation that the free halogen concentration in the complex solutions was the same as the total halogen concentration. Tentative  $K$  values were then determined from the linear plots of the data (equation 3). Using these  $K$  values the concentration of uncomplexed halogen was determined, and corrected values of  $d_c$  were evaluated. These were used to calculate the  $K$  and  $\epsilon_c$  values reported in Table I.

Although the spectrum of bromine in carbon tetrachloride solutions of *n*-butyl bromide shows an indication of halogen-organic halide interaction, the equilibrium constant is very small and cannot be evaluated by the procedures described here.

**The Relative Stabilities of the Complexes.**—The equilibrium constants for formation of the alkyl iodide-iodine complexes in heptane solution decrease with change in the structure of the alkyl group in the order *t*-butyl > *i*-propyl > ethyl > methyl. This stability series is the reverse of that for the relative inductive effects of the alkyl groups. It therefore seems likely that the halogen molecules function as electron acceptors in these interactions. A structure for the complexes based on a resonance hybrid of  $R:\ddot{X}:\ddot{X}:\ddot{X}$  and related electronic forms appears reasonable. The spatial geometry of the complexes may be similar to that proposed by Pauling<sup>5</sup> for trihalide ions.

Inspection of Table I reveals several other points of interest. The equilibrium constants for formation of the ethyl iodide-iodine complexes in heptane and in carbon tetrachloride solutions are of the

(4) In the wave length region 260 to 420  $m\mu$ , iodine in carbon tetrachloride or heptane solutions does not obey Beer's law. Through this range the extinction coefficient of iodine is given by  $\epsilon_{12} = \epsilon_0 + k(I_2)$  where  $\epsilon_{12}$  refers to the extinction coefficient of iodine,  $\epsilon_0$  is the extrapolated value of  $\epsilon_{12}$  at zero iodine concentration and  $k$  is a constant. Values of  $\epsilon_{12}$  used in eq. 1 to calculate  $d_c$  values were estimated from the above equation.

(5) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 111.

same order of magnitude. Bromine shows less tendency for complex formation than does iodine, but the equilibrium constant for the *n*-butyl bromide-iodine reaction is of about the same order of magnitude as that for the interaction of iodine with alkyl iodides. It should be noted, therefore, that the equilibrium constants reported previously for double bond interaction of 1-bromopropene and iodine<sup>2d</sup> may in part reflect organic bromide-halogen interaction. Experimental evidence suggesting organic halide-halogen interaction in solutions of bromine in bromo- and iodobenzenes has previously been reported.<sup>6</sup> It is doubtful that aromatic halides show as pronounced a capacity for interaction with halogen as do the alkyl halides. The organic iodides form complexes with iodine which are in general more stable than the iodine-toluene complex.

An attempt was made to locate the ultraviolet absorption maximum for the ethyl iodide-iodine complex by making measurements on a very dilute ethyl iodide solution ( $8.18 \times 10^{-3} M$  ethyl iodide and  $9.27 \times 10^{-4} M$  iodine in carbon tetrachloride). This solution was measured down to a lower wave length limit of 283  $m\mu$  against a blank solution of the same ethyl iodide concentration.

The free iodine concentration of this solution was calculated using the experimentally determined value of the equilibrium constant ( $K = 0.29$ ) for iodine-ethyl iodide interaction. Using the known extinction coefficients for iodine in carbon tetrachloride the measured optical densities were then corrected to represent only the absorption of the complex. The corrected readings were small and gave no sure indication of a true maximum. However the corrected densities were reasonably constant in the 300-283  $m\mu$  region (varying from 0.069 to 0.066), an indication that the absorption curve shows a plateau at these wave lengths. The extinction coefficient of the complex in the region of the plateau was estimated to be of the order of magnitude of  $3 \times 10^4$ . It is of interest to recall that aqueous triiodide ion solutions show an absorption maximum at 289  $m\mu$  with an extinction coefficient of 35000.<sup>7</sup>

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(6) R. M. Keefer and L. J. Andrews, *THIS JOURNAL*, **72**, 4677 (1950).

(7) Custer and Natelson, *Anal. Chem.*, **21**, 1005 (1949).