computed according to equation 1 and according to the limiting law 2 practically coincide.

The same method of subtracting the heat capacity contributions of the 2 Na oscillators, when applied to the heat capacity of glassy anhydrous tetraborate according to the data of the same paper by Westrum and Grenier and for the same value of $\theta_{Na} = 256°$, yields points which do not fall on a straight line, as is evident from Fig. 2.

Moscow, U.S.S.R.

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

A Spectrophotometric Study of the Interaction of Bromine with Tetrakis-(*p*-methoxyphenyl)-ethylene[1]

BY ROBERT E. BUCKLES AND W. DALE WOMER

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When mixed with bromine in ethylene chloride tetrakis-(*p*-methoxyphenyl)-ethylene (TAE) gave a blue solution immediately. This solution had an absorption peak at 575 mμ which was not characteristic of bromine nor of TAE. Standing produced a new absorbing species (490 mμ). Both of these species acted as if they were complexes in that the bromine was easily removed from each by copper. Less easily removed was bromine held by a third species which was in equilibrium with the complexes. An equilibrium constant (based on concentration) of $(6.8 \pm 0.5)10^2$ l. per mole was measured for the formation of the blue complex in ethylene chloride at 26°. The value for this equilibrium constant increased as the temperature was lowered. No changes in spectra were observed when TAE was mixed with bromine in dilute solutions in carbon tetrachloride. In ethylene chloride other tetraarylethylenes failed to give instantaneous spectral changes when mixed with bromine.

Donor-acceptor complexes[2] have generally come to be accepted as the most useful description of the type of interaction which characterizes the solutions of iodine in the so-called "brown" solvents.[3] Of particular interest has been the interaction of halogens with aromatic compounds.[4] Considerable data have been accumulated in connection with the shifts in the visible and ultraviolet absorption spectra and with the equilibrium constants associated with the formation of the complexes.[5] Also, observations which support the formation of donor–acceptor complexes have been made concerning changes in the infrared spectra[6] and in the dipole moments[7] which accompany solvent interaction with halogens. Consistent with the view that the interaction of halogens with arylethylenes as electron donors gives rise to complexes are the observations reporting the formation of colored solutions,[8] colored, salt-like solids[8e–g] and conducting solutions.[8g]

The present investigation involves the changes in the visible and ultraviolet absorption spectra of tetrakis-(*p*-methoxyphenyl)-ethylene (tetraanisylethylene or TAE) on interaction with bromine.

A solution of TAE in ethylene chloride in the presence of bromine turned blue immediately as had been reported[8a,e] for this interaction. This sort of change is presumed to involve complex formation. As shown in Fig. 1, these blue solutions of TAE with bromine in ethylene chloride also underwent slow changes and the blue color (575 mμ) gradually disappeared as the peak characteristic[9] of the conjugated double bond (330 mμ) also disappeared. At the same time a new peak appeared at 490 mμ. A second complex apparently was formed as a result of a slow but favorable equilibrium with the first complex. Copper powder removed this new peak from the solution. If the copper was kept in contact with the solution for only a short time the resulting solution contained a third absorbing species with a spectrum the same as that of the second complex, within experimental error, except that the peak at 490 mμ was removed. This third species may have been a third complex or the dibromide of TAE. In any event the solution turned yellow on standing. The peak at 490 mμ was again observed in the spectrum but the rest of the spectrum was the same as before the 490 mμ peak returned. Thus, the third complex (or dibromide) was in slow equilibrium with the second complex. Finally all changes could be wiped out and the spectrum of the solution returned to that characteristic of the original ethylene by extended treatment with copper powder. This solution had the spectrum characteristic of the blue complex when mixed with a fresh portion of bromine solution.

This behavior of TAE with bromine to form a blue complex immediately and a yellow complex more slowly is reminiscent of the complexes re-

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[1] From the Ph.D. Thesis of W. Dale Womer. This investigation was sponsored by the Office of Ordnance Research, U. S. Army.

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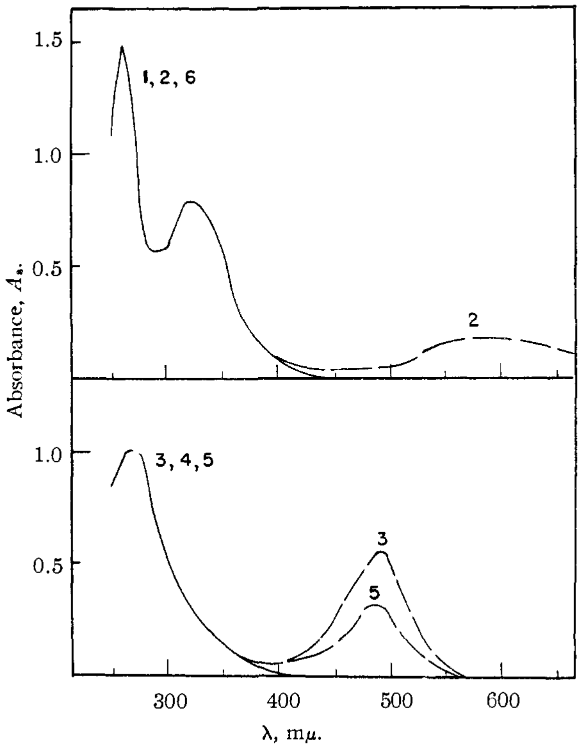

Fig. 1.—The absorption spectra of tetrakis-(*p*-methoxyphenyl)-ethylene TAE with bromine in ethylene chloride under various sets of conditions. The cells had path lengths of 1.00 cm. Pure solvent was used as a blank. In each case the initial concentration of TAE was 5.0×10^{-6} *M* and that of bromine was 2.5×10^{-4} *M*, except for curve 1 when no bromine was present. For 2 the spectrum was taken on a freshly mixed solution. For 3 the solution was allowed to stand 8 days. For 4 the solution of curve 3 was shaken with copper powder for 3 hr. and the spectrum taken immediately. For 5 the solution of curve 4 was allowed to stand 8 hr. For 6 any of the solutions with copper powder for 4 days gave curve 6 essentially the same as curve 1.

ported[10] between dianisylethylene and trichloroacetic acid. In that case, however, the complex which absorbed at shorter wave lengths (498 mμ) was formed rapidly and the complex which absorbed at longer wave lengths (680 mμ) was formed more slowly.

The type of changes in absorption spectrum associated with the addition of halogen to the double bond of a tetraarylethylene is illustrated by the spectrum of 1,2-dichloro-1,1,2,2-tetraphenylethane. This compound showed very little absorption (a_m was no greater than 340) in the neighborhood of 300 mμ and at higher wave lengths. At shorter wave lengths the absorbance increased sharply. Tetraphenylethylene on the other hand is reported[11] to have an absorption peak of $a_m = 1.42 \times 10^4$ at 312 mμ. Also two derivatives of TAE brominated on the rings, tetrakis-(3-bromo-4-methoxyphenyl)-ethylene and tetrakis-(3,5-dibromo-4-methoxyphenyl)-ethylene, each had the relatively intense absorption peak around 325 mμ which is characteristic of the conjugated double bond.[9,11] Thus, bromination of the rings of TAE did not affect the general pattern of the ultraviolet spectra. Neither of these brominated compounds showed a change in spectrum characteristic of complex formation with bromine in ethylene chloride as TAE did, however. A qualitative observation of this sort has been reported[8e] with tetrakis-(3-chloro-4-methoxyphenyl)-ethylene. The halogens on the ring either shifted the absorption peak of the complex to a region where it could not be measured or they decreased the tendency of the complex to form so that its concentration was too low for measurement.

Eleven other arylethylenes (listed in the Experimental Part) also failed to exhibit immediate spectral changes characteristic of complex formation with bromine in ethylene chloride. Most did undergo changes on standing with bromine which were somewhat similar to the results with TAE on standing in that the conjugation peak around 330 mμ was lowered. The investigations were not carried past the preliminary stages, however.

Dilute solutions of TAE in carbon tetrachloride containing as much as 100 times as much bromine (on a molar basis) had spectra characteristic only of the TAE and the bromine. No spectral evidence for complex formation was observed. Mixed solvents containing varying amounts of carbon tetrachloride and ethylene chloride also were used in qualitative experiments. It was found that when solutions with much less than 50% ethylene chloride by weight were used the extent of complex formation was too small to be measured spectrophotometrically. Thus, effective complex formation appeared to be dependent upon the polarity of the ethylene chloride and not on a specific reaction with this solvent.

At the low concentrations used for the observation of complex formation in ethylene chloride, the spectrum of bromine (411 mμ, a_m 206)[12] could not be observed effectively except when a large excess was used. Because of extensive absorption by TAE and the complexes, the characteristic[13] absorption peak of tribromide ion at 273 mμ could not be observed either. Thus, ionization of one of the complexes could not be established spectrophotometrically. Correlation of absorption spectra with electrical conductance will be necessary in order to clarify this point.

The equilibrium constants for the formation of the complex of TAE with bromine in ethylene chloride were measured spectrophotometrically at four temperatures ranging below room temperature. Equation 1 was used at room temperature (26°) to calculate K_c for solutions with bromine in excess. This equation is an adaptation of that suggested by Scott.[14] Since the values of the constants were relatively large compared with those usually found for complexes of this sort and since the concentrations were relatively small, either a combination of equations 1 and 2 or equation 3 could be used to calculate K_N. In these equations K_c and K_N are the equilibrium constants based on molar concentrations and mole fractions, respectively, C_x

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and N_x are the concentration and mole fraction of bromine, C_{Bt} and N_{Bt} are the initial concentration and initial mole fraction of the arylethylene, b is the path length of the cell, a_C is the molar absorbancy index (molar extinction coefficient) of the complex, A_S is the absorbance (optical density) of the solution and V_S is the molar volume of the solvent.

In each case the equilibrium constant obtained was based on the formation of a 1:1 complex. The values at 26° were essentially constant over an 800-fold change in concentration in bromine and a 10-fold change in the concentration of TAE.

$$\frac{C_x C_{Bt} b}{A_S} = \frac{C_x}{a_C} + \frac{1}{K_C a_C} \qquad (1)$$

$$K_C = V_S K_N \qquad (2)$$

$$\frac{N_x N_{Bt} b}{A_S} = \frac{V_S N_x}{a_C} + \frac{V_S}{K_N a_C} \qquad (3)$$

In Table I are listed the values of K_C and a_C obtained at various wave lengths, at 26°. The average value for K_C from 74 measurements was $(6.79 \pm 0.53)10^2$ liters per mole where the precision sets the 95% confidence limits of the average. In Table II are given values of K_N at various temperatures. From these data ΔH for the complex formation was calculated to be -9.56 ± 0.64 kcal./mole; $\Delta F°_{26}$ was -5.38 ± 0.05 kcal./mole; and $\Delta S°_{26}$ was -14.0 ± 2.1 cal./degree mole. The precision in each case sets the 95% confidence limits of the values.

TABLE I

EQUILIBRIUM CONSTANTS FOR THE FORMATION OF A 1:1 COMPLEX BETWEEN TAE AND BROMINE IN CARBON TETRACHLORIDE AT 25°

$K_C \times 10^{-2}$	λ, mμ	$a \times 10^{-4}$
6.14	575	2.04
6.46	586	1.91
6.54	600	1.82
6.99	612	1.69
7.34	625	1.55
7.27	650	1.39

TABLE II

EQUILIBRIUM CONSTANTS FOR THE FORMATION OF THE 1:1 COMPLEX BETWEEN TAE AND BROMINE IN ETHYLENE CHLORIDE AT VARIOUS TEMPERATURES

The precision sets the 95% confidence limits of the values.

Temp., °C.	$K_N \times 10^{-4}$
26.0 ± 0.4	0.854 ± 0.067
2.5 ± .2	3.72 ± 0.52
−11.5 ± .3	7.7 ± 2.7
−17.5 ± .3	14.1 ± 4.6

The formation constants observed for TAE are higher than those reported[5] for other aromatic compounds. The reaction appears to be more exothermic and the standard entropy of reaction has a higher negative value as well. The values appear to be quite comparable to those reported[2d] for the iodine–pyridine complex in hexane. The spectrum of the complex differs from those reported for these cases, however, in that the peak is at a higher wave length (575 mμ)—higher in fact than the wave lengths of the peaks associated with either TAE or bromine. The usual charge transfer spectrum[2] associated with donor–acceptor complexes of the aromatic compounds with halogens has an intense absorption peak in the range from 200 to 300 mμ. In fact if this peak at 575 mμ is a charge transfer peak it would be correlated[15] with a relatively low ionization potential (around 6 e.v.) for TAE.

Experimental Part

Tetrakis-(*p*-methoxyphenyl)-ethylene (TAE).—A mixture of 24 g. (0.10 mole) of 4,4′-dimethoxybenzophenone and 8.5 ml. (12.7 g., 0.10 mole) of oxalyl chloride was allowed to react at room temperature for 30 minutes. The reaction mixture was then heated to about 80° to ensure removal of the carbon dioxide and carbon monoxide. The dichloride formed was not isolated but was dissolved in 100 ml. of benzene and heated under reflux with excess copper bronzing powder for 2 hr. The reaction mixture was filtered and the filter cake was washed several times with hot benzene. The combined benzene solution was concentrated by distillation. A yield of 20.4–21.5 g. (90–95%) of the TAE, m.p. 183–184°, was obtained after crystallization from the benzene solution. Only 4–6% of the product could be obtained when phosphorus pentachloride was used for the synthesis of the dichloride from 4,4′-dimethoxybenzophenone. Only the copper bronzing powder used in gilt paints was satisfactory. All other types of powdered copper gave little or no product. The method of preparation of the dichloride is an adaptation of one in the literature.[16] In that case the TAE was prepared by the action of mercury on the dichloride.

Tetrakis-(*p*-hydroxyphenyl)-ethylene.—A solution of 2.5 g. (0.0056 mole) of TAE and 25 ml. of 57% hydriodic acid in 200 ml. of glacial acetic acid was boiled under reflux for 4 hr. Steam distillation removed the acetic acid and the hydriodic acid. The crude product (2 g.) was separated from the residue by filtration. Crystallization was carried out in aqueous methanol. Additional crops were obtained by concentration of mother liquors. The total yield was 1.0 g. (45%) of product of m.p. above 335°. This product had properties consistent with those reported.[17]

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.8; H, 5.08. Found: C, 78.6; H, 5.34.

Tetrakis-(3,5-dibromo-4-hydroxyphenyl)-ethylene.—A solution of 2.0 g. (0.0051 mole) of tetrakis-(*p*-hydroxyphenyl)-ethylene in 15 ml. of 95% ethyl alcohol was mixed with 2.0 ml. (6.0 g., 0.033 mole) of bromine in 40 ml. of glacial acetic acid. The reaction mixture was heated gently for a few minutes and then 10 ml. of water was added. Crude tan crystals (3.6 g.) of m.p. 155–170° precipitated. Successive crystallization from aqueous methanol and then from chloroform yielded 2.5 g. (45%) of crystals, m.p. 240–242° (slight dec.). This compound appeared to be either a complex with hydrogen bromide or an addition product. Alcoholic silver nitrate gave an immediate precipitate in the cold.

Anal. Calcd. for $C_{26}H_{13}O_4Br_9$: C, 28.2; H, 1.17. Found: C, 28.3; H, 1.17.

The product was heated under reduced pressure at 100° for 24 hr. The resulting material had an m.p. of 246–247° (no dec. evident) and gave no reaction with alcoholic silver nitrate.

Anal. Calcd. for $C_{26}H_{12}O_4Br_8$: C, 30.3; H, 1.18. Found: C , 29.8; H, 0.92.

Tetrakis-(3,5-dibromo-4-methoxyphenyl)-ethylene.—Diazomethane from the action of alcoholic potassium hydroxide on 1.0 g. of N-methyl-N-nitroso-*p*-toluenesulfonamide in ether was distilled into an ether solution of 0.15 g. (1.5×10^{-4} mole) of tetrakis-(3,5-dibromo-4-hydroxyphenyl)-ethylene. The ether was evaporated and the residue crystallized from chloroform to give 0.15 g. (93%) of tetrakis-(3,5-dibromo-4-methoxyphenyl)-ethylene, m.p. 228.5–230°.

Anal. Calcd. for $C_{30}H_{20}O_4Br_8$: C, 33.2; H, 1.86. Found: C, 32.7; H, 1.73.

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Attempts to prepare either tetrakis-(3,5-dibromo-4-methoxyphenyl)-ethylene or tetrakis-(3-bromo-4-methoxyphenyl)-ethylene from the corresponding benzophenone by way of the dichloride as used for the synthesis of TAE were unsuccessful.

Direct Bromination of Tetrakis-(*p*-methoxyphenyl)-ethylene (TAE).—A solution of 9.5 g. (0.021 mole) of TAE and 22 ml. (65 g., 0.36 mole) of bromine in 600 ml. of carbon tetrachloride was boiled under reflux as it was stirred with 110 g. of calcium carbonate. The mixture was heated for 45 hr. The excess bromine was then removed by reaction with aqueous sodium thiosulfate solution. Crystallization of 7.0 g. of crude product was induced by the addition of methanol to the carbon tetrachloride solution. Four crystallizations from chloroform and absolute ethyl alcohol gave a 4.0-g. yield of a bright yellow product of m.p. 256–257°. This compound was not identical with either tetrakis-(3,5-dibromo-4-methoxyphenyl)-ethylene, or tetrakis-(3-bromo-4-methoxyphenyl)-ethylene. From its ultraviolet absorption spectrum (peaks at 282 mμ of $a_m = 3.82 \times 10^4$ and at 328 mμ of $a_m = 1.68 \times 10^4$) this compound appeared to be something other than a tetraarylethylene, but its structure was not established.

4,4′-Dimethoxy-3,3′,5,5′-tetrabromobenzophenone.—Direct bromination of 4,4′-dimethoxybenzophenone in glacial acetic acid gave a 97% yield of 3,3′-dibromo-4,4′-dimethoxybenzophenone, m.p. 174–178°.[18] Demethylation of 4,4′-dimethoxybenzophenone was accomplished by the action of 57% hydriodic acid in glacial acetic acid to give a 90% yield of 4,4′-dihydroxybenzophenone, m.p. 205–207°. This cleavage gave results similar to those carried out with aluminum bromide.[19] The dihydroxybenzophenone was brominated directly in glacial acetic acid to give an 85% yield of 4,4′-dihydroxy-3,3′,5,5′-tetrabromobenzophenone, m.p. 224–226°.[20] A solution of 3.0 g. (0.0057 mole) of this ketone in 75 ml. of methylene chloride was treated with excess diazomethane in methylene chloride. The solvent was evaporated and the residue was crystallized from chloroform–ethyl alcohol to give 3.1 g. (94%) of 4,4′-dimethoxy-3,3′,5,5′-tetrabromobenzophenone, m.p. 205–210°.

Anal. Calcd. for $C_{15}H_{10}O_3Br_4$: C, 32.3; H, 1.81. Found: C, 31.7; H, 1.85.

Arylethylenes.—The following arylethylenes were either available from earlier investigations or were synthesized by the methods described in the references: 1,1-bis-(*p*-bromophenyl)-2,2-dibromoethylene,[21] m.p. 120–121°; 1,2-bis-(*p*-bromophenyl)-1,2-dibromoethylene,[21] m.p. 234–236°; 1,1,2-tris-(*p*-bromophenyl)-2-bromoethylene,[21] m.p. 184–185°; tetrakis-(*p*-bromophenyl)-ethylene,[21] m.p. 248°; 1,2-bis-(*p*-bromophenyl)-1,2-bis-(*p*-chlorophenyl)-ethylene,[8g] m.p. 231.5°; *cis*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene,[8g] m.p. 157–158.5°; *trans*-1,2-bis-(*p*-chlorophenyl)-1,2-diphenylethylene,[8g] m.p. 205°; *cis*-1,2-bis-(4-biphenylyl)-1,2-diphenylethylene,[8g] m.p. 219°; 1,2-bis-(*p*-dimethylaminophenyl)-1,2-diphenylethylene,[8g] m.p. 217°; and 1,2-bis-(*p*-dimethylaminophenyl)-1,2-bis-(*p*-methoxyphenyl)-ethylene,[8g] m.p. 218°. 1,2-Bis-(*p*-methoxyphenyl)-1,2-diphenylethylene was synthesized as before[8g] but the m.p. obtained was 200–200.5° instead of 185–186.5°. As in the earlier investigation[8g] attempts were made to separate *cis* and *trans* isomers of the tetraarylethylenes by chromatography and fractional crystallization, but no new separations were accomplished. Tetrakis-(3-bromo-4-methoxyphenyl)-ethylene, m.p. 265–267°, was kindly supplied by Mr. R. E. Erickson and 1,2-dichloro-1,1,2,2-tetraphenylethane, m.p. 183–184°, by Dr. D. F. Knaack, both of this Laboratory.

Purification of Solvents.—The problems of obtaining pure ethylene chloride which does not react with bromine have been discussed in connection with earlier investigations.[13,22] The same general methods were applied for this work. Carbon tetrachloride was purified as described for earlier investigations.[12,23]

Spectrophotometric Measurements.—All measurements at room temperature were carried out on a Cary, Model 11, Recording Spectrophotometer in calibrated silica cells of path lengths 1.00 ± 0.01 cm. as well as in 2, 5 and 10 cm. cells of corresponding precision. Pure solvent was used in the blank cells. The qualitative observations of spectra were carried out on solutions made up with the concentration of the arylethylene about 5×10^{-5} *M* and amounts of bromine varying from 0 to 25 moles per mole of arylethylene. The solutions were allowed to stand varying lengths of time. In a number of experiments all or part of the bromine was removed when the solution was shaken with copper powder for varying lengths of time. The excess copper and the copper bromide were removed by filtration.

Although oxidizing agents have been reported[8a] to react with TAE to give colored products none of the tetraarylethylenes used changed color on extended exposure to oxygen except for those with dimethylamino groups in the *p*-positions. The extent of complex formation between TAE and bromine was not increased when oxygen was bubbled into the solution.

In the dilute solutions used for spectrophotometric measurements little or no aromatic substitution was observed. No hydrogen bromide was detected even though careful analyses were carried out. In more concentrated solutions (*e.g.*, 1 *M*) substitution was an important reaction.

Low temperature spectrophotometric measurements were carried out with a cell surrounded by a cooling chamber which was in turn surrounded by a silvered, vacuum jacket. The optical windows were of Corex glass and they were double at each end with an evacuated space between. The entire cell except for the windows was packed in vermiculite and dry nitrogen was blown into the cell compartment of the instrument. Glycol-water mixtures from a refrigerated bath were circulated through the cell. The temperature in the cell was measured with a pentane thermometer. At a bath temperature of −30° the temperature gradient between the cell and the bath was about 13°, but it was relatively constant. The path length of the cell was determined as 7.496 ± 0.003 cm. by measurements with a travelling microscope. From the absorption spectrum of standard aqueous potassium permanganate a value of 7.490 ± 0.14 cm. was obtained. The cell was best standardized against three Corex cells (5 cm., 2 cm., and 1 cm.) containing solvent. With this cell reproducible measurements of absorption spectra of solutions down to −17.5° were possible.

Measurement of Equilibrium Constants.—Stock solutions of bromine and TAE were prepared. From these and pure solvent the solutions of desired concentrations were prepared. Initial concentrations of TAE were varied from 2×10^{-5} *M* to 2×10^{-4} *M* while those of bromine were varied from 10^{-5} *M* to 8×10^{-3} *M*. The volumes of ethylene chloride were corrected for temperature changes using a linear extrapolation of the data available.[24]

Calculations of the constants at room temperatures were carried out graphically with equations 1, 2 and 3. From the molar absorbancy indices found at 26° (assumed to be temperature independent) the constants were calculated at the lower temperatures. In all 74 measurements of *K* were made at room temperature and 24 at each of the other temperatures. The heat of reaction was obtained graphically from the temperature dependence of the equilibrium constant. The standard entropy and standard free energy for the reaction at 26° were calculated from the equilibrium constant and the heat of reaction.

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