attributed to this same effect.[16] The difference in the temperature coefficients of dielectric constant of acetic acid and ethyl N-methylcarbamate is also of interest. Acetic acid shows very unusual behavior in this respect in that its dielectric constant increases slightly with increasing temperature. This can be explained as due to dissociation of the dimer in sufficient amount to counteract the effects which normally cause dielectric constant

(16) C. P. Smyth and H. E. Rogers, THIS JOURNAL, **52**, 1824 (1930); R. J. W. LeFevre, Trans. Faraday Soc., **34**, 1127 (1938).

to decrease with increasing temperature. The dielectric constant of ethyl N-methylcarbamate shows a normal decrease in dielectric constant with increasing temperature. Since the temperature coefficient of density is very nearly the same for both compounds, this may be taken to indicate little change in the degree of dissociation of the dimer of ethyl N-methylcarbamate with change in temperature, and hence a small heat content change for the dimerization process.

LEXINGTON, KY.   RECEIVED JUNE 8, 1951

The Argentation of Organic Iodides

BY L. J. ANDREWS AND R. M. KEEFER

By measurement of the solubilities in aqueous silver nitrate of the 1,2-diiodoethylenes, o- and m-diiodobenzene and methylene iodide, equilibrium constants for the formation of water soluble organic halide–silver ion complexes have been obtained. All of these iodo compounds show a marked tendency to undergo such coördination to form complexes containing either one or two silver ions, except for methylene iodide which forms only a 1:1 complex in measurable amounts. Structurally related dichlorides and dibromides are only feebly disposed to interact with silver ion. Possible structures for the several organic iodide complexes are discussed in this report.

In determining aromatic ring argentation constants by measuring the solubilities of a series of substituted benzenes in aqueous silver nitrate it was noted that iodobenzene and p-diiodobenzene showed a pronounced capacity for coördination with silver ion.[1] The argentation constants found for these compounds were considerably larger than those for benzene, while the constants for the corresponding chloro- and bromobenzenes were less than those for benzene. These observations were interpreted as an indication that in the complexes of the iodine compounds the silver ions are bonded preferentially to the iodine atoms rather than to the aromatic nucleus.

Experiments have now been performed which were designed to demonstrate that vinyl iodides and saturated iodides as well as aromatic iodides will coördinate silver ions in aqueous solution. This report presents evidence for the iodine atom argentation of cis- and trans-1,2-diiodoethylenes and of methylene iodide as based on measurements of the solubilities of these diiodides in aqueous silver nitrate.[2] The results of similar measurements on related organic chlorides and bromides and also on o- and m-diiodobenzene are reported.

Experimental

The Dihaloethylenes.—Samples of the 1,2-dichloroethylenes remaining from earlier work[3] were refractionated (trans, b.p. 47.9–48.5°; cis, b.p. 60.0°). A sample of 1,2-dibromoethylene (Eastman Kodak Co.) was distilled and a cut of b.p. 111–112°, $n^{25}D$ 1.5395 was collected. On the basis of its refractive index[4] it was estimated that this cut was approximately 35% of the trans configuration. The cis- and trans-diiodoethylenes were prepared by the methods of

previous investigators.[4,5] The trans isomer melted at 71.5–72.0° and the cis at −13°.[6]

The Halomethanes.—Methylene iodide, b.p. 71.0–71.5° (18 mm.), and methylene bromide, b.p. 96.5–98.0° (763 mm.), were prepared, respectively, from iodoform and bromoform.[7] Mallinckrodt Analytical Reagent grade chloroform was used without purification.

o- and m-Diiodobenzene.—The ortho (m.p. 23–24°) and meta (m.p. 34–35°) diiodides were prepared from Eastman o- and m-nitroaniline.[8]

The Solubility Measurements.—Saturated solutions of the several organic halides in aqueous silver nitrate solutions of varying concentrations were prepared at 25° by methods described previously.[1,9] The ionic strengths of the original silver nitrate solutions were adjusted to unity by the addition of potassium nitrate. The organic halide concentrations of these saturated solutions were determined by extracting measured volumes with known volumes of hexane and determining the halide concentrations of the hexane phases by spectrophotometric methods, using the previously devised techniques.[1,9]

Table I contains the wave length and slit width settings of the Beckman spectrophotometer used in measuring the optical densities of the hexane solutions of the halides and also contains the corresponding experimentally determined extinction coefficients of solutions of the halides in hexane. The compounds for which extinction coefficients are reported obeyed Beer's law in hexane solution in the concentration range in which analytical measurements were made.

Recovery of the Diiodoethylenes from Silver Nitrate Solution.—To check the possibility that cis–trans isomerization may have been induced when trans-diiodoethylene was dissolved in aqueous silver nitrate, 50 ml. of a saturated solution of the diiodide in 1 N silver nitrate was extracted repeatedly with a total of 50 ml. of hexane. The hexane extract was evaporated to dryness at room temperature under a stream of air. Only white needles of the trans-dihalide (m.p. 70–71°) remained as residue. The quantitative aspects of the experiment were destroyed by the

(1) Andrews and Keefer, THIS JOURNAL, **72**, 3113 (1950).

(2) Sabanejeff, Ann., **216**, 275 (1883), reported the isolation of a solid addition compound, C₂H₂I₂·4AgNO₃. Scholl and Steinkopf, Ber., **39**, 4393 (1906), obtained a solid, CH₂I₂·AgNO₃. In both compounds the silver ions presumably were coördinated with the iodine atoms.

(3) Volman and Andrews, THIS JOURNAL, **70**, 457 (1948).

(4) Cf. Noyes, Noyes and Steinmetz, ibid., **72**, 33 (1950).

(5) Noyes, Dickinson and Schomaker, ibid., **67**, 1319 (1945).

(6) Miller and Noyes, ibid., **73**, 2376 (1951), have presented evidence suggesting that this so-called "cis" isomer as prepared in this investigation is a eutectic mixture containing about 20% of the trans isomer.

(7) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 349, 350.

(8) (a) Baeyer, Ber., **38**, 2760 (1905); (b) Körner, Gazz. chim. ital., **4**, 385 (1874); (c) Körner and Wender, ibid., **17**, 491 (1887).

(9) Andrews and Keefer, THIS JOURNAL, **71**, 3644 (1949); **72**, 5034 (1950).

TABLE I

OPTICAL DATA FOR HEXANE SOLUTIONS OF THE DIHALIDES

| Compound	λ, mμ	Slit width, mm.	ϵ^d
cis-Dichloroethylene	239	1.25	4.60
trans-Dichloroethylene	240	1.20	7.85
cis-Diiodoethylene[a]	300	0.50	168
trans-Diiodoethylene[b]	280	.56	330
Dibromoethylene[c]	268	.60	.....
Methylene iodide	360	0.36	65.2
Methylene bromide	272	1.15	53.8
Chloroform	224	1.55	.....
o-Diiodobenzene	248	2.0	4800
m-Diiodobenzene	244	1.26	5650

[a] See footnote 6. [b] By hexane extraction procedures and use of the data of the table, the concentration of trans-diiodoethylene in its saturated aqueous solution at 25° was found to be 0.0169 g./100 cc. [c] cis–trans mixture, approximately 35% trans. [d] The extinction coefficient is defined by the equation $d = \log_{10} I_0/I = \epsilon l c$ where l is the light path length, 1 cm. in these studies, and c is the molar concentration of dihalide in the hexane solvent.

marked tendency of the diiodide to sublime in air during the evaporation and drying process. When first weighed the crystals totaled 0.0851 g. The spectrophotometric procedure indicated that the aqueous solution contained, before extraction, 0.141 g. of the diiodide. When a 1 N silver nitrate solution of the cis-diiodide was similarly extracted only liquid diiodide was recovered.

Results

The Argentation Constants.

—The solubilities in aqueous silver nitrate of all of the iodides which were investigated increased markedly with increasing silver nitrate concentration of the solvent. For the chlorides and bromides which were studied only small increases in solubility with increasing silver ion concentration of the solvent were observed.

The solubility data for all of the dichlorides and dibromides, as well as for chloroform were interpreted on the assumption that equilibrium (1) was established in the saturated solutions (D = dihalide).

$$Ag^+ + D = AgD^+ \quad K_1 = (AgD^+)/(Ag^+)(D) \quad (1)$$
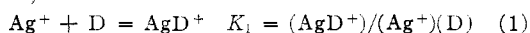
In the analytical procedure 10 ml. of the aqueous silver and potassium nitrate solutions of these halides were extracted with 10 ml. of hexane. The organic halide concentrations were then determined from the optical densities of the hexane extracts at the wave lengths specified in Table I. The K_1 values were then calculated from equation (1a) in which d_0 represents the optical density of the hexane extract of the dihalide saturated solution of 1 N potassium nitrate.

$$K_1 = (d - d_0)/d_0(Ag_t^+)$$

This equation is valid in these cases since the quantity of complexed halide in these solutions was very small.

Table II presents the K_1 values for these bromides and chlorides. The constants for the dichloro- and dibromoethylenes are very much smaller than those observed by Winstein and Lucas[10] for the double bond argentation of alkyl substituted olefins and reflect the strong inductive effects of halogen atoms on the π-electrons of double bonds to which they are attached.

(10) Winstein and Lucas, THIS JOURNAL, 60, 836 (1938).

TABLE II

ARGENTATION CONSTANTS FOR THE CHLORIDES AND BROMIDES (25°)

(Ag$_t$ $^+$) mole/liter	trans-C$_2$H$_2$Cl$_2$ d	K	cis-C$_2$H$_2$Cl$_2$ d	K	C$_2$H$_2$Br$_2$ d	K
0.000	0.264	..	0.245	..	0.266	..
.400	.301	0.35	.261	0.16	.316	0.47
.600	.313	.31	.272	.18	.346	.50
.800	...	..	...	..	.376	.52
1.000	.333	.26	.281	.15	.412	.55
Av.		0.31		0.16		0.51

	CH$_2$Br$_2$[a] d	K	CHCl$_3$ d	K
0.000	0.309	..	0.225	..
.200	.353	0.74	.233	0.2
.400	.396	.72	...	..
.600	.440	.72	.251	.19
.800	.498	.77	...	..
1.000	.540	.75	.272	.21
Av.		0.74		0.2

[a] Silver bromide precipitated very slowly during the course of saturation of the silver nitrate solutions. These data were recorded after rotating the methylene bromide with the silver solutions for seven hours, a much shorter time than is usually employed for the saturation process.

The data for the dibromoethylene sample were taken originally in an exploratory study prior to separating the pure cis and trans isomers for individual consideration. The observed degree of complex formation was, however, so small that it was deemed not worthwhile to undertake the arduous separation of isomers.

To explain the solubility data for the diiodoethylenes and for o- and m-diiodobenzene it was necessary to assume that in addition to equilibrium (1) a second equilibrium, (2), was established in these saturated solutions.

$$Ag^+ + AgD^+ = Ag_2D^{++}$$
$$K_2 = (Ag_2D^{++})/(Ag^+)(AgD^+) \quad (2)$$
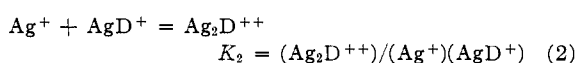
The constant K needed to determine K_1 and K_2 was evaluated from equation (3) by the same procedure used in the aromatic argentation studies.[1,9]

$$K = (D_c)/[(Ag_t^+) - (D_c) - (Ag_2D^{++})](D) = K_1 + K_1K_2(Ag^+) \quad (3)$$

where

(D_c) = the molar concentration of complexed diiodide = $(D_t) - (D)$

(D_t) = the molar concentration of all diiodide containing species

(D) = the molar concentration of free diiodide = the solubility of diiodide in 1 N potassium nitrate

(Ag_t^+) = the molar concentration of silver ion in free and complexed form

Table III presents the argentation data for these diiodides. The K values reported were calculated by use of equation (3) on the assumption that the (Ag_2D^{++}) term might be disregarded. The points obtained by plotting these constants, K, against the corresponding silver ion concentrations fit a straight line from which values of K_1 and K_2 were obtained. In the diiodoethylene solutions the Ag_2D^{++} concentrations contributed appreciably to the total silver ion concentration. Therefore, the tentative K_1 and K_2 values were used to re-

estimate the concentration of uncomplexed silver ion in the several solutions, and new K values were then calculated. These slightly modified K values were again treated graphically according to the right hand expression of equation (3) to yield K_1 and K_2 as reported in Table III.

TABLE III

ARGENTATION CONSTANTS FOR THE DIIODOETHYLENES AND THE DIIODOBENZENES (25°)

	trans-$C_2H_2I_2$		cis-$C_2H_2I_2$	
(Ag⁺) mole/ liter	(Dₜ) mole/liter × 10³	K	(Dₜ) mole/liter × 10³	K
0.000	0.527	..	1.65	..
.200	1.39	8.2	..	..
.400	2.74	10.5	16.5	23.4
.600	4.54	12.7	28.0	26.6
.800	6.99	15.5	40.5	29.6
1.000	10.09	18.1	54.1	31.8

$K_1 = 5.5$ $\quad\quad\quad$ $K_1 = 17.8$
$K_2 = 2.3$ $\quad\quad\quad$ $K_2 = 1.06$

	o-$C_6H_4I_2$		m-$C_6H_4I_2$	
	Mole/liter × 10⁴		Mole/liter × 10⁴	
0.000	0.452	..	0.293	..
.020	.625	19.1ᵃ	...	..
.080	....	...	.457	7.0
.120	....	...	.550	7.3
.160	....	...	.701	8.7
.200	2.40	21.5	.816	8.9
.400	5.14	26.0	1.71	12.1
.600	8.95	31.4	3.00	15.4
.800	13.86	37.1	5.00	20.1ᵇ

$K_1 = 16.5$ $\quad\quad\quad$ $K_1 = 5.7$
$K_2 = 1.53$ $\quad\quad\quad$ $K_2 = 2.9$

ᵃ This value appears somewhat too high when compared with K values at higher silver ion concentrations. However, the experimental error is largest for solutions of low silver ion concentration. ᵇ This K value which was confirmed by a repeat experiment lies somewhat above the best straight line drawn through the points obtained by plotting K against (Ag⁺).

The choice of saturated organic iodides suitable for these argentation studies is seriously limited by the fact that most of these compounds react rapidly with aqueous silver nitrate to precipitate silver iodide. Originally it was planned to investigate the dimethyl esters of the 9-haloanthracene-9,10-endo-succinic acids, a group of compounds which should be resistant to reaction with silver nitrate to form silver halide.[11] However, the bromo compound proved to be so insoluble in aqueous media that the spectrophotometric method of analysis used in the argentation studies could not be applied to its aqueous solutions. Therefore, plans for further study of this group of compounds were abandoned.

Methylene iodide was the only saturated iodide investigated which proved satisfactory for the argentation studies. Even this compound reacted rapidly enough with silver nitrate so that the silver nitrate concentrations of the solutions which were saturated with the iodide had to be kept small

(11) (a) Barnett, Goodway, Higgins and Lawrence, J. Chem. Soc., 1224 (1934); (b) Bartlett and Cohen, THIS JOURNAL, 62, 1183 (1940).

(0.04–0.20 M). After the reaction flasks were rotated overnight, enough silver iodide had formed so that it was necessary to analyze the aqueous phases not only for organic iodide but also for total silver ion concentration. The data taken for these solutions could be interpreted satisfactorily on the assumption that only a 1:1 complex of silver ion and the diiodide was formed. Values of K_1 calculated from the methylene iodide data using equation (1) are given in Table IV.

TABLE IV

ARGENTATION CONSTANTS FOR METHYLENE IODIDE (25°)

(Agₜ⁺)ᵃ	(Ag⁺)ᵇ	(CH₂I₂)ₜ mole/liter × 10²	K_1
0.0000	0.0000	3.11	..
.0372	.0350	5.32	20.3
.0720	.0677	7.38	20.3
.1048	.0984	9.54	21.0
.1393	.1312	11.2	19.8
.1673	.1576	12.8	19.8

Av. 20.2

ᵃ As measured by volumetric analysis at the end of the saturation period. A sample of the aqueous silver ion–diiodide solution was added to excess standard potassium chloride solution, and the resultant mixture was back titrated with standard silver nitrate solution. ᵇ (Ag⁺) = (Agₜ⁺) − (CH₂I₂)ₜ + 3.11 × 10⁻³.

The Evidence for Iodine Atom Argentation.— The results of the argentation studies seem to indicate unquestionably that methylene iodide forms a 1:1 complex in which silver ion is bonded to halogen. The studies on methylene bromide indicate that this compound also can undergo this type of complex formation. However, the equilibrium constant for methylene bromide argentation is much smaller than that for methylene iodide. Chloroform shows only a meager tendency to form such a complex ion.

In view of these results on the saturated halides the highly specific capacity for coördination with silver ion manifested by the 1,2-diiodoethylenes as compared with the analogous dichlorides and dibromides is regarded as strong evidence that the centers of coördination for silver ion in these diiodides are also the iodine atoms rather than the carbon–carbon double bonds.[12]

A structure has been postulated for the iodo-

(12) It is entirely possible that the equilibrium constants for the diiodoethylenes describe in part interactions between silver ion and the carbon–carbon double bond. With the corresponding chlorides and bromides the tendency for such interactions is either small or nonexistent whereas with methyl substituted ethylenes it is larger than that for the diiodoethylenes.[10] Admittedly an iodine substituent at the carbon–carbon double bond would probably be somewhat less deactivating on the π electrons of that bond than would a chlorine or bromine substituent. Then qualitatively, at least, even if the interactions of the diodoethylenes with silver ion involved only the carbon–carbon double bond rather than the iodine atoms, one would predict that K_1 for the diiodides should be intermediate between those values for the dichlorides and dibromides and those for the methylethylenes. However, it should be noted that iodine substituted benzenes display larger argentation constants than do the corresponding methylated benzenes, facts which have previously been presented in favor of the supposition that the iodine atoms attached to the ring are highly susceptible to argentation. These observations and the fact that methylene iodide also shows a strong tendency to coördinate silver ion lead the authors to believe that the K_1 and K_2 values for the diiodoethylenes represent for the most part reactions leading to the formation of bonds between silver ion and iodine atoms.

benzene–silver ion complex which is stabilized by resonance forms involving the benzene ring. A similar structure based on resonance forms of the type

$$\text{>}C\text{=}C\text{<}_{I-Ag}^{+} \qquad \text{>}C\text{—}C\text{<}_{I-Ag}^{+}$$
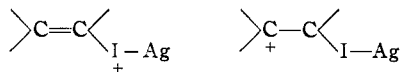
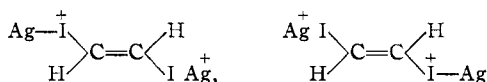may be appropriate to describe the argentation of the vinyl bound iodine atom.

The equilibrium constants indicate that the tendency for monoargentation is considerably higher for the *cis* than for the *trans* isomer of 1,2-diiodoethylene. On the other hand the K_2 value for the *cis* compound is approximately one-half that of the *trans*. This suggests that a steric effect opposing addition of a second silver ion is operative with *cis* AgD^+ which is lacking for the corresponding complex ion of the *trans* isomer.[13]

It occurred to the authors that *o*-diiodobenzene,

(13) The fact that the K_1 value for the *cis* diiodide is so much larger than that for the *trans* isomer suggests that in the *cis* AgD^+ ion the silver may be located in a position such that it may bond to either of two iodine atoms. The geometry of such a structure is indicated by the formula

$$\begin{matrix} H & & H \\ & \text{>}C\text{=}C\text{<} & \\ I & & I \\ & Ag^+ & \end{matrix}$$
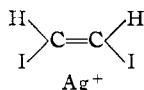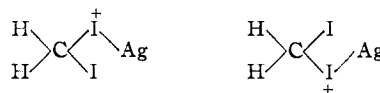
Professor George Scatchard has pointed out to the authors that from statistical considerations one would predict that these diiodides would have K_1 values not more than one-fourth as large as their K_1 values, provided only Ag^+-iodine atom complexes were formed. It is possible that the Ag_2D^{++} complex for the *trans* isomer derives some stabilization energy from the contribution of equivalent no bond resonance forms

$$\begin{matrix} Ag\text{—}\overset{+}{I} & & H \\ & \text{>}C\text{=}C\text{<} & \\ H & & I\ \overset{+}{Ag}, \end{matrix} \qquad \begin{matrix} \overset{+}{Ag}\ I & & H \\ & \text{>}C\text{=}C\text{<} & \\ H & & I\text{—}Ag \end{matrix}$$

A similar explanation may be presented in the cases of the *m*- and *p*-diiodobenzenes. A correct prediction as to the relative magnitudes of K_1 and K_2 is in this case difficult, since double bond or ring argentation must occur at least to a small extent with the diiodo-ethylenes and -benzenes.

in which the two iodine atoms are oriented with respect to each other in much the same manner as are the two iodine atoms in *cis*-1,2-diiodoethylene, might have a K_1 value much larger than those for the *m*- and *p*-diiodides. Experiment confirmed this supposition. Values of K_1 for the *o*-, *m*- and *p*-isomers were, respectively, 16.5, 5.7 and 5.5[1]. The K_2 value for the ortho compound was lower than that for either the *m*- or *p*-derivative. Indeed the K_1 and K_2 values for *o*-diiodobenzene and for the *cis*-diiodoethylene were closely similar. It should be noted, however, that too close a comparison of these values is not justified since there is some doubt as to the purity of the "*cis*" diiodo-ethylene sample.[6]

It is interesting to note that while the K_1 value for methylene iodide is of the same order of magnitude as those values for *cis*-diiodoethylene and for *o*-diiodobenzene, there seems to be no evidence of an appreciable reaction to form a 2:1 silver ion–methylene iodide complex. It is probable that the lack of evidence for this 2:1 complex may be ascribed to the very close proximity of the two iodine atoms in the saturated diiodide. The structure of the 1:1 methylene iodide complex actually may be stabilized sufficiently by resonance forms of the type

$$\begin{matrix} H & & \overset{+}{I} & \\ & \text{>}C\text{<} & & \text{\textbackslash}Ag \\ H & & I & \end{matrix} \qquad \begin{matrix} H & & I & \\ & \text{>}C\text{<} & & \diagup Ag \\ H & & \underset{+}{I} & \end{matrix}$$

so as to inhibit strongly reaction to coördinate a second silver ion.

Experiments to determine the degree to which saturated alkyl monoiodides form argentation complexes would be most interesting in connection with some of the postulates as to the structure of the complexes. Unfortunately no iodide suitable for such a study has yet been discovered.

DAVIS, CALIFORNIA   RECEIVED JUNE 29, 1951

Copolymerization. XVIII.[1,2] The Reactivity of Butadiene in Emulsion Copolymerization at 5°

BY CHEVES WALLING[3] AND JOHN A. DAVISON

The compositions of synthetic rubbers derived from butadiene have been studied. Monomer reactivity ratios have been determined for the copolymerization of butadiene with methyl methacrylate, methyl acrylate, butyl acrylate, methacrylonitrile and vinylidene chloride in emulsion at 5°. In the copolymerization of butadiene with acrylate esters there is a tendency toward alternation. Butadiene is shown to behave much like styrene in copolymerization. Styrene therefore serves as a substitute for butadiene in oil-phase polymerizations, where the polymerization of butadiene is inconveniently slow.

Despite the importance of butadiene as a component of synthetic rubbers, the composition of butadiene copolymers has received little quantitative study. Thus, the only systems for which monomer reactivity ratios are available are those containing, as the other monomer, styrene,[4,5,6]

p-chlorostyrene,[7] 2,5-dichlorostyrene,[7] 1-cyanobutadiene,[7] methyl methacrylate,[4] acrylonitrile[6,7,8] and 2-chlorobutadiene.[8] Accordingly, we have recently determined the monomer reactivity ratios in the copolymerization of butadiene with several rates in the copolymerization of butadiene with

(1) For the preceding paper in this series see C. Walling and E. A. McElhill, THIS JOURNAL, **72**, 2927 (1950).

(2) This work was carried on under Quartermaster Contract W44-109-QM-2030.

(3) Present address, Lever Brothers Co., Cambridge, Mass.

(4) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and W. J. Wenisch, THIS JOURNAL, **70**, 1527 (1948).

(5) E. J. Meehan, *J. Polymer Science*, **1**, 318 (1946).

(6) J. M. Mitchell and H. L. Williams, *Can. J. Research*, **27F**, 35 (1949).

(7) F. T. Wall, R. W. Powers, G. D. Sands and G. S. Stent, THIS JOURNAL, **70**, 1031 (1948).

(8) L. M. Gindin, A. D. Abkin and S. S. Medvedev, *J. Phys. Chem.* (*U. S. S. R.*), **21**, 1267 (1947).