[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds. VI. The Argentation of Substituted Benzenes

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From the solubilities of certain aromatic hydrocarbons (Ar) in aqueous silver nitrate, equilibrium constants for the formation of water-soluble complexes $AgAr^+$ and Ag_2Ar^{++} have been calculated.[1] In the present study the methods of the previous investigation have been used to measure the solubility of certain mono- and disubstituted benzenes in aqueous silver nitrate. The results have been examined to determine the influence of the various substituents on the magnitude of the argentation constants.

Experimental

Materials.—The benzene derivatives used were all Eastman Kodak Co. white label products. Anisole (b. p. 153.4–153.8°), ethyl benzoate (b. p. 212.3–212.8°), fluorobenzene (b. p. 84.4°), chlorobenzene (b. p. 131.9–132°), bromobenzene (b. p. 156.3°) and nitrobenzene (b. p. 211.0°) were fractionated before use. The acetophenone (m. p. 19.4°) was purified by fractional freezing. The iodobenzene (b. p. 188.3°) was washed with dilute sodium thiosulfate, dried over calcium chloride and fractionated. *p*-Dichloro- and *p*-dibromobenzene were used without further purification. The *p*-diiodobenzene (m. p. 87–88°) was recrystallized twice from ethanol.

The Solubility Measurements.—Saturated solutions of the benzene derivatives in aqueous silver nitrate solutions of varying concentrations were prepared at 25.0° as described previously. The ionic strength of the original silver nitrate solutions was adjusted to unity by the addition of appropriate amounts of potassium nitrate. Measured volumes of the saturated solutions were extracted with measured volumes of hexane to remove the aromatic matter from the aqueous layer. The concentration of the aromatic substance in the hexane layer was measured spectrophotometrically. From these results the concentration of aromatic material (both free and complexed) in the saturated silver nitrate solutions was calculated. The details of the method are described in the earlier publication.[1]

TABLE I

EXTINCTION COEFFICIENTS OF HEXANE SOLUTIONS AND WATER SOLUBILITIES AT 25.0° OF THE SUBSTITUTED BENZENES

Compound	λ, mμ	Optical data slit width, mm.	ε	Water solubility, g./100 cc. satd. soln. at 25.0°
Anisole	237	0.48	538	0.014
Acetophenone	300	.22	30.2	.630
Ethyl benzoate	284	.30	139	.072[a]
Fluorobenzene	235	.56	50.0	.155[b]
Chlorobenzene	265	.28	253	.050[c]
Bromobenzene	265	.38	195	.041[d]
Iodobenzene	258	.32	685	.018[e]
Nitrobenzene	320	.24	147	.193[f]
p-Dichlorobenzene	234	.64	2750	.0076[g]
p-Dibromobenzene	228	.64	14500	.0020
p-Diiodobenzene	242	.44	23700	.00014

[a-g] Solubilities (g./100 g. of water) reported in Seidell, "Solubilities of Organic Compounds," Vol. II, Third Edition, D. Van Nostrand Co., New York, N. Y., 1941, are [a] 0.08 (20°), [b] 0.154 (30°), [c] 0.0488 (30°), [d] 0.0446 (30°), [e] 0.034 (30°), [f] 0.205 (30°), [g] 0.00791 (25°).

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 benzene derivatives. The corresponding experimentally determined molar extinction coefficients are included. The solubilities of the benzene derivatives in water at 25.0° as determined by this procedure are also included to demonstrate further the reliability of the method.

Results

It has been shown[1] that the solubility of aromatic hydrocarbons in aqueous silver nitrate solutions may be explained quantitatively in terms of the equilibria

$$Ag^+ + Ar = AgAr^+ \quad K_1 = (AgAr^+)/(Ag^+)(Ar) \quad (1)$$

$$Ag^+ + AgAr^+ = Ag_2Ar^{++}$$
$$K_2 = (Ag_2Ar^{++})/(Ag^+)(AgAr^+) \quad (2)$$

The constant K, introduced to facilitate calculation of K_1 and K_2, has been defined as

$$K = \frac{(Ar_c)}{[(Ag_t^+) - (Ar_c) - (Ag_2Ar^{++})](Ar)} = K_1 + K_1K_2(Ag^+) \quad (3)$$

where (Ar_c) = the molar concentration of complexed hydrocarbon = $(Ar_t) - (Ar)$
(Ar_t) = the molar concentration of all hydrocarbon containing species
(Ar) = the molar concentration of free hydrocarbon = solubility of hydrocarbon in 1 N potassium nitrate
(Ag_t^+) = the molar concentration of silver ion in free and complexed form

As a first approximation in the evaluation of K it may be assumed that (Ag_2Ar^{++}) is sufficiently small compared to $(Ag_t^+) - (Ar_c)$ so that it may be neglected. In all cases investigated it has proved to be small enough so that a reëvaluation of K has not been necessary. Values of K_1 and K_2 have been determined from the straight line obtained by plotting K against (Ag^+).

The solubility data for the mono- and disubstituted benzenes obtained in the present investigation may also be satisfactorily explained in terms of these same equilibria. The solubility data and K values for the several compounds studied are given in Table II.

In most cases the K values calculated from equation (3) showed only slight upward drifts with increasing silver ion concentration indicating that the contribution of reaction (2) to complex formation was small. In the case of iodo- and *p*-diiodobenzene, however, significant quantities of Ag_2Ar^{++} were formed in addition to $AgAr^+$.

In Table III are listed K_1 and K_2 values for the

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[1] Andrews and Keefer, THIS JOURNAL, **71**, 3644 (1949).

several compounds determined as previously explained. The accuracy of K_2 values which are as low as 0.1 is not great, since the variations in K for these particular compounds were small. In certain of these cases isolated points on the plot of K against (Ag^+) did not fit too closely the best straight line which could be constructed. In the cases of anisole, nitrobenzene and *p*-dichlorobenzene the K_1 values reported are averages of the K values from Table II. In the cases of the iodo compounds which displayed relatively large trends in K with changing silver ion concentration the graphical treatment gave straight lines which fit the experimental points very well.

Table II

The Solubility of Substituted Benzenes in Aqueous Silver Nitrate at 25°

	Anisole		Acetophenone		Ethyl benzoate	
(Ag_t^+) mole/liter	(Ar_t) mole/liter $\times 10^2$	K	(Ar_t) mole/liter $\times 10^2$	K	(Ar_t) mole/liter $\times 10^3$	K
0.000	1.06	..	4.55	..	4.00	...
.200	1.59	2.50	5.05	0.55	4.40	0.50
.400	2.14	2.54	5.58	.58	4.95	.59
.600	2.64	2.49	6.19	.62	5.40	.58
.800	3.10	2.41	6.78	.63	5.99	.62
1.000	3.80	2.58	7.42	.65	6.51	.63

	Fluorobenzene		Chlorobenzene		Bromobenzene	
	(Ar_t) $\times 10^2$)		(Ar_t) $\times 10^3$		(Ar_t) $\times 10^3$	
0.000	1.36	..	3.62	..	2.09	...
.200	1.49	0.48	4.10	0.66	2.50	0.98
.400	1.63	.50	4.65	.71	2.90	.97
.600	1.79	.53	5.32	.78	3.34	1.00
.800	1.96	.55	5.75	.74	3.86	1.06
1.000	2.14	.57	6.35	.75	4.31	1.06

	Iodobenzene		Nitrobenzene		*p*-Dichlorobenzene	
	(Ar_t) $\times 10^3$		(Ar_t) $\times 10^2$		(Ar_t) $\times 10^4$	
0.000	0.774	..	1.66	..	4.28	...
.200	1.67	5.81	1.73	0.21	4.54	0.30
.400	2.82	6.62	1.78	.18	4.94	.38
.600	4.21	7.41	1.85	.19	5.24	.37
.800	5.87	8.24	1.91	.19	5.48	.35
1.000	7.79	9.08	1.98	.19	5.80	.35

	p-Dibromobenzene		*p*-Diiodobenzene	
	(Ar_t) $\times 10^5$		(Ar_t) $\times 10^6$	
0.000	6.98	..	3.15	...
.100	....	..	6.08	9.3
.200	8.04	0.76	10.32	11.4
.400	8.85	.67	21.62	14.7
.600	9.89	.69	38.20	18.5
.800	11.05	.73	58.20	21.8
1.000	12.35	.77	86.20	26.4

Table III

The Equilibrium Constants for Argentation of the Benzene Derivatives

Compound	K_1	K_2
Anisole	2.50	...
Acetophenone	0.54	0.11
Ethyl benzoate	.56	.12
Fluorobenzene	.46	.24
Chlorobenzene	.69	.09
Bromobenzene	.97	.12
Iodobenzene	5.00	.81
Nitrobenzene	0.19	...
p-Dichlorobenzene	.35	...
p-Dibromobenzene	.61	0.25
p-Diiodobenzene	7.50	2.34
Benzene[a]	2.41	0.212
Toluene[a]	2.95	.214
Phenol[b]	1.5	...

[a] From Ref. 1. [b] From Keefer, Andrews and Kepner, This Journal, **71**, 3906 (1949); measured at $\mu = 0.1$. Winstein and Lucas, *ibid.*, **60**, 836 (1938), report a value of $K_1 = 2.19$ for the phenol complex, measured at $\mu = 1.0$.

The Structures and Relative Stabilities of the Complexes.—The relative magnitudes of the argentation constants for aromatic hydrocarbons have been discussed[1] in terms of the structure proposed by Winstein and Lucas[2] for the silver perchlorate–benzene complex. In the 1:1 complex, $AgAr^+$, silver ion is pictured as being bonded to the aromatic nucleus from a position above the ring and on the six-fold symmetry axis of the ring.[3] In the case of Ag_2Ar^{++} it is presumed[1] that the two silver ions are bonded to opposite sides of the plane of the ring. It seems likely that, with certain exceptions, the complexes studied in the present investigation are of these same structural types.

These complexes are of particular interest in view of their possible close structural similarity[4] to the π complexes, presumably formed by attack of an electrophilic reagent on the aromatic nucleus, which have been proposed by Dewar[5] as intermediates in aromatic substitution reactions.[6]

With these observations in mind it is interesting to recall that Hammett,[7] in terms of the ρ,σ substituent constant method, has interpreted successfully, kinetic data for the relative rates of substitution at different positions in the ring

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(2) Winstein and Lucas, This Journal, **60**, 836 (1938).

(3) Favorable evidence for this structure is found in the results of Raman spectra measurements by Taufen, Murray and Cleveland, *ibid.*, **63**, 3500 (1941).

(4) Rundle and Holman, *ibid.*, **71**, 3264 (1949).

(5) Dewar, *J. Chem. Soc.*, 777 (1946); 468 (1949).

(6) It has already been noted[1] that the silver ion–aromatic complexes are closely related to the iodine–aromatic complexes studied by Benesi and Hildebrand, This Journal, **70**, 2832 (1948); **71**, 2703 (1949). Kinetic experiments indicate that halogen–aromatic complexes are intermediates in aromatic halogenation reactions; *cf.* De la Mare and Robertson, *J. Chem. Soc.*, 276 (1943); Lambourne and Robertson, *ibid.*, 1167 (1948); Robertson, Allan, Haldane and Simmons, *ibid.*, 933 (1949).

(7) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 198.

for a variety of substituted benzenes.[8] It has, therefore, seemed worth while to attempt to fit the argentation data for the monosubstituted benzenes obtained in this investigation to the Hammett equation

$$\log K_1 - \log K_{1_0} = \rho\sigma \qquad (4)$$

where K_1 is the argentation constant for benzene and K_{1_0} that for the particular substituted benzene under consideration. However, it is difficult to make a choice between σ meta and σ para values for the various ring substituents in attempting this treatment, since there is no justification for the assumption that silver ion is bonded preferentially to any particular ring carbon. Indeed a value intermediate between the two σ values might be most correct.

However as shown in Fig. 1, with the exception of the constant for iodobenzene, the points obtained by plotting log K_1 values against σ meta values for the ring substituents fit reasonably well a straight line as required by equation (4). The line drawn, as based on the method of least squares excluding the point for iodobenzene, gives log K_{1_0} and ρ values of 0.390 and −1.60, respectively; the probable error in log K_1 values has been calculated as 0.088. In this plot σ values for the OH and $COOC_2H_5$ groups are those listed by Hammett[9] for the OCH_3 and COOH groups, respectively.[10]

In attempting a similar plot of log K_1 values against σ para values only those points for nitro-, chloro- and bromobenzenes, benzene and toluene conform at all well to a straight line. Since the σ para values given by Hammett for CH_3CO and COOH groups may be applicable only to aniline and phenol derivatives, it is perhaps not justifiable to include them in the graphical treatment of the data. It should be mentioned that for those ring substituents cited above which fit the σ para treatment, the σ para and σ meta values are not greatly different. At present the significance of the observation that the argentation constants may be treated successfully in terms of the σ meta values is not completely apparent, although a reasonable explanation is based on the assumption that a ring substituent alters the electron density at the position meta to that substituent more through an inductive than a resonance effect. Consequently the σ meta values for various ring substituents are probably better measures of the inductive effects of these substituents on the π electrons of the ring than are σ para values. It might, then, be concluded that the relative stabilities of the argentation complexes are associated primarily with the relative inductive effects of ring substituents.

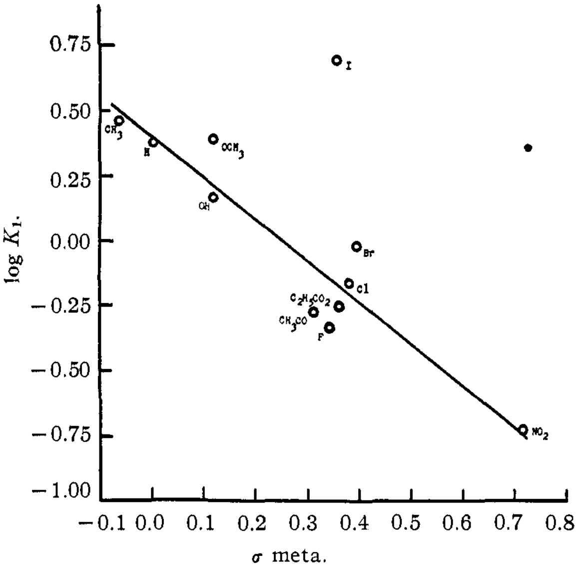
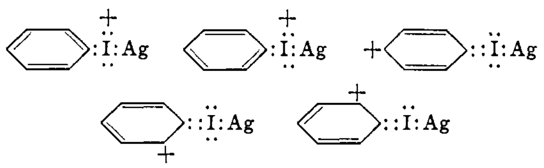


Fig. 1.—Graph of log K_1 against σ meta values.

The value of K_1 for iodobenzene is much larger than that for the other monohalobenzenes; and in contrast to the other halobenzenes, iodobenzene has a K_2 value of appreciable magnitude. Since the magnitude of log K_1 for iodobenzene is much too high to fit the straight line of the log K_1–σ meta plot, it would appear that in addition to the usual π complex a type of complex is formed from iodobenzene which is different from that of the other benzene derivatives. The argentation constants for *p*-dichloro- and *p*-dibromobenzenes are somewhat lower than those for their monohalogen analogs. On the other hand, *p*-diiodobenzene has a significantly larger K_1 value than does iodobenzene.

A reasonable explanation for this anomalous behavior of the iodo compounds is based on the assumption that complexes in which silver ion bonds to the iodine atom may form. The structure of such an ion is indicated by the resonance forms



The existence of such complexes is not surprising since structurally similar compounds typified by diphenyliodonium iodide and iodobenzene dichloride are readily prepared.

Although addition compounds similar to those pictured above have been suggested as intermediates in reactions in which silver ion removes iodide ion from an aliphatic iodide, no positive evidence for their existence is known.[11] In the

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[8] The data of Bird and Ingold, *J. Chem. Soc.*, 918 (1938), for certain aromatic nitration reactions.

[9] Ref. 7, p. 188.

[10] *Cf.* Hammett[7] and Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1945, p. 418.

[11] Wheland, "Advanced Organic Chemistry," second edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 490.

case of aromatic iodides it is possible that the complex ions may be stabilized by resonance forms as pictured above in which iodine accommodates ten electrons in its valence shell. Since the other halogen atoms probably cannot readily accommodate more than the normal octet of valence electrons, it is not too surprising that the other halobenzenes do not form the silver ion–halogen type complex.

Undoubtedly the K_1 values for the iodo compounds measure in part the reaction in which silver ion bonds to the aromatic ring. In forming Ag_2Ar^{++} from iodobenzene it is probable that one silver ion bonds to the iodine atom and the other to the aromatic nucleus. The K_2 value for *p*-diiodobenzene probably measures equilibria for the formation of several different structures of the type Ag_2Ar^{++}

Summary

Argentation constants for a variety of mono- and disubstituted benzene derivatives have been obtained by measurement of the solubilities of the aromatic substance in aqueous silver nitrate at 25°. The relative magnitudes of the constants have been discussed in terms of Hammett's ρ,σ substituent constants. The structures of the silver–aromatic complexes have been discussed and are suggested as being similar to those of intermediates in aromatic substitution reactions.

Evidence has been presented that iodo- and *p*-diiodobenzene form complexes with silver ion in which the metallic ion coördinates with the iodine atoms of the organic molecules.

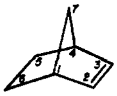
DAVIS, CALIFORNIA RECEIVED OCTOBER 31, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY OF NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Reaction of Norbornylene with N-Bromosuccinimide. Nortricyclene and its Derivatives[1,2]

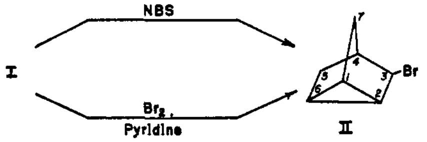
BY JOHN D. ROBERTS, E. R. TRUMBULL, JR., WINIFRED BENNETT AND ROSE ARMSTRONG

N-Bromosuccinimide (NBS) reacts with camphene, a compound whose only allyl hydrogen atom is located at a bridgehead of a bicyclic ring system, to give principally 8-bromocamphene,[3] a vinyl bromide derivative. In order to determine the scope of this abnormal bromination[4] the reaction of NBS with norbornylene (bicyclo-[2.2.1]-2-heptene, I) was investigated.



I

The reaction of I with NBS in the presence of benzoyl peroxide in boiling carbon tetrachloride was about twice as fast as that of camphene with NBS,[3] being complete in four hours. Hydrogen bromide appeared to be an effective catalyst and in one experiment using carbon tetrachloride saturated with dry hydrogen bromide the reaction was complete in fifteen minutes. The yield of monobromide (II) ranged from 27–40%. II, b. p. 70–74° (19 mm.), reacted rapidly with alcoholic silver nitrate and absorbed very little hydrogen over platinum oxide.[5] The elemental analysis was satisfactory for C_7H_9Br, a monosubstitution product of I. The saturated character and analysis of II are suggestive of a tricyclic ring system, while the facile reaction with silver nitrate indicates that the halogen atom is not located at a bridgehead position.[6] From these inferences and consideration of possible modes of reaction between I and NBS (*vide infra*) the most likely structure for II appears to be 3-bromonortricyclene (3-bromotricyclo[2.2.1.$0^{2,6}$]-heptane).



II

The conversion of I to II is not unique to NBS. The reaction of I with bromine in carbon tetrachloride was found to give mono- and dibromide fractions. The monobromide fraction consisted of about equal quantities of II and of norbornyl bromide resulting from the addition of hydrogen bromide to I. When excess pyridine was added to the reaction mixture to combine with the hydrogen bromide formed by the substitution reaction, the monobromide fraction was essentially

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[1] Supported in part by the joint program of the Office of Naval Research and the Atomic Energy Commission.

[2] Presented in part at the St. Louis Meeting of the American Chemical Society, Sept. 7, 1948.

[3] Roberts and Trumbull, THIS JOURNAL, **71**, 1630 (1949).

[4] *Cf.* Djerassi, *Chem. Revs.*, **43**, 271 (1948), for discussion of the usual course of the reaction.

[5] Most of the preparations of II contained sufficient quantities of an isomeric unsaturated bromide to react with dilute alcoholic potassium permanganate solution. This fact led to the supposition that II was in reality an unsaturated bromide and that on attempted hydrogenation the catalyst was rapidly poisoned by impurities. II was previously assigned the structure, 7-bromonorbornylene (*cf.* Abstracts of St. Louis Meeting of the American Chemical Society, September, 1948, p. 43L.)

[6] Bartlett and Knox, THIS JOURNAL, **61**, 3184 (1939).