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

Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds. IV. The Argentation of Aromatic Hydrocarbons[1]

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Detailed information concerning the argentation of aromatic hydrocarbons is lacking. The results of studies of the phase relationships in the systems silver perchlorate–benzene–water and silver perchlorate–toluene–water[2] suggest that the tendency for such complex formation is appreciable.

In the present investigation, which represents an extension of the work reported previously,[3] the solubilities of several aromatic hydrocarbons in aqueous silver nitrate solutions have been measured. The data have been interpreted on the assumption that from each hydrocarbon two water-soluble complexes, $AgAr^+$ and Ag_2Ar^{++}, are formed.[4] Equilibrium constants for reactions leading to their formation have been calculated.

Experimental

The Aromatic Hydrocarbons.—All of the hydrocarbons used were of the best grade obtainable from Eastman Kodak Co. The benzene and toluene were washed successively with concentrated sulfuric acid, water and dilute sodium hydroxide and, after drying, were fractionated. Cuts of b. p. 80.1° (benzene) and 110.4° (toluene) were used in the solubility experiments. The xylenes were fractionated and samples of the following b. p. used: *o*-xylene (144.3–144.5°), *m*-xylene (139.5°), *p*-xylene (138.5°). The naphthalene was recrystallized from ethanol, m. p. 80.5°. The biphenyl was used directly, m. p. 70.0–70.5°. The diphenylmethane was purified by fractional freezing,[5] m. p. 25.0°. Phenanthrene was recrystallized twice from ethanol, m. p. 101.0°.

The Solubility Measurements.—To aqueous silver nitrate solutions of varying silver ion concentration contained in glass-stoppered Erlenmeyer flasks were added 0.1–1.0-g. samples of aromatic hydrocarbon. In all cases sufficient potassium nitrate was contained in the aqueous solution to maintain an ionic strength of unity. The mixtures were rotated twenty hours in a constant temperature bath at 25.0° to saturate the aqueous phase with hydrocarbon.

Pipet samples (5–20 ml.) of the aqueous phase were then removed and extracted with measured volumes of hexane (10–50 ml.) by shaking in glass-stoppered Erlenmeyer flasks. The optical density of the hexane phase was measured against a hexane blank on the Beckman spectrophotometer at a wave length and slit width setting for each particular hydrocarbon for which values of the molecular extinction coefficient of such solutions had previously been determined. In all cases investigated one extraction with hexane removed all of the hydrocarbon, both free and complexed, from the aqueous phase, as was indicated by the fact that hexane samples used in a second extraction of the aqueous phase gave negligible optical density readings. The volumes of the aqueous and hexane phases were adjusted insofar as possible to obtain optical density readings between 0.200 and 0.800. Thus the data were available to calculate the aromatic hydrocarbon content of the saturated aqueous solutions.

Samples of aqueous silver nitrate and potassium nitrate were extracted with hexane. The hexane phase contained no light absorbing materials as evidenced by measurement of its spectrum against a hexane blank.

The hexane was Skellysolve B rendered optically pure for purposes of the experiments by two washings with fuming sulfuric acid, followed by washings with water and dilute sodium hydroxide solution, drying and distillation.

The wave lengths and slit width settings used in the optical density measurements of the hexane solutions of the hydrocarbons with corresponding values of the molecular extinction coefficients are given in Table I. In each case the solutions obeyed Beer's law. Included in this table are values of the water solubilities of the hydrocarbons at 25.0°, determined by the method described above as a check on the extraction procedure, with corresponding data from the literature.

Attempts at a determination of the argentation constants for anthracene by this method were unsuccessful. Reproducible results were not obtainable, since difficulty was encountered with contamination during sampling of the saturated solutions.

To check on the possibility that silver nitrate may have distributed to the aromatic hydrocarbon phase in the solubility experiments, equal volumes of benzene and 1 *N* silver nitrate solution were shaken for several hours. Samples of the benzene were removed and shaken with dilute aqueous potassium chloride. No silver chloride was formed.

Results

The solubility of the several hydrocarbons in aqueous solutions increased with increasing silver ion concentration to a greater degree than was consistent with the supposition that only a 1–1 complex, $AgAr^+$, was formed. Accordingly the data were interpreted on the assumption that equilibria (1) and (2) were established in these solutions.

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

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

An additional constant K was defined in terms of the several species postulated as present in the saturated aqueous solutions as follows

$$K = \frac{(Ar_c)}{[(Ag_t^+) - (Ar_c) - (Ag_2Ar^{++})](Ar)} = \frac{(AgAr^+) + (Ag_2Ar^{++})}{[(Ag_t^+) - (AgAr^+) - 2\,(Ag_2Ar^{++})](Ar)} = K_1 + K_1K_2\,(Ag^+) \quad (3)$$

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 = the concentration of hydrocarbon in its saturated solution in 1 *N* potassium nitrate

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

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[1] Presented before the Organic Division of the American Chemical Society, San Francisco, California, March, 1949.

[2] Summarized in Seidell, "Solubilities of Inorganic and Metal-Organic Compounds," Third Edition, Vol. I, D. Van Nostrand Company, Inc., New York, N. Y., 1940.

[3] For the preceding paper in this series see Keefer, Andrews and Kepner, THIS JOURNAL, **71**, 2381 (1949).

[4] The symbol Ar is used to represent the aromatic hydrocarbon molecule.

[5] DeVries and Stow, THIS JOURNAL, **61**, 1797 (1939).

TABLE I

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

Hydrocarbon	λ, mμ	Optical properties Slit width, mm.	ε	Solubility Measured g./100 cc. satd. soln.	Solubility Literature values[a] g./100 cc. H_2O
Benzene	250 or 262	0.40 or 1.425	106 or 28.5	0.174	0.180
Toluene	260	1.27	183	.053	.054
o-Xylene	263	0.36	267	.0204	.013[b]
m-Xylene	265	.36	268	.0173	
p-Xylene	275	.35	554	.0200	
Naphthalene	275	.34	5.50×10^3	.00315	.0030
Biphenyl	252	.48	1.58×10^4	5.94×10^{-4}	.....
Diphenylmethane	222	1.10	7.69×10^3	1.41×10^{-4}	.....
Phenanthrene	252	0.42	7.16×10^4	9.94×10^{-5}	1.6×10^{-4} (27°)[c]

[a] Values, except as noted, from Seidell, "Solubilities of Organic Compounds," Third Edition, Volume II. [b] For a xylene mixture of unrecorded composition. [c] Results of Davis, Krake and Clowes, THIS JOURNAL, 64, 108 (1942), as based on the nephelometric method.

To calculate K the concentrations of substances as defined above were substituted in the left-hand expression of equation (3). It was assumed that (Ag_2Ar^{++}) was sufficiently small as compared to the concentration of uncomplexed silver ion so that it could be neglected in calculating K. In every case the K_2 values obtained as described below indicated that (Ag_2Ar^{++}) was very small as compared to uncomplexed silver ion concentration, so that the values of K needed no correction.

Values of K calculated from the data recorded for each compound are summarized in Table II.

TABLE II

THE SOLUBILITY OF THE HYDROCARBONS IN AQUEOUS SILVER NITRATE AT 25.0°

(Ag_t^+) mole/liter	(Ar_t) mole/liter $\times 10^3$	K	(Ar_t) mole/liter $\times 10^3$	K	(Ar_t) mole/liter $\times 10^6$	K
	Benzene		Toluene		Phenanthrene	
0.000	16.5	..	4.30	..	4.05	...
.100	20.5	2.52	5.55	2.94	....	...
.200	24.3	2.46	6.93	3.10	8.10	5.00
.400	33.3	2.66	9.68	3.18	14.52	6.45
.600	42.1	2.70	12.8	3.34	22.5	7.57
.800	51.0	2.82	...	..	33.0	8.94
1.000	62.0	2.90	19.4	3.57	45.6	10.27
	o-Xylene		*m*-Xylene		*p*-Xylene	
					$\times 10^3$	
0.000	1.48	..	1.12	..	1.29	...
.100	1.92	2.99	1.48	3.16	1.64	2.72
.200	2.35	2.96	1.86	3.28	2.02	2.86
.400	3.40	3.26	2.66	3.42	2.81	2.96
.600	4.51	3.43	3.52	3.57	3.72	3.15
.800	5.75	3.62	4.52	3.79	4.71	3.32
1.000	7.06	3.79	5.60	4.00	5.78	3.50
	Naphthalene		Biphenyl		Diphenylmethane	
			$\times 10^5$		$\times 10^4$	
0.000	0.191	..	2.46	..	0.781	...
.200	.328	3.58	4.82	4.80	1.43	4.20
.400	.514	4.23	7.90	5.53	2.32	4.93
.600	.746	4.85	11.56	6.17	3.41	5.61
.800	.986	5.20	16.58	7.18	4.75	6.35
1.000	1.31	5.86	21.97	7.94	6.30	7.06

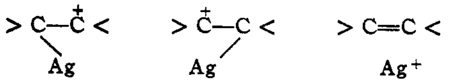
If reaction (1) were the only one contributing appreciably to complex formation, K should equal K_1 and values of K for any particular hydrocarbon should be independent of silver ion concentration of the medium. The marked increase in K values observed indicates an appreciable contribution of reaction (2). As would be expected, if equations (1) and (2) account for all complexes formed, plots of K against the silver ion concentration in the saturated solutions should give straight lines. This was found to be true for all the compounds investigated. In such plots the ordinate intercept is K_1, and K_2 may be obtained from the slope of the lines which is equal to K_1K_2. The values of K_1 and K_2 obtained are given in Table III.

TABLE III

THE EQUILIBRIUM CONSTANTS FOR ARGENTATION OF THE HYDROCARBONS AT 25.0°

Hydrocarbon	K_1	K_2
Benzene	2.41	0.212
Toluene	2.95	.214
o-Xylene	2.89	.315
m-Xylene	3.03	.320
p-Xylene	2.63	.331
Naphthalene	3.08	.909
Biphenyl	3.94	1.01
Diphenylmethane	3.46	1.04
Phenanthrene	3.67	1.80

The Structures of the Complexes.—The complex formed between silver ion and a molecule containing an unconjugated double bond has been described[6] in terms of resonance formulas



A similar structure in which silver ion is bonded to one particular double bond of a ring might be postulated for aromatic systems. This seems unattractive since such a structure would entail the loss of considerable ring resonance energy within the aromatic system itself. An attractive

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[6] Winstein and Lucas, THIS JOURNAL, 60, 836 (1938).

modification of the above structure, as applied to the singly argentated benzene molecule, pictures the silver ion as being located above the plane of the ring at a position equidistant from the six-ring carbon atoms. This silver ion would be in a position to utilize the π-electrons of the ring to form covalent bonds of the type indicated above with any of the six ring carbons. The structure of the complex would then be represented by eighteen equivalent single-bonded structures in addition to two no-bond structures as contributors to a resonance hybrid.[6,7] The loss of ring-resonance energy when such a complex is formed would be compensated to a large degree by the resonance energy associated with the complex itself. In the doubly argentated benzene complex the second silver ion could bond to the plane of the ring from the side opposite to which the first silver ion is attached. A synchronized resonance[8] in which two silver–carbon bonds resonate among six equivalent positions might then exist. One can calculate, using the tetrahedral covalent radii for the ring-carbon atoms and for silver,[9] that the silver ion in the complex would not penetrate the plane of the ring, thus eliminating the possibility of steric interference between two silver ions in the doubly argentated complex. It is interesting to note that the covalent radius of silver is sufficiently large so that the silver ion would overlap the perimeter of the carbon–carbon bond skeleton of the ring. With these postulates as to structure in mind it is interesting to consider the tendencies for complex formation of the several hydrocarbons.

It appears that a methyl substituent enhances slightly the basic strength of the benzene ring, as reflected in the values of the equilibrium constants for benzene and toluene. The presence of two methyl groups on the ring (see the data for the xylenes) apparently causes no marked increases in basicity over that for toluene, which suggests that a steric effect opposing complex formation may be present in these molecules.[10]

In the case of the multiple ring systems the K_1 values are higher than those for benzene. One might expect for biphenyl, in which the two phenyl groups are on the average in the same plane,[11] a K_1 value approximately double that for benzene. The interaction between rings in biphenyl is at least partially responsible for the fact that K_1 observed is less than the predicted value.

For diphenylmethane, in which the two rings are not coplanar, steric influences should effectively eliminate one of the four positions of attack available to silver ion. On this basis K_1 should be approximately $^3/_2\ K_1$ for benzene, and the observed value is only slightly less than the predicted value.

A lower value of K_1 is obtained for naphthalene than for biphenyl. Since there are only five double bonds in naphthalene as compared to six in biphenyl, naphthalene might be expected to be less basic than biphenyl.

The K_1 value for phenanthrene is greater than that for naphthalene but less than that for biphenyl. In addition to the possibility that silver ion may coördinate with any of the three rings in this molecule, the possibility that it may coördinate with the carbon–carbon bond at the 9,10-position should be considered. This bond has a high degree of double bond character, and in other reactions preferential substitution or addition occurs at this point.[12]

The K_2 values for the single ring compounds are small as compared to those for multiple-ring systems. This seems reasonable since the presence of a silver ion in $AgAr^+$ must considerably reduce the basicity of the ring with respect to addition of a second silver ion. This effect would be much less pronounced in the multiple-ring systems since the second silver may bond to a ring other than that to which the first silver ion is attached.

Assuming that the first silver ion attached to benzene does not alter the ability of a molecule to coördinate a second silver ion, the predicted value of K_2 for benzene (on a statistical basis) would be $^1/_4\ K_1$. The observed value is about $^1/_3$ the predicted value.

There are three positions at which a silver ion might add to the $AgAr^+$ complex of biphenyl. The position on the side of the ring opposite to that at which the first silver ion is attached might be expected to be roughly equivalent in base strength to the $AgAr^+$ complex of benzene. Two alternate bonding positions are available on the other ring, each of which should be roughly equivalent in basicity to one of the four positions available when silver ion coördinates with biphenyl. The ease of loss of a silver ion should be twice as great from Ag_2Ar^{++} as from $AgAr^+$. Combining the above observations one might predict that K_2 for biphenyl would be $^1/_4\ K_1$ for biphenyl plus K_2 for benzene. The observed value of 1.01 is less than the value of 1.2 predicted on the above basis.[13]

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[7] Taufen, Murray and Cleveland, THIS JOURNAL, **63**, 3500 (1941).

[8] Pauling, *J. Chem. Soc.*, 1461 (1948).

[9] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940.

[10] Benesi and Hildebrand, THIS JOURNAL, **70**, 2832 (1948), have described a 1-1 complex for certain aromatic hydrocarbons and iodine and report evidence that increasing methyl substitution on the benzene ring appears to result in an increased tendency for complex formation. Undoubtedly these iodine complexes are closely associated structurally with those under consideration in this report. It is further interesting in this connection to note that if benzene solutions of iodine are treated with anhydrous silver salts, reaction occurs to yield iodobenzene and silver iodide; *cf.* Birckenbach and Goubeau, *Ber.*, **66B**, 1280 (1933). One cannot overlook the possibility that these silver complexes may be very closely related structurally to the transition state intermediates in certain aromatic substitution reactions; *cf.* Dewar, *J. Chem. Soc.*, 777 (1946); 463 (1949).

[11] Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 160.

[12] Price, THIS JOURNAL, **58**, 2101 (1936).

[13] This treatment assumes that the front and rear faces of the free ring in the $AgAr^+$ complex of biphenyl offer equivalent bonding positions for the second silver ion. Considering the coplanarity of biphenyl this assumption is open to question insofar as the silver–silver repulsions would be different for the two possible forms of

A maximum value of K_2 for diphenylmethane of $^1/_3$ K_1 (for diphenylmethane) is predicted if it is assumed that the position sterically prohibited is the other side of the ring containing the first silver ion. The observed value of K_2 is 1.04 as compared to a maximum calculated value of 1.15.

In attempting to predict K_2 values for the fused ring systems, as represented by naphthalene and phenanthrene one cannot overlook the possibility that structures for Ag_2Ar^{++} in which two silver ions are coördinated with adjacent rings on the same side of the plane of the molecule are sterically unfavorable. Neglecting such structures values of K_2 may be calculated which are considerably less than the observed values. For fused ring systems, the structural nature of the Ag_2Ar^{++} complex may be somewhat different from those suggested for non-fused ring molecules.

Summary

By measurement of the solubilities of several aromatic hydrocarbons in aqueous silver nitrate solutions, evidence has been obtained for the formation of two water-soluble complexes, $AgAr^+$ and Ag_2Ar^{++}. Equilibrium constants for the reactions to form these complexes at 25° have been calculated. Structures for the complexes are suggested, and the tendencies for the various hydrocarbons to undergo argentation have been considered in terms of these structures.

A method of analysis for the aromatic hydrocarbon content of aqueous solutions is described in which the hydrocarbon is extracted from the solution with hexane, and its concentration in the hexane phase determined by spectrophotometric measurement.

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RECEIVED MAY 3, 1949

Ag_2Ar^{++} in which one silver ion is coördinated with each ring. The method used in predicting a value for K_2 is similar to that used in approximating dissociation constants for dibasic acids; *cf.* Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall Inc., New York, N. Y., 1945, p. 200.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Absorption Spectra of ortho-Substituted Aldehydes. I. The *o*-Hydroxynaphthaldehydes[1]

BY NORTEN C. MELCHIOR[2]

The difficulties encountered in attempts to correlate the molecular structures of compounds with their absorption spectra makes careful comparisons of the spectra of closely related compounds important. During an investigation[3] of some of the metal derivatives of the *o*-hydroxynaphthaldehydes, the absorption spectra of these aldehydes and their negative ions was measured in methanol–water solutions. The striking differences in these spectra led to this extension of the measurements.

Experimental

Absorption Measurements.—All measurements were made with a Beckman model DU spectrophotometer in silica cells having a 10-mm. light path. The temperature of the cells was controlled by hollow metal plates, pierced by a small opening for the light beam, which were placed on opposite sides of the cell compartment. Water from a controlled temperature bath was circulated through these plates. A slow stream of dry air passed into the cell compartment prevented fogging of the cell windows at temperatures below the dew point of the laboratory air. Small differences in the measurements due to the volume change of the solvent were eliminated by making final dilutions at the temperature at which the spectrum was run, or by calculation from the measured temperature–volume coefficient of the solvent. Measurements at a given wave length were made with the same slit width, which was kept as small as possible.

Solvents.—Methanol was reagent grade, octane and heptane mixtures were purified by standard procedures. In all cases blanks were prepared from the same sample of solvent used for dissolving the compound studied.

Aldehydes.—The preparation of these compounds has been reported.[3,4] Each sample was sublimed several times at pressures below 0.001 mm., once immediately before use.

Results.—The more pertinent results are shown in Figs. 1 to 5. It is evident in Fig. 1 that the first band of the negative ion of 3-hydroxy-2-naphthaldehyde appears at a lower frequency but with considerably lower intensity, than do those of its isomers. It is easily seen by comparing Figs. 2, 3 and 4 that this is also the case in the neutral molecule, regardless of solvent. It is also apparent that solvent change has a greater effect on the spectrum of the 3-2-compound than upon that of either of its isomers. In addition, Fig. 5 shows the striking effect of temperature change on the absorption spectrum of the 3-2-compound in 80 mole per cent. methanol.

[1] Presented at the meeting of the American Chemical Society in San Francisco, March, 1949.

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[3] (a) Calvin and Melchior, THIS JOURNAL, **70**, 3273 (1948); (b) Thesis, N. C. Melchior, University of California, 1946.

[4] Arnold and Sprung, THIS JOURNAL, **60**, 1163–1164 (1938).