must await a more complete study of the effect of molecular weight and molecular weight distribution on these curves. It appears, in any case, that all amorphous polymers of similar molecular weights in reasonably good solvents will show very similar behavior, and that the shape of the dispersion curve is characteristic of a loose entanglement of flexible molecules.

Summary

1. The propagation of transverse waves in solutions of an unfractionated polyvinyl acetate ($\bar{M}_n$ = 140,000) in 1,2,3-trichloropropane, methyl isobutyl ketone, methyl ethyl ketone, cyclohexanone and diisopropyl ketone, and of three fractions of different molecular weights in trichloropropane, has been studied as a function of temperature, concentration and frequency.

2. The wave rigidity, $\tilde{G}$, increases with frequency, decreases with increasing temperature, and increases with concentration.

3. In each solvent, the reduced wave rigidity, $\tilde{G}T_0/Tc$, plotted against the reduced frequency, $\omega\eta T_0/Tc$ (where ω is the circular frequency, η the steady flow viscosity, c the concentration in g./cc., T the absolute temperature, and T_0 = 298° K.) gives a single dispersion curve on which data for all concentrations and temperatures superpose.

4. The dispersion curves for the unfractionated polymer in different solvents lie very close together and resemble in shape the corresponding curves obtained previously for polystyrene and polyisobutylene.

5. When the dispersion curves for samples of different molecular weight are reduced to comparison at c = 0.25, they appear to converge at high frequencies, while with decreasing frequency they diverge, the rigidity falling off more rapidly the lower the molecular weight.

MADISON, WISCONSIN RECEIVED JANUARY 12, 1950[12]

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[12] Original manuscript received January 20, 1949.

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

Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds. VII. Further Studies on the Argentation of Substituted Benzenes

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

In previous communications[1,2] the solubilities of certain aromatic hydrocarbons and substituted benzenes in aqueous silver nitrate have been reported. These data have been used to calculate equilibrium constants for the formation of the water soluble complexes, $AgAr^+$ and Ag_2Ar^{++}. It has been postulated[1,3] that the aromatic nucleus donates electrons to silver ion in forming such complexes and that the magnitude of the equilibrium constant for the formation of $AgAr^+$ may be considered a measure of the basicity of the aromatic ring in question.[4] Supporting these postulates is the observation that the magnitudes of the argentation constants for the formation of $AgAr^+$ using a variety of monosubstituted benzenes increase with increasing capacity of the substituents to furnish electrons to the ring.[2] In this regard it is of interest to note that the logarithms of these argentation constants yield a straight line when plotted against the Hammett[5] σ_{meta} values for the various ring substituents.

With these facts in mind the argentation studies have been extended, as described in this report, to include a number of other aromatic substances. In particular the solubilities in aqueous silver nitrate of mesitylene, several monoalkylbenzenes, styrene and a few of its derivatives have been investigated.

Experimental

Materials.—The following Eastman Kodak Co. white label materials were fractionated for use in the solubility measurements: mesitylene, b. p. 165.0°; ethylbenzene, b. p. 136.0°; isopropylbenzene, b. p. 151.5–152.0; *n*-propylbenzene, b. p. 157.8–158.1°; *t*-butylbenzene, b. p. 167.8–168.0°; *n*-butylbenzene, b. p. 182.0–183.0°; *s*-butylbenzene, b. p. 175.0–175.8°; *t*-amylbenzene, b. p. 188.0–189.0°. Eastman Kodak Co. white label styrene was distilled shortly before it was used. A sample (11.9 g.) of the distillate, b. p. 76° at 78 mm., was treated with 0.1 g. hydroquinone to stabilize it. In terms of the available absorption spectrum of hydroquinone[6] this quantity of the antioxidant should not be expected to introduce appreciable error into the spectrum measurements used in investigating the solubility of the styrene sample. Even though a sample of styrene so prepared was exposed to aqueous silver nitrate for twenty hours in the solubility measurements, no visible evidence of polymerization was observed. Eastman Kodak Co. white label bibenzyl, m. p. 51–52°, was used without further purification. Ethyl cinnamate, b. p. 131–132° at 7 mm., and ethyl hydrocinnamate, b. p. 121.9° at 11 mm., were prepared from the corresponding acids by the method of Fischer and Speier.[7] Samples of *trans*-stilbene, m. p. 120–121° and of 1,1-diphenylethylene, b. p. 125–127° at 6 mm.,

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

[2] Andrews and Keefer, *ibid.*, **72**, 3113 (1950).

[3] Winstein and Lucas, *ibid.*, **60**, 836 (1939).

[4] Several other methods recently have been suggested as being useful in the measurement of relative base strengths of aromatic substances; *cf.* Benesi and Hildebrand, *ibid.*, **70**, 3978 (1948); **71**, 2702 (1949); Brown and Brady, *ibid.*, **71**, 3573 (1949); McCaulay and Lien, Abstracts of Papers Presented to the Division of Physical and Inorganic Chemistry, Detroit, Mich., April, 1950.

[5] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 198.

[6] "International Critical Tables," Volume V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 361.

[7] Fischer and Speier, *Ber.*, **28**, 3252 (1895).

kindly furnished by Dr. Robert E. Buckles of the State University of Iowa, were used.

The Solubility Measurements.—Saturated solutions of the above compounds in aqueous silver nitrate solutions (ionic strength adjusted to unity by the addition of potassium nitrate) at 25° were prepared as described previously. Samples of these solutions were extracted with hexane, and the aromatic content of the resultant hexane solutions were determined spectrophotometrically. The details of the experimental techniques and the methods by which the data are used to calculate the concentrations of aromatic substances in the saturated aqueous solutions are outlined in the earlier publications.[1,2]

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 substituted benzenes and also the corresponding experimentally determined extinction coefficients. The solubilities of the benzene derivatives in water at 25° as determined by this procedure are also included as a matter of interest since most of these data are not available elsewhere.

TABLE I

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

Compound	Optical data λ, mμ	Slit width, mm.	ε	Water solubility g./100 cc. satd. soln. at 25.0°
Mesitylene	230	0.64	575	9.7×10^{-3}
Ethylbenzene	262	0.42	204	1.68×10^{-2a}
n-Propylbenzene	221	1.3	590	5.5×10^{-3}
n-Butylbenzene	220	1.4	1,680	1.26×10^{-4}
Isopropylbenzene	262	0.38	165	7.3×10^{-3}
s-Butylbenzene	224	0.92	876	3.09×10^{-2}
t-Butylbenzene	219	1.55	1,350	3.4×10^{-3}
t-Amylbenzene	219	1.35	2,460	1.05×10^{-3}
Styrene	287	0.30	318	3.0×10^{-2}
trans-Stilbene	295	0.28	26,400	2.9×10^{-5}
Bibenzyl	219	1.5	10,500	4.3×10^{-4}
1,1-Diphenylethylene	250	0.44	11,100	6.6×10^{-4}
Ethyl cinnamate	304	0.24	1,023	1.78×10^{-2}
Ethyl hydrocinnamate	259	1.5	401	2.2×10^{-2}

[a] A value of 0.014 g./100 cc. at 15° is reported by Fühner, *Ber.*, **57B**, 510 (1924).

Results

It has been shown[1,2] that the solubility of aromatic compounds in aqueous silver nitrate may be explained in terms of the equilibria

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

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

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

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

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 *M* potassium nitrate

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

The solubility data for the substituted benzenes obtained in the present investigation may be explained in terms of equilibria 1 and 2. The measured solubilities and values of K for the various compounds studied are given in Table II. Values of K_1 and K_2 obtained by graphical interpretation of eq. 3 are tabulated in Table III.

TABLE II

THE SOLUBILITY OF THE SUBSTITUTED BENZENES IN AQUEOUS SILVER NITRATE AT 25.0°

(Ag^+_t) mole/liter	(Ar_t) mole/liter $\times 10^4$	K	(Ar_t) mole/liter $\times 10^3$	K	(Ar_t) mole/liter $\times 10^4$	K
	Mesitylene		Ethylbenzene		*n*-Propylbenzene	
0.000	6.4	..	1.31	...	3.6	..
.200	8.7	1.8	2.03	2.8	5.8	3.1
.400	11.1	1.8	2.75	2.8	7.3	2.6
.600	13.2	1.8	3.59	2.9	9.8	2.9
.800	15.3	1.8	4.46	3.0	12.0	2.9
1.000	17.4	1.7	5.45	3.1	14.5	3.0
	n-Butylbenzene		*iso*-Propylbenzene		*s*-Butylbenzene	
	$\times 10^5$		$\times 10^4$			
0.000	7.3	..	4.77	...	1.71	..
.200	11.9	3.1	7.34	2.7	2.54	2.4
.400	16.1	3.0	10.2	2.9	3.40	2.5
.600	20.1	2.9	13.3	3.0	4.35	2.6
.800	24.7	3.0	16.8	3.1	5.34	2.6
1.000	29.4	3.0	19.7	3.1	6.31	2.7
	t-Butylbenzene		*t*-Amylbenzene		*trans*-Stilbene	
	$\times 10^4$				$\times 10^6$	
0.000	1.96	..	0.56	...	1.17^5	..
.200	2.78	2.1	0.86	2.7	3.25	8.8
.400	3.90	2.5	1.14	2.6	4.88	7.9
.600	5.14	2.7	1.47	2.7	7.1	8.4
.800	6.16	2.7	1.82	2.8	10.0	9.4
1.000	7.46	2.8	2.24	3.0	13.2	10.3
	Bibenzyl		1,1-Diphenylethylene		Ethyl cinnamate	
	$\times 10^5$		$\times 10^5$		$\times 10^4$	
0.000	1.58	..	3.02	...	8.22	..
.200	4.64	9.7	4.79	2.9	9.96	1.1
.400	8.31	10.6	7.20	3.5	11.8	1.1
.600	13.2	12.2	10.5	4.1	14.0	1.2
.800	18.4	13.3	14.4	4.7	16.1	1.2
1.000	25.0	14.8	19.0	5.3	18.5	1.3
	Ethyl hydrocinnamate		Styrene			
	$\times 10^3$		(Ag^+_t) mole/liter		$\times 10^3$	
0.000	0.98	..	0.000		2.22	..
.200	1.32	1.7	.020		3.00	18.3
.400	1.70	1.8	.040		3.82	18.8
.600	2.09	1.9	.080		5.48	19.2
.800	2.58	2.0	.120		7.34	20.1
1.000	3.00	2.1	.160		9.23	20.6
			.200		11.06	20.8

TABLE III

THE EQUILIBRIUM CONSTANTS FOR ARGENTATION OF THE BENZENE DERIVATIVES AT 25°

Compound	K_1	K_2
Mesitylene	1.8	..
Ethylbenzene	2.7	0.15
n-Propylbenzene	2.9	..
n-Butylbenzene	3.0	..
Isopropylbenzene	2.8	.41
s-Butylbenzene	2.4	.12
t-Butylbenzene	2.3	.22
t-Amylbenzene	2.4	.25
Styrene	18.2	.81
trans-Stilbene	6.3	.63
Bibenzyl	8.0	.85
1,1-Diphenylethylene	2.3	1.3
Ethyl cinnamate	1.0	0.3
Ethyl hydrocinnamate	1.6	.3

It has been noted previously that a single methyl substituent on the benzene ring enhances the basic strength of the ring with respect to argentation. The values of K_1 observed for benzene and toluene are 2.41 and 2.95, respectively. In the case of the xylenes, however, the measured K_1 values are very close to those obtained for toluene. Since in other work[4] it has been observed that each successive methyl substitution increases the basicity of the aromatic nucleus, it has been suggested[1] that in the argentation reaction of polymethylbenzenes a steric effect opposing complex formation may exist. This supposition is strengthened by the results of the present study of mesitylene which has even a lower K_1 value than does benzene and a K_2 value too small to be determined.

In the structure proposed for $AgAr^+$[1,3] the silver ion is bonded to the ring from a position on the six-fold symmetry axis of the ring with the aromatic nucleus coördinated to the metallic ion at a position previously occupied by a water molecule. Since silver ion in aqueous solution has been pictured as a dihydrate[8] and tends to form linear bond types[9] when doubly coördinated, the second water molecule should offer no steric interference in the ring coördination process. Estimates of the bond distances in the argentation complexes based on the covalent radii of the atoms in question[1,10] suggest that interference between silver ions and methyl groups may exist in polymethylbenzenes. If, however, several water molecules remain coördinated with silver ion in the complex a serious steric barrier to complex formation should exist.

The monoalkylbenzenes were considered in this investigation to determine whether or not any significant changes in the tendency for argentation were associated with changes in the nature of the alkyl group. Berliner and Berliner[11] have reported noticeable downward trends in the rates of bromination of alkylbenzenes as hydrogen atoms available for hyperconjugation with the aromatic ring at the alpha and beta carbon atoms of the side chain are replaced by alkyl radicals. In the present study no large deviations in K_1 or K_2 values for the several alkylbenzenes as compared with those obtained for toluene (2.95 and 0.21, respectively) were observed. The K_1 values for *s*-butyl- and *t*-amylbenzene were noticeably lower than those for the other compounds of this series. However, it is possible that the observed lowering results from steric rather than electronic effects. It is noteworthy that the σ values listed by Hammett[5] for CH_3, C_2H_5, i-C_3H_7 and t-C_4H_9 groups are very nearly the same, indicating that these groups have closely similar electronic influences on the aromatic nucleus. The accuracy of the K_1 and K_2 values reported for the propyl-, butyl- and amylbenzenes is less than that of those reported previously, since the solubilities of these compounds in aqueous media were small and considerable difficulty was experienced in avoiding contamination during sampling of these solutions for analysis. In general the K_2 values, presumably representing the tendency for formation from $AgAr^+$ of complexes in which silver ions are coördinated to the aromatic nucleus from positions above and below the plane of the ring, are of the same order of magnitude as those for benzene and toluene.

Several compounds have been studied in this investigation to obtain information concerning the argentation constants for compounds in which a phenyl group is conjugated with an ethylenic bond. For styrene a K_1 value of 18.2 was obtained as compared with a value of 2.7 for ethylbenzene. Thus styrene is comparable in reactivity to certain of the less reactive types of alkenes.[12] On the basis of these results it appears that in the styrene molecule the vinyl group, even though its reactivity is reduced by the phenyl substituent, is the primary center for coördination of silver ion. It is probable that for the Ag_2Ar^{++} complexes of styrene, the most likely structure is that in which one silver ion is coördinated at the side chain and the other at the aromatic nucleus. It should be pointed out that Winstein and Lucas[3] have previously noted that propenylbenzene appears to be considerably less reactive with respect to argentation than are the alkenes.

As demonstrated by the K_1 value (6.3) for *trans*-stilbene the introduction of a second phenyl group in the styrene molecule reduces its base strength appreciably. Indeed the dihydro derivative of *trans*-stilbene, bibenzyl, has a higher K_1 value (8.0) in the argentation reaction than does *trans*-stilbene itself.

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(8) Schmidt and Keller, *Z. physik. Chem.*, **A141**, 331 (1929).

(9) Wells, "Structural Inorganic Chemistry," Oxford University Press, London, England, 1945, p. 504.

(10) Pauling, "Nature of Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(11) Berliner and Berliner, THIS JOURNAL, **71**, 1195 (1949).

(12) Winstein and Lucas[3] list K_1 values of 61.7 and 18.2, respectively, for *iso*-butene and trimethylethylene.

In the case of 1,1-diphenylethylene the K_1 value is much lower than that for *trans*-stilbene. In this compound there is undoubtedly appreciable steric interference between rings[13] which is effective in reducing the basicity of the molecule. A complete interpretation of the K_1 and K_2 values for *trans*-stilbene and 1,1-diphenylethylene is difficult since the relative contributions of the phenyl groups and the ethylenic bonds in these molecules in forming bonds with silver ion is not known.

By the methods employed previously[1] a K_1 value for bibenzyl of 6 (twice that for toluene) would be predicted, using the assumption that there is no steric interference between the two phenyl groups of bibenzyl with respect to the coördination of silver ion.[14] A K_2 value for bibenzyl ($^1/_4\, K_1$ for bibenzyl + K_2 for toluene) of 2.2 would also be predicted as compared with an observed value of 0.85. These deviations between predicted and observed values are more marked than those found for other compounds of this type. In terms of the observed K_1 value ethyl cinnamate is a weaker base even than benzene or ethyl hydrocinnamate. Thus the introduction of the carbethoxy group deactivates the styrene molecule with respect to argentation to a considerable extent. It is probable that both steric and electronic effects of the carbethoxy group are responsible for this diminished reactivity. In the case of ethyl hydrocinnamate, with a K_1 value somewhat lower than that for the monoalkylbenzenes, it is probable that the diminished reactivity of the aromatic nucleus results from a steric effect of the somewhat bulky ring substituent.

Summary

In an extension of earlier work the equilibrium constants for the formation of argentation complexes of the type $AgAr^+$ at 25° have been determined for several benzene derivatives. Mesitylene behaves in these reactions as a weaker base than benzene, toluene and the xylenes in contrast to its behavior in other reactions in which the aromatic nucleus is acting as an electron donor. It is possible that the methyl groups in mesitylene, through steric effects, inhibit the argentation reaction. It has been found that for a variety of monoalkylbenzenes the argentation constants are comparable to those for benzene and toluene. Styrene complexes readily with silver ion, probably with the vinyl side chain acting as the electron donor portion of the organic molecule. With *trans*-stilbene, 1,1-diphenylethylene and ethyl cinnamate a much lower reactivity is observed. In fact *trans*-stilbene and ethyl cinnamate coördinate to form $AgAr^+$ less readily than do the corresponding dihydro derivatives, and 1,1-diphenylethylene shows a reactivity comparable with that of benzene.

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[13] Coates and Sutton (*J. Chem. Soc.*, 567 (1942)) calculate on the basis of dipole moment measurements that the rings in biphenyl are twisted 30° out of a common plane. In this configuration ortho hydrogen atoms would effectively eliminate one face of each ring as potential positions for coördination of silver ion.

[14] Jeffrey, *Nature*, **156**, 82 (1945), reports data for crystalline bibenzyl which are in harmony with this assumption.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYDNEY UNIVERSITY]

Sexadentate Metal Complexes. II. Magnetic Studies

BY FRANCIS P. DWYER, FRANCIS LIONS AND DAVID P. MELLOR

The recent resolution of a cobalt(III) complex of 3,6-dithia-1,8-bis-(salicylideneamine)-octane[1] has been interpreted as showing that it is possible for a single molecule to attach itself to a metal atom through six atoms. Since this appears to be the first instance in which experimental evidence, other than that provided by the preparation of a compound of the appropriate composition, has been obtained indicating that a molecule is able to function in such a manner[2] it was thought worth while to obtain verification of its sexadentate character by investigating some further physical consequences of this mode of attachment.

Magnetic susceptibility measurements of compounds of the transition elements can, in certain favorable instances, be used not only to determine the oxidation state but also the number, character and configuration of the chemical bonds formed by these elements.

With such information it is then possible to discover whether a multidentate molecule in a complex of known composition, utilises all of its available coördinating groups in attaching itself to a metal atom.[3] It has been abundantly proved[4] that octahedrally (d^2sp^3) coördinated complexes of Co(III) are invariably diamagnetic. We should therefore expect a sexadentate cobalt

[1] F. P. Dwyer and F. Lions, THIS JOURNAL, **69**, 2917 (1947), and *ibid.*, in press.

[2] A sexadentate function has been proposed for ethylene diamine tetra-acetic acid (YH_4) in the compound $NaCoY_4H_2O$ by Brintzinger, Thiele and Muller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943). Klemm, *ibid.*, **252**, 225 (1944), has shown that $NaCoY_4H_2O$ is diamagnetic but since it is not known whether any of the four water molecules is attached to the cobalt, the sexadentate function of the chelating molecule is, to that extent, a matter of uncertainty. For more recent work on complexes of YH_4 see F. A. Long, S. S. Jones and M. Burke, *Brookhaven Conference Report, Chemistry Number*, **2**, 106 (1948).

[3] D. P. Mellor, *Aust. J. Science*, **3**, 120 (1941); F. P. Dwyer and D. P. Mellor, THIS JOURNAL, **63**, 81 (1941).

[4] F. Rosenbohm, *Z. physik. Chem.*, **93**, 693 (1919).