boxy-9,10-dihydrophenanthrene was determined by oxidation to 9-phenanthroic acid and to phenanthraquinone.

The acid was shown to be *trans* since upon treatment with acetic anhydride or by heating to fusion, it was converted into an anhydride which on hydrolysis gave a new acid, the *cis* form. The *cis* acid was readily reconverted to the *trans* merely by heating in glacial acetic acid or by warming in sodium hydroxide solution.

The *trans* acid is oxidized with difficulty, the *cis* acid or anhydride with great ease. The latter gives as a product, 9,10-dicarboxyphenanthrene anhydride which shows reactions similar to those of phthalic anhydride.

The identification of 9-fluorenecarboxylic acid is based on the correspondence of its properties with those of a previously described compound of established structure and upon its characteristic conversion into fluorene and fluorenone. The fluorene has been proved to be an impurity present in all natural phenanthrenes that have not been especially treated to remove this impurity.

A theoretical discussion is given of several phases of the work: (1) the mechanism of inversion of the geometrical isomers of the 9,10-dicarboxy-9,10-dihydrophenanthrene; (2) the ease of formation of 9,10-dicarboxyphenanthrene from the *cis*-dihydro acid; (3) the ease of formation of the anhydride of 9,10-dicarboxyphenanthrene from the corresponding acid; (4) the mechanism of the addition of sodium to phenanthrene; (5) the role of the solvent, ethylene glycol dimethyl ether.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Dissociation of Hexa-*p*-alkylphenylethanes[1]

BY MAX F. ROY AND C. S. MARVEL

In a previous paper,[2] the preparation of a series of hexa-*p*-alkylphenylethanes in toluene solution was reported. Also, on the basis of the fact that the depth of color of the ethane solutions increased with the weight of the alkyl group, it was postulated that the dissociation of the ethanes increased as the weight of the alkyl groups increased.

The degrees of dissociation of these hexa-*p*-alkylphenylethanes in one-tenth molar benzene solution at 20° have now been measured by the magnetic method. This method, first suggested by Taylor[3] and more recently elaborated by Müller[4] and his associates, consists in measuring the magnetic susceptibility of a solution of a dissociated hexaarylethane. The molecular susceptibility of the ethane in solution may then be calculated, and a comparison of this observed value with that calculated from Pascal's diamagnetic atomic susceptibilities gives the paramagnetic contribution of that part of ethane which is dissociated. The degree of dissociation of the ethane is then the ratio of this observed paramagnetic contribution to that which might be expected if dissociation were complete.

One-tenth molar solutions of the ethanes were prepared by shaking two-tenths molar benzene solutions of the appropriate tri-*p*-alkylphenylchloromethanes with a large excess of molecular silver. Complete conversion of chloromethane to ethane was assumed in this operation. This assumption is reasonable, because the work of Gomberg and Sullivan[5] has shown that similarly prepared solutions of tetraphenyl-di-β-naphthylethane absorbed 99.6, 102, 102, and 100% of the theoretical amount of oxygen.

The magnetic mass susceptibilities of the ethane solutions were measured by the Quincke hydrostatic method, and the degrees of dissociation were calculated as indicated. The degree of dissociation of hexaphenylethane in one-tenth molar benzene solution at 20° was determined and found to be $2.1 \pm 0.5\%$. This value is in good agreement with the value 2.4% calculated for one-tenth molar solution from the equilibrium constant at 23° found by Müller.[4]

The colors of the solutions and the degrees of dissociation of the hexa-*p*-alkylphenylethanes in one-tenth molar benzene solution at 20° are given in Table I.

It may now be stated with certainty that increasing the weight of the aryl groups in a hexa-

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[1] This is the fifth paper in the series. For the fourth paper see THIS JOURNAL, **59**, 1176 (1937).

[2] Copenhaver, Roy and Marvel, *ibid.*, **57**, 1311 (1935).

[3] Taylor, *ibid.*, **48**, 858 (1926).

[4] Müller, *et al.*, *Ann.*, **520**, 235 (1935); **521**, 89 (1935).

[5] Gomberg and Sullivan, THIS JOURNAL, **44**, 1810 (1922).

TABLE I

DISSOCIATION OF HEXA-p-ALKYLPHENYLETHANES

Alkyl group	Color of solution[a]	Degree of dissociation, %
Ethyl	Orange	3.5 ± 0.3
n-Propyl	Orange-red	4.2 ± .8
Isopropyl	Orange-red	4.5 ± .6
n-Butyl	Orange-red	4.9 ± .4
s-Butyl	Wine-red	5.9 ± .4
Isobutyl	Wine-red	6.7 ± .4

[a] There was a slight increase in the depth of color from *n*-propyl through isopropyl to *n*-butyl and from *s*-butyl to isobutyl.

arylethane by introducing various alkyl groups in the *para* position causes a small but definite increase in the dissociation of the ethane. Also, branched chain groups are more effective in producing dissociation than are the corresponding straight chain groups.

These results contradict the prediction of Burton and Ingold[6] that the presence of *o,p*-orienting groups such as alkyl groups in the *para* positions of hexaarylethanes should inhibit radical formation. Actually, all of the hexa-p-alkylphenylethanes studied are more dissociated than hexaphenylethane.

The applicability of the theory of Kharasch[7] which postulates that the electronegativity of the aryl group of a hexaarylethane is the only important factor in its dissociation cannot be tested in this series of hexa-p-alkylphenylethanes, because the relative electronegativities of the various p-alkylphenyl groups are not known.

Nor can the theory of Pauling,[8] that the resonance in the aryl group is the important factor, be tested. It would be predicted that the resonance energy contributed by the different p-alkylphenyl groups would be the same, because varying the alkyl group should not alter the resonance in the p-alkylphenyl group as a whole. However, if resonance is possible in alkanes, and thus in alkyl groups, as later suggested by Wheland,[9] then the theory might apply, but since no quantitative estimations of the effects to be expected from the various alkyl groups are available, the actual applicability of the theory cannot be evaluated.

An attempt was made to prepare a one-tenth molar solution of hexa-p-tolylethane in the manner described. At first, the solution was a light orange, but this color rapidly faded to a light yellow. Magnetic susceptibility measurements on this light yellow solution showed that no free radical was present. This confirms the previous observation of Gomberg[10] that a similarly prepared solution did not have the properties of a free radical solution.

Experimental

The mass susceptibilities of the hexaarylethane solutions were measured by the Quincke hydrostatic method. An all-glass apparatus (Fig. 1) was designed in which the ethane solutions could be prepared and contained throughout the susceptibility measurements.

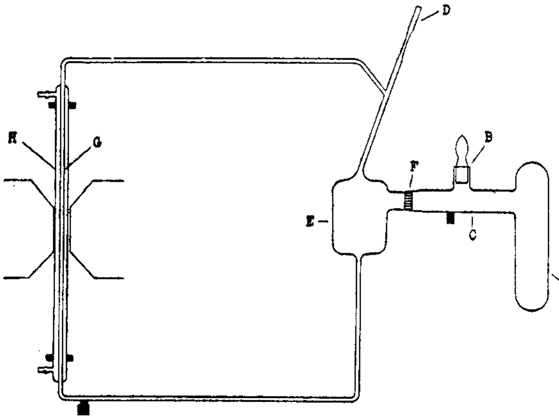

Fig. 1.

The necessary magnetic fields were supplied by the electromagnet described by Shaw.[11] The magnet was fitted with auxiliary conical pole pieces which reduced the diameter of the effective field to 2 inches (5 cm.). With a pole gap of approximately 1 cm., this arrangement gave fields of 22,000–24,000 gausses with currents of 12–15 amperes through the magnet coils. The current through the coils was measured by means of a Weston Model 1 DC ammeter of range 1–25 amperes. On calibration this ammeter was found to give readings reproducible to within 0.5%.

A convenient quantity of a 0.2 molar benzene solution of a triarylchloromethane was introduced into tube A through the glass-stoppered opening B. In order to reduce the vapor pressure of the solvent and prevent evaporation, the solution was cooled (frozen) to a temperature approaching −80° by surrounding tube A with an acetone–dry-ice bath. An eight-fold excess of molecular silver was introduced through B into tube C and the glass stopper was sealed in with de Khotinsky cement. The entire apparatus was then evacuated through tube D to a pressure of 0.1–0.2 mm. and sealed off at the constriction in D. The solution was allowed to warm up to room temperature and was thus contained in the apparatus under its own vapor only.

The entire apparatus was placed in a shaking machine with tube A in a horizontal position, and the solution of

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[6] Burton and Ingold, *Proc. Phil. Soc. Leeds*, **1**, 421 (1929).

[7] Kharasch, *et al.*, *J. Chem. Ed.*, **5**, 404 (1933); THIS JOURNAL, **48**, 3130 (1926); **54**, 674 (1932).

[8] Pauling and Wheland, *J. Chem. Phys.*, **1**, 363 (1933).

[9] Wheland, *ibid.*, **2**, 474 (1934).

[10] Gomberg, *Ber.*, **37**, 1626 (1904).

[11] Shaw, *Rev. Sci. Instruments*, **2**, 611 (1931).

the chloromethane was shaken with the molecular silver for twenty-four hours.

The resulting 0.1 molar hexaarylethane solution was filtered into the large tube E through the sintered glass plate F which effectively held back the silver chloride and excess silver.

The apparatus was mounted on adjustable brass supports with the small tube G in the pole gap of the magnet as indicated in the diagram, and with the plane of the apparatus inclined at an angle to the axis of the poles so that the large tube E was removed as far as conveniently possible from the field of the magnet. The supports were then adjusted so that the meniscus of the solution in tube G was within 1 mm. of the center of the poles. The solution in tube G was kept at 20 ± 0.05° by circulating water from a thermostat through the outer jacket H. Room temperature was generally within one or two degrees of 20° so that little distillation of solvent from one liquid surface to the other could occur.

The procedure outlined above was used where a hexaarylethane solution was prepared in the apparatus for subsequent measurement of its magnetic susceptibility.

Pure liquids and externally prepared solutions in which no reaction was to occur, were introduced in a similar manner in order that they might be observed under their own vapors only. In such cases the addition of molecular silver and the twenty-four-hour shaking period were, of course, omitted.

It will be noted that no dimensions for the glass apparatus are given. In this connection it will suffice to say that tubes E and G had internal diameters of 50 mm. and 3 mm., respectively, and that the rest of the apparatus was of dimensions such that 25 cc. was a convenient quantity of liquid to be used in order to fill partially the large tube E and to give a meniscus about the middle of small tube G.

The changes in meniscus height in tube G on applying fields of different strength were observed by means of a cathetometer. The vernier scale of the cathetometer could be read directly to 0.02 mm., and with some practice the readings could be estimated to 0.01 mm. For the field strengths used (22,000–24,000 gausses) the changes in meniscus height were of the order of 2 mm.

In order to minimize the effects of errors inherent in the method, the mass susceptibility of water at 20°, -0.720×10^{-6} e. s. u.,[12] was taken as standard, and the mass susceptibilities of other liquids (solutions) were obtained by comparing the change in meniscus height of the liquid directly with the change in meniscus height for water in a field of the same strength. The mass susceptibility of the liquid is given by the equation

$$-\chi_x = 0.720 \times 10^{-6} \frac{h_x}{h_{\text{water}}}$$

where χ_x is the mass susceptibility of the liquid in e. s. u., h_x is the change in height of the meniscus for a given field strength, and h_{water} is the change in meniscus height for water in a field of the same strength.

It was assumed that the field strength of the magnet was reproducible with respect to the current through the magnet coils as recorded by the ammeter. In the course of calibrating the field strength in terms of the change in meniscus height for water on several different occasions, it was found that this assumption was valid in that the field strengths at different currents were reproducible within 0.5%. However, in order to minimize the effect of residual magnetism in the magnet as well as any effects due to changes in temperature of the magnet coils during use, the calibrations with water and the subsequent observations on the other liquids were always carried out in the same current-time sequence in so far as possible.

The mass susceptibility of the benzene used to make up the hexaarylethane solutions was measured and the average of sixteen determinations was -0.708×10^{-6} e. s. u.

To test the adequacy of the method for determining the molecular susceptibilities of the hexaarylethanes in benzene solution, the mass susceptibilites of approximately 0.2 molar benzene solutions of several of the structurally similar triarylchloromethanes were determined. The mass susceptibilities of the triarylchloromethanes in solution were calculated by means of the mixture rule and these values multiplied by their respective molecular weights gave their molecular susceptibilities. Also, from these observed molecular susceptibilities of the chloromethanes and the atomic susceptibility of chlorine (-20.1×10^{-6} e. s. u.[12]), the molecular susceptibilities to be expected for the corresponding ethanes in the undissociated state were estimated.

From the results summarized in Table II, it

TABLE II

MOLECULAR SUSCEPTIBILITIES OF TRIARYLCHLOROMETHANES AND HEXAARYLETHANES .

	$-\chi_{\text{mol.}} \times 10^{-6}$	
	Obsd.	Calcd.[a]
Triphenylchloromethane	184 ± 4	183
Tri-*p*-ethylphenylchloromethane	247 ± 4	254
Tri-*p*-*n*-propylphenylchloromethane	287 ± 4	289
Tri-*p*-*n*-butylphenylchloromethane	329 ± 4	325
Hexaphenylethane	328 ± 8	325
Hexa-*p*-ethylphenylethane	454 ± 8	467
Hexa-*p*-*n*-propylphenylethane	534 ± 8	538
Hexa-*p*-*n*-butylphenylethane	618 ± 8	610

[a] Calculated from Pascal's empirical atomic susceptibilities.[13]

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(12) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. VI, p. 345.

TABLE III

DISSOCIATION OF HEXAARYLETHANES IN 0.1 *M* BENZENE SOLUTION AT 20°

Aryl group	A % ethane	B $-\chi \times 10^6$ solution	C $-\chi \times 10^6$ ethane	D $-\chi_{\text{mol.}} \times 10^6$ ethane	E $-\chi_d \times 10^6$ ethane	F $\chi_p \times 10^6$	G α (%)
Phenyl	5.49	0.700 ± 0.002	0.56	272	325	53	2.1 ± 0.5
p-Ethylphenyl	7.41	.698 ± .001	.58	379	467	88	3.5 ± .3
p-*n*-Propylphenyl	8.37	.698 ± .003	.585	432	538	106	4.2 ± .8
p-Isopropylphenyl	8.36	.697 ± .002	.575	424	538	114	4.5 ± .6
p-*n*-Butylphenyl	9.32	.697 ± .001	.59	485	610	125	4.9 ± .4
p-Isobutylphenyl	9.32	.692 ± .001	.535	440	610	170	6.7 ± .4
p-*s*-Butylphenyl	9.32	.694 ± .001	.56	460	610	150	5.9 ± .4
p-Tolyl (?)	6.51	.712 ± .001	.78	445	396	−49	......

may be seen that the agreement between the observed values and those calculated from Pascal's empirical atomic susceptibilities is remarkably good, particularly if it is remembered that the calculations for the observed values involved the use of the mixture rule.

One-tenth molar benzene solutions of the hexaarylethanes, in which the aryl group was phenyl, *p*-tolyl, *p*-ethylphenyl, *p*-*n*-propylphenyl, *p*-isopropylphenyl, *p*-*n*-butylphenyl, *p*-isobutylphenyl and *p*-*s*-butylphenyl, were prepared in the apparatus as previously described. The mass susceptibilities of these solutions were measured at 20° and the degrees of dissociation of the ethanes in solution were calculated.

The results are collected in Table III. The various columns may be explained as follows:

A. The percentage concentration of ethane in the one-tenth molar solution was calculated from the weights of benzene and chloromethane used to make the 0.2 molar chloromethane solution. Complete conversion of chloromethane to ethane was assumed with no loss in weight of solvent.

B. The mass susceptibility of each ethane solution as recorded is the average of eight separate determinations each of which is based on six observations of the change in meniscus height at a given current: three with the cathetometer moving down, *i. e.*, no field to field and three with the cathetometer moving up, *i. e.*, field to no field.

C. The mass susceptibility of the ethane in solution was calculated by means of the mixture rule. The mass susceptibility of the solvent benzene previously was observed to be -0.708×10^{-6} e. s. u.

D. The molecular susceptibility ($\chi_{\text{mol.}}$) of the ethane in solution was calculated by multiplying its mass susceptibility in solution by its molecular weight.

E. χ_d is the diamagnetic molecular susceptibility for the undissociated ethane as calculated from Pascal's empirical atomic susceptibilities.

F. χ_p is the paramagnetic contribution of that part of the ethane which is dissociated in solution and is obtained by subtracting χ_d from χ_{mol}.

G. The degree of dissociation (α) is the ratio of χ_p to 2540×10^{-6} e. s. u. which is the paramagnetic contribution to be expected at 20° if dissociation of ethane were complete.[4]

Summary

1. The degrees of dissociation in 0.1 molar benzene solution of the hexa-*p*-alkylphenylethanes in which the alkyl group was ethyl, *n*-propyl, isopropyl, *n*-butyl, *s*-butyl and isobutyl were determined by the magnetic method.

2. The dissociation of the ethanes increased as the weight of the alkyl group increased.

3. The branched-chain alkyl groups were more effective in producing dissociation than were the corresponding straight-chain groups.

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