of 4.31 × 10^{-10} sec. and 1.29 × 10^{-10} sec., respectively. Values calculated from Stokes' formula by assuming that the molecules are rigid spheres are 2.45 × 10^{-10} sec. and 1.4 × 10^{-10} sec., respectively. From the general agreement of these two sets of values we conclude that the molecules orient as rigid bodies in response to the applied electric field, and that there is no significant internal rotation in either molecule in periods shorter than those corresponding to the critical frequencies.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 23, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Heats of Dissociation of Some Hexaarylethanes[1]

BY RALPH PRECKEL AND P. W. SELWOOD

The purpose of this investigation was to measure the equilibrium constants, the heats, and the entropies of dissociation of several hexaarylethanes, with the primary object of testing experimentally some of the current theories of free radical stability. The data presented were obtained from measurements of magnetic susceptibilities on the ethanes in solution at several temperatures and at several dilutions.

The applicability of the magnetic method to free radical studies has been amply demonstrated by Müller,[2] by Marvel,[3] and by others,[4] including work done[5] in this Laboratory. There appears, however, to have been only one previous attempt to obtain the heat of dissociation of a hexaarylethane by magnetic measurements. Müller[6] obtained a value of 11.6 kcal. for the heat of dissociation of hexaphenylethane, in agreement with the photometric determination of Ziegler,[7] and in fair agreement with the colorimetric determination of Wooster.[8]

Current theories of free radical stability are discussed by Bachmann.[9] Among the theories of most interest at the present time are the "steric" theory, the "resonance" theory, and the attempt by Conant to predict the heats of dissociation of several substituted ethanes. The steric theory has been shown to be inadequate to explain, for instance, the instability of tricyclohexylmethyl. The resonance theory[10,11] has yielded encouraging results with respect to major stability differences among various free radicals, but has been shown[12] to be unable to explain many relatively minor differences in stability. Conant's[13] theory is based on the assumption that the entropy change during dissociation is independent of substituent. The present work lends little support to the resonance theory; it suggests that the differences in stability among the radicals studied are due to steric effects; and it shows that the entropy change is not independent of substituent.

Experimental

Preparation of Materials.—The quantities of triarylmethyl chlorides required for this investigation were obtained, for the most part, through the courtesy of Professor C. S. Marvel and Mr. C. M. Himel of the University of Illinois. The sample of triphenylmethyl chloride was prepared by Dr. J. D. Malkemus, formerly of this University. All of these materials were supplied in a high state of purity, as attested by sharp melting points and their appearance as nearly white powders or crystalline solids. They were obtained vacuum sealed into glass ampoules which, upon being opened, were either immediately evacuated and resealed or stored in a vacuum desiccator.

"Molecular" silver was prepared by internal electrolysis, substantially as described by Gomberg.

Toluene was prepared from "C. P." toluene by repeated extraction with pure concentrated sulfuric acid until the extract no longer showed color. Subsequently this extracted toluene was shaken with successive portions of dilute sodium hydroxide solution and distilled water, dried over phosphorus pentoxide, shaken with C. P. mercury and distilled from sodium, the middle half being collected.

The radical solutions were prepared by shaking a solution of triarylmethyl chloride with a tenfold excess of molecular silver under an atmosphere of toluene vapor at the vapor pressure of the solution. The shaking was continued for a

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[1] Presented at the Symposium on Magnetism and Molecular Structure at the Atlantic City Meeting of the American Chemical Society, September 8–12, 1941.

[2] Müller, Müller-Rodloff and Bunge, *Ann.*, **520**, 235 (1935), *et seq.*

[3] Roy and Marvel, THIS JOURNAL, **59**, 2622 (1937), *et seq.*

[4] Michaelis and Fetcher, *ibid.*, **59**, 2460 (1937), *et seq.*

[5] Selwood, *ibid.*, **61**, 3168 (1939), *et seq.*

[6] Müller and Müller-Rodloff, *Ann.*, **521**, 89 (1935).

[7] Ziegler and Ewald, *ibid.*, **473**, 163 (1929).

[8] Wooster, THIS JOURNAL, **58**, 2156 (1936).

[9] Bachmann in Gilman, "Treatise on Organic Chemistry," Vol. I, John Wiley and Sons, New York, N. Y., 1938, p. 489.

[10] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

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

[12] Marvel, Mueller and Ginsberg, THIS JOURNAL, **61**, 2008 (1939).

[13] Conant, *J. Chem. Phys.*, **1**, 427 (1933).

longer or shorter period depending on the chloride used, though in no case was the shaking period less than two hours. The solution was then filtered through a sintered glass disk into the bulb from which the expansion pycnometer and magnetic sample tube were filled. In order to wash the silver chloride precipitate and excess silver, as well as the preparation bulb, some of the solvent toluene was distilled back into the preparation bulb. After the third washing further washings were never colored, so a threefold washing was considered sufficient.

Filling the Sample Tubes.—The apparatus evolved for use in filling the expansion pycnometer and the magnetic sample tube is shown in Fig. 1. It was sealed at A to an evacuation system consisting of a mercury vapor pump backed by a Cenco Megavac and was mounted on a board to facilitate shaking. The first step was to seal the apparatus, without the sample tubes attached, under high vacuum for 12 hours with freshly melted sodium in B in order to destroy water vapor. The required amount of molecular silver was placed in bulb C. Then the sample tubes were sealed into their respective positions with 2–3 cc. portions of anhydrous toluene in them. Subsequently, this toluene was distilled back through the apparatus and out at A into a dry-ice–toluene trap. Toluene was introduced into B over the sodium, the toluene being heated to the point of reflux several times to melt the sodium, thus ensuring removal of traces of water. The quantities of molecular silver and triarylmethyl chloride required were introduced through the addition tube at D, which was later sealed off at E. The apparatus was then vigorously evacuated, the toluene in B being protected against extensive evaporation by cooling in a dry-ice–toluene bath. After evacuation, the apparatus was sealed off at A and the toluene in B distilled into C by allowing it to warm to room temperature and by sharply cooling C with solid dry-ice. When the distillation was complete, the bulb B was sealed off from the remainder of the apparatus at F. The resulting triarylmethyl chloride solution was shaken with the tenfold excess of molecular silver for several hours, the solution becoming colored immediately owing to formation of free radical. The solution, containing the ethane, free radical and unreacted chloride, was filtered through the sintered glass disk into bulb H. Bulb C and the molecular silver were washed by distilling 2–3-cc. portions of the solvent using the same technique as previously. Then the preparation of the solution was complete, and proper tipping and tilting of the apparatus served to fill the sample tubes, which were washed with the solution before the final filling. After the proper amount of solution had been introduced into the magnetic sample tube, a seal was made at I by melting some Wood's metal on the side of the tube and allowing it to flow into a constriction. This was done so that the solution in the sample tube could be manipulated satisfactorily without danger of changing its concentration; thus, solvent was distilled up and down to clean the walls of the filling tube, and the solution was cooled with dry-ice before the tube was sealed off at J. Similarly, after the pycnometer had been filled a metal seal was made at K and the pycnometer subsequently sealed off at L. Finally, in order to make the apparatus less unwieldy for weighing operations, etc., the filling arm was sealed off at M.

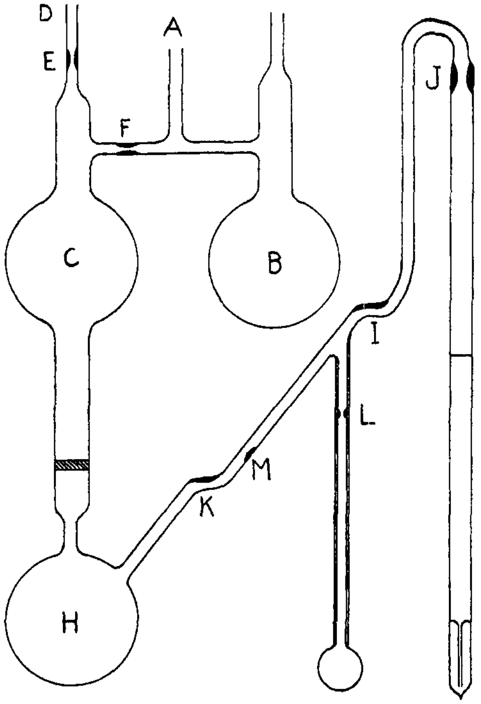

Fig. 1.—Apparatus for preparation of free radical solutions and for filling pycnometer and magnetic sample tube. The magnetic tube, at extreme right, is out of proportion in order to show internal construction.

Density Measurements.—Densities of the solutions over the temperature ranges employed were determined by means of an expansion pycnometer of about 10-ml. capacity with calibrated expansion neck some 10 cm. long. The neck was semi-capillary tubing of about 3 mm. internal diameter with a steel scale securely attached alongside so that it could be read with a cathetometer telescope. The scale was marked in sixty-fourths of an inch or approximately 0.4-mm. divisions. With the cathetometer telescope, readings could be made to half a scale division or ±0.02 cm. It will be seen that this corresponds to less than 0.0014 ml. error, which, in a total volume of 10 ml., gives a tolerance in density of less than ±0.0002. Calibration of the pycnometer was performed with freshly redistilled water, and no measurable hysteresis was observable; the reading at a given temperature was the same whether the temperature was approached from above or below. The pycnometer was immersed in a tall cylindrical oil bath equipped with an efficient variable speed electrical stirrer and heated with a 250-watt knife heater whose heating rate was controlled with a Variac. The temperature was held constant to ±0.1° throughout a period of about ten minutes for each reading. Temperature indication was by means of a calibrated copper–constantan thermocouple used in connection with a Rubicon potentiometer and a Leeds and Northrup HS galvanometer. For the measurements below room temperature, it was found quite satisfactory to make measurements on the solution at 30, 40, etc., and at 0°, and to obtain intermediate values and that for −10° by interpolation and extrapolation, respectively.

Analytical Measurements.—The pycnometer solution was analyzed for total solute by evaporation. The pycnometer was cleaned by dipping it in successive baths of methyl alcohol and benzene until a standardized procedure gave weighings reproducible to ±0.1 mg. The sealed tip was then broken open, care being taken to collect all pieces resulting from the break, and the toluene distilled into a dry-ice–toluene trap under vacuum, using a Cenco Megavac. Thus air was excluded, preventing formation of peroxides, and evaporation was ensured. As the evaporation proceeded, heat was gradually applied to the pycnometer until a temperature of about 100° was attained. Then it was allowed to cool, still under vacuum, and weighed along with the pieces from the break of the seal. Then the pycnometer was cleaned of ethane and chloride and weighed again. The aggregate error in weight of the solute was not more than ±0.2 mg., which, in a total solute weight of 100–300 mg., would not exceed 0.2%. A similar weight error in a total of about 8.5 g. of solution would obviously contribute a negligible error in the density calculation.

In order to obtain the concentration of ethane in the solution, the preparation part of the apparatus (Fig. 1), sealed at points E, F and M, was weighed to 0.01 g. The solution was then removed after breaking the seal between bulbs C and H, care being taken to account for all pieces of glass from the break. After the apparatus was washed with toluene, the weight of solution was obtained by reweighing the dismembered apparatus, again to 0.01 g. The concentration of ethane was obtained from the weight of silver chloride obtained by the reaction producing the ethane. Thus the silver chloride–molecular silver mixture remaining in bulb C was extracted repeatedly with 3 *N* ammonium hydroxide solution, giving a solution which was filtered and from which the silver chloride was reprecipitated by addition of a slight excess of concd. nitric acid. After being cooled, the precipitated silver chloride was collected in a sintered glass Gooch crucible, washed with slightly acidified distilled water and a little pure acetone, dried in an oven at 120° and weighed to ±0.05 mg. The error here is aggregated to 0.1 mg. in 200–400 mg., which is less than 0.05% or less than the error in weighing the solution, which was ±0.02 g. in 20–60 g. or less than 0.1%. Thus the tolerance in concentration of ethane may be reported as less than 0.2%; the concentration of the triarylmethyl chloride, obtained by difference, may be in somewhat larger percentage error, since it was generally present in smaller concentration than the ethane. However, little significance attaches to this fact, since the diamagnetic susceptibility of the chloride is not very different from that of the solvent.

Magnetic Measurements.—The magnetic measurements were performed with the Gouy balance previously described.[14] A new modification was the heating coil of fine nichrome wire wound about the lead heat reservoir in the dewar system. This, in conjunction with a Variac, was used for control above room temperature in an entirely satisfactory manner. Control to ±0.1° was quite simple and could easily be refined to ±0.01° if necessary.

Below room temperature, the previously described technique of cooling the heat reservoir by dropping oxygen liquified in a liquid nitrogen condenser into a copper tube imbedded in the reservoir was again used. However, at the relatively high temperatures here employed, −10° or above, it was found advantageous to maintain the temperature, once it had been reached, by passing a stream of tank nitrogen through the cooling system. At the temperatures used this procedure permitted much better control than did the use of liquid oxygen; here, also, the control to ±0.1° was very easy and doubtless susceptible to further refinement.

The magnetic sample tube was of a modified Freed and Kaspar[15] type which permitted use of rising or falling temperature during the course of a series of measurements. The modification embodied the use of a thin capillary tube communicating between the lower half of the sample tube and the bottom of the partly empty toluene reservoir. In the original Freed and Kaspar tube, communication to the liquid reservoir was through a capillary, necessitating the use of constant or rising temperature.

Treatment of Data.—The measured quantity in the Gouy method is Δw, the apparent change in weight of the sample on application of the magnetic field. From this quantity the susceptibility may be calculated. In this research, using the double ended sample tube modified from Freed and Kaspar's original design, it was necessary first to measure the "tube constant" over the range of temperatures used. These data were obtained by filling both ends of the tube with toluene and measuring Δw at 12.5 amperes, the standard field coil current producing 13,100 oersteds, at the various temperatures. These values correspond to the magnetic dissymmetry of the two ends of the sample tube which was of constant internal diameter (about 5 mm. ±0.01 mm., Pyrex).

The relative susceptibilities of the toluene at various temperatures were then measured by emptying and evacuating one end of the tube and again measuring Δw as a function of temperature. These measurements supplemented by an absolute value of the susceptibility of toluene obtained at 25° gave the absolute susceptibilities of toluene over the desired temperature range.

In order to obtain α, the degree of dissociation of the ethane in solution, it is necessary first to calculate the susceptibility of the solution in question. For example, taking a datum for a solution of di-α-naphthyltetraphenylethane at 0.0410 molal and at 50°: here $\Delta w = 1.222$ mg. using the equation

$$\chi^t{}_{\text{soln.}} = \chi^{25}{}_{\text{toluene}} \times \frac{d^{25}{}_{\text{toluene}}}{d^t{}_{\text{soln.}}} \times \frac{\Delta w^t{}_0 - \Delta w^t{}_{\text{soln.}}}{\Delta w^{25}{}_0 - \Delta^{25}{}_{\text{toluene}}}$$

where χ^t represents the gram susceptibility at temperature t, d the density and Δw the measured change in weight. Δw_0 represents the tube constant and the quantity $\Delta w^{25}{}_0 - \Delta w^{25}{}_{\text{toluene}}$ is

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[14] Haller and Selwood, THIS JOURNAL, **61**, 85 (1939).

[15] Freed and Kaspar, *Phys. Rev.*, **36**, 1002 (1930).

proportional to the gram susceptibility of toluene at 25°. Then, for the datum given above

$$\chi^{50}_{\text{soln.}} = -0.7060 \times 10^{-6}\,\frac{0.8615}{0.8464}\left(\frac{10.588 - 1.222}{10.827 - 0.534}\right)$$
$$= -0.6538 \times 10^{-6} \text{ c. g. s. units}$$

According to Wiedemann's additivity law, the susceptibility of the solution is the algebraic sum of the susceptibilities of solvent and solute multiplied by their respective fractions present. The susceptibility of toluene at 50° is -0.7081×10^{-6}, and of the α-naphthyldiphenylmethyl chloride -0.6697×10^{-6} as computed from Pascal's constants. Hence

$$-0.6538 \times 10^{-6} = 0.9615(-0.7081 \times 10^{-6}) + 0.0152(-0.6697 \times 10^{-6}) + 0.0232\,\chi^{50}_{\text{ethane}}$$

The term $\chi^{50}_{\text{ethane}}$ is the apparent susceptibility of the ethane at 50°. This is actually the resultant of the diamagnetic part and of the paramagnetic contribution of that part of the ethane which is dissociated into radicals.

From the above equation $\chi^{50}_{\text{ethane}} = 1.6024 \times 10^{-6}$, the positive value indicating that dissociation to free radicals has proceeded so far that the paramagnetism of the radicals outweighs the original diamagnetism of the ethane. The diamagnetism of the ethane, computed from Pascal's constants, is -0.6821×10^{-6}, hence the paramagnetic part of the susceptibility is $(1.6024 + 0.6821) \times 10^{-6} = 2.2845 \times 10^{-6}$. This is a direct measure of p, the fraction of solute particles present as free radicals. The total change in susceptibility for 100% dissociation at 50° would be $[(2 \times 1280 \times 298)/(M \times 323)] \times 10^{-6} = 3.9950 \times 10^{-6}$, where 1280×10^{-6} is the molar paramagnetism of a single unpaired electron spin at 25° and M is the molecular weight. The fraction p is then $(2.2845/3.9950) \times 10^{-6} = 0.572$. Since the dissociation proceeds "ethane $\rightleftarrows$ 2 radicals," $p = 2\alpha/(1 + \alpha)$, where α is the degree of dissociation. Then $\alpha = p/(2 - p) = 40.0\%$.

The equilibrium constant is given by

$$K = \frac{4\alpha^2[\text{concn. of ethane}]}{1 - \alpha} = \frac{4(0.400)^2(0.0410)}{0.600} = 0.0438$$

The heat of dissociation, ΔH, is obtained from the van't Hoff expression

$$\mathrm{d}\ln K/\mathrm{d}T = \Delta H/RT^2$$

after integration

$$\Delta H = \frac{2.303\,R(\log K_2 - \log K_1)T_2 \times T_1}{T_2 - T_1}$$

For the above solution at 10°, $K = 0.003947$, which combined with the 50° value gives

$$\Delta H = \frac{2.303 \times 1.98\,(1.0455)\,323.1 \times 283.1}{40} = 11.0 \text{ kcal.}$$

ΔS is calculated according to the thermodynamic equations $\Delta F = \Delta H - T\Delta S$ and $\Delta F = -RT\ln K$.

The Δw obtained originally is accurate to ±0.003 mg., which combined with the tolerance in density of ±0.0002 leads to a tolerance in the calculated susceptibility of the solution of about $\pm 0.0005 \times 10^{-6}$ unit. This in turn leads to not more than a 1% error in the calculation of the apparent susceptibility of the solute ethane. Hence p and α, as well as K, are also subject to this same tolerance. However, since the logarithms of numbers such as were shown above, log 0.0109, are subject to only about 0.5% error for a 1% error in the number, ΔH should also be subject to a maximum tolerance of ±1%. ΔS being almost proportional to ΔH is also uncertain by ±1%. However, disproportionation and other effects make the actual uncertainty considerably greater.

Results

The Disproportionation Reaction.—Marvel and his co-workers have recently in several publications[16] drawn attention to the disproportionation of hexaarylethanes to form substituted methanes and olefinic compounds with the consequent disappearance of the free radical. This reaction was soon encountered in the present work, and, although incidental to the main purpose of the work, necessitated some preliminary investigations which will be described.

The reaction is evidenced as a gradual decrease of magnetic susceptibility with time when a solution containing a free radical is warmed, or, in some cases, simply held at room temperature or lower. The effect is shown in Fig. 2 for a 0.0397 *M* solution of di-*o*-tolyltetraphenylethane in toluene. The measurements were made with rising temperature over an interval of several hours. When the temperature was held near 100° for several hours the apparent degree of dissociation fell to 5% or less. In some cases the free radical disappeared entirely. It is evident, therefore, that accurate determination of the degree of dissociation becomes hazardous above about 50° for this particular ethane.

Different ethanes disproportionated[17] at differ-

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[16] Marvel, Rieger and Mueller, THIS JOURNAL, **61**, 2769 (1939), *et seq.*

[17] The reactions are referred to as disproportionation, although there is no proof of this except in those studied by Marvel.

TABLE I

APPARENT DEGREE OF DISSOCIATION OF SOME HEXAARYLETHANES AT SEVERAL TEMPERATURES

Ethane	Concentration, molal	Degree of dissociation (α) at												
		−10°	0	10	20	25	30	40	50	60	70	80	90	100
Hexaphenyl	0.0163	..	..	..	..	..	0.064	..	0.101	..	..	0.170	..	..
	.0231	..	..	..	..	..	.057	..	.083	..	..	.159	..	..
	.0497	..	..	..	..	..	..	0.042	..	0.073	..	.113	..	..
Di-*o*-tolyltetraphenyl	.0144	..	..	..	..	0.239	.253	.304	.354	.369	0.373	.384	0.406	0.415
	.0156	..	..	0.160	..	.245	..	..	.446	..	..	..	..	..
	.0397	..	..	..	..	.170	.211	.301	.383	.462	.535	.584	.578	.512
	.0648	..	0.090	.117	0.154	..	.204	.274	.346	..	..	..	..	..
Di-α-naphthyltetraphenyl	.0109	0.144	..	..	.352	..	..	..	.591	..	..	..	..	..
	.0278	..	.102	..	..	.261	..	..	.478	..	..	..	..	..
	.0410	..	..	.144	..	.227	..	..	.400	..	..	..	..	..
Tetra-*o*-tolyldiphenyl	.0239	.513	.573	.670	..	..	..	..	..	..	..	..	..	..
	.0699	.529	.635	..	..	..	..	..	..	..	..	..	..	..

ent rates. Of the four compounds studied hexaphenylethane was the most stable, but even in this case the free radical almost entirely disappeared on heating the solution at 100° for twenty-four hours. This thermal decomposition was in all cases carried out in the original magnetic susceptibility sample tube so that the solution was not removed or handled in any way during the reaction. Tetra-*o*-tolyldiphenylethane was the least stable of the four compounds. With this compound measurements had to be restricted to below 10° or less, and even then the determinations proved to be less accurate than anticipated. Table I shows the complete data obtained on all four ethanes at several temperatures and several concentrations. Except for di-*o*-tolyltetraphenylethane data are not given above temperatures at which fairly rapid disproportionation starts. Data obtained at higher temperatures are, of course, useless for calculating equilibrium constants and heats of dissociation.

The importance of this phase of the work is that it raises serious doubts about the significance of ebullioscopic determinations of free radical concentration. In all cases disproportionation takes place at the boiling point of benzene and rapid disproportionation takes place at the boiling point of toluene. It is evident, therefore, that ebullioscopic measurements cannot be relied on for accurate determination of free radical concentration. In some cases the same is true of cryoscopic determinations. There are some reasons for believing that the apparent molecular weight may not greatly change during disproportionation.

The Color Effect.—One of the most interesting observations made during this work had to do with the color of the solutions before and after disproportionation had completely destroyed the free radical. For a long time colorimetric measurements have been used in the study of free radicals, and it has often been assumed that color in a solution is evidence for the presence of a free radical. Gomberg[18] has, however, stated that "the color does not parallel the dissociation," and Marvel[19,20] has several times recently pointed out that colorimetric measurements cannot be relied upon for accurate determination of free radical concentration. The present authors are prepared to go even further and to say that the color of the solution does not necessarily bear any relationship to the presence or absence of a free radical. In all cases studied the color of the solution was the same before and after complete destruction of the free radical as evidenced by magnetic measurements. The intensity of color was definitely diminished by about one-half during disproportionation, but in spite of that the solutions all remained richly col-

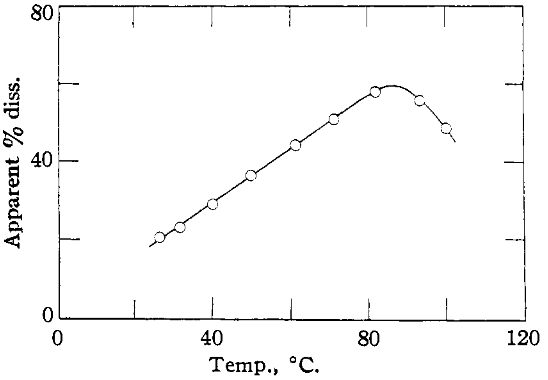

Fig. 2.—Apparent percentage dissociation of a 0.0397 *M* solution of di-*o*-tolyltetraphenylethane in toluene, showing disproportionation becoming rapid above 80°.

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[18] Gomberg and Sullivan, THIS JOURNAL, **44**, 1810 (1922) Gomberg and Forrester, *ibid.*, **47**, 2373 (1925).

[19] Marvel, Mueller, Himel and Kaplan, *ibid.*, **61**, 2771 (1939),

[20] Marvel, Kaplan and Himel, *ibid.*, **63**, 1892 (1941).

TABLE II

EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF SOME HEXAARYLETHANES AT SEVERAL TEMPERATURES

Ethane	Concentration, molal	Equilibrium constant ($K \times 10^3$) at −10°	0	10	20	25	30	40	50	60	70	80	90	100
Hexa-phenyl	0.0163	..	..	..	..	..	0.289	..	0.733	..	..	2.28	..	..
	.0231	..	..	..	..	..	.313	..	.696	..	..	2.78	..	..
	.0497	..	..	..	..	..	..	3.64	..	1.15	..	2.85	..	..
Di-*o*-tolyl-tetra-phenyl	.0144	..	..	..	..	4.13	4.91	7.63	11.15	12.38	12.70	13.78	15.93	16.86
	.0156	..	..	1.91	..	4.96	..	..	22.46	..	..	..	..	..
	.0397	..	..	..	..	5.70	8.96	16.22	29.91	49.84	77.80	102.4	..	..
	.0648	..	2.28	4.02	7.25	..	13.60	26.76	47.47	..	..	..	..	..
Di-α-naph-thyltetra-phenyl	.0109	1.05	..	..	8.34	..	..	..	37.18	..	..	..	..	..
	.0278	..	1.14	..	..	10.28	..	..	48.56	..	..	..	..	..
	.0410	..	..	3.95	..	10.90	..	..	43.83	..	..	..	..	..
Tetra-*o*-tolyl-diphenyl	.0239	51.6	73.4	129.7	..	..	..	..	..	..	..	..	..	..
	.0699	165.8	309.2	..	..	..	..	..	..	..	..	..	..	..

ored even when the free radical was completely destroyed. It is well known that the color of a hexaarylethane is dependent upon the temperature. After disproportionation, however, the color was no longer dependent on the temperature. As disproportionation was generally carried on at a somewhat elevated temperature it often occurred that the solution at room temperature after destruction of the free radical was more intensely colored than the same solution before destruction of the free radical. It is worth mentioning that exposure to air almost instantly bleached the solutions both before and after destruction of the free radical.

The importance of these observations is that they raise serious doubts about the utility of colorimetric studies of free radicals. Apparently the excellent results of Ziegler and of others mentioned above must be regarded as fortuitous. The free radical with which they worked happened to be rather more stable than most. It should be emphasized that even magnetic measurements may be worthless unless they are continued over a period of time to see if disproportionation is taking place.

This work also explains the many contradictory results in the literature on the color of free radicals. It doubtless also explains the interesting observation of Gomberg and Sullivan[18] that the color of β-naphthyldiphenylmethyl upon cooling does not decrease beyond a certain limit. The residual color must have been due to a trace of the similarly colored disproportionation product.

Equilibrium Constants.—Apparent degrees of dissociation for all four ethanes at several concentrations and temperatures are shown in Table I. It is worth mentioning that the commonly accepted value of 60%[9] for the degree of dissociation of di-α-naphthyltetraphenylethane in benzene solution at 5° is probably quite wrong. This raises some doubts concerning the corresponding value for the β-naphthyl. Di-β-naphthyltetraphenylethane is being investigated by the authors at the present time because of the interest these two compounds have in connection with the resonance theory of free radical stability.

Equilibrium constants are shown in Table II. Values are, of course, omitted where disproportionation makes the data useless for calculating heats of dissociation.

Free Energies, Heats, and Entropies of Dissociation.—These values are shown in Table III. The only compound for which earlier data are available is hexaphenylethane. The present values for the heat of dissociation are slightly lower. This is not surprising because even in the previous magnetic determination no precautions were taken to correct for disproportionation. The value for the tetra-*o*-tolyldiphenylethane is for reasons discussed above less accurate than might be desired. From these results it is not yet possible to say that ΔH and ΔS are independent of temperature although they appear to be so.

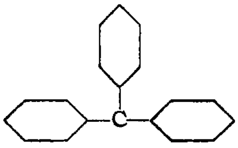
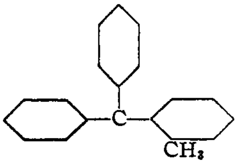
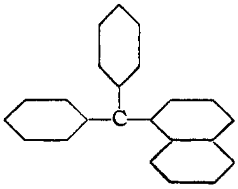
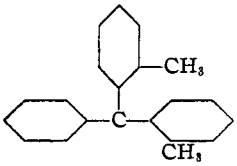
TABLE III

FREE ENERGIES, HEATS AND ENTROPIES OF DISSOCIATION OF SOME HEXAARYLETHANES

Ethane	Concn., molal	Temp. range, °C.	ΔF_{20}, kcal.	ΔH_{20}, kcal.	ΔS_{20}, cal./°C.
Hexa-phenyl	0.0163	30 to 80	5.3	8.9	12.4
	.0231	30 to 80	5.2	9.0	12.8
	.0497	40 to 80	5.1	11.4	21.5
Di-*o*-tolyl-tetra-phenyl	.0144	25 to 50	...	(7.3)	..
	.0156	25 to 80	2.5	10.8	28.2
	.0397	20 to 50	3.9	11.9	27.3
	.0648	10 to 50	2.3	11.3	30.7
Di-α-naph-thyl-tetra-phenyl	.0109	−10 to 50	2.7	10.1	25.3
	.0278	0 to 50	2.8	13.2	35.4
	.0410	10 to 50	2.3	11.0	29.8
Tetra-*o*-tolyldi-phenyl	.0239	−10 to 10	0.9	6.9	20.5
	.0699	−10 to 0	−0.2	8.6	29.9

TABLE IV

BEST PROBABLE VALUES FOR THE DEGREE, FREE ENERGY, HEAT, AND ENTROPY CHANGE OF DISSOCIATION FOR SOME HEXAARYLETHANES

Free radical				
α for 0.03 molal solution at 20°	2.8	19.7	25.2	90.8
ΔF_{20}, kcal.	5.2	2.9	2.7	0.7?
ΔH_{20}, kcal.	9.9	11.4	11.5	8.6?
ΔS_{20}, cal./°C.	16	29	30	27?

Discussion of Results.—The authors' estimates as to the best probable results of this work are indicated in Table IV. Some of the results have been obtained by interpolation, some by extrapolation, and they do not necessarily represent arithmetical means of all data obtained.

These results show first that the entropy change of dissociation is not independent of substituent, although it may yet appear that hexaphenylethane is the only irregular hexaarylethane in this respect. This conclusion with respect to the entropies confirms the observations of Wooster[8] and of Bent,[21] and shows that Conant's interesting attempt to predict degrees of dissociation rests upon a faulty assumption. His theory would also suggest that the heat of dissociation of di-α-naphthyltetraphenylethane would be 4 kcal. less than that of hexaphenylethane. Such is not the case.

In connection with the resonance theory of free radical stability it has often been pointed out that α-naphthyldiphenylmethyl with thirteen "contributing" resonance structures[22] is much more stable than β-naphthyldiphenylmethyl with twelve. The present work shows that this difference in stability may or may not exist. It also shows that di-*o*-tolyltetraphenylethane with only nine contributing resonance structures per radical has the same heat of dissociation as di-α-naphthyltetraphenylethane with thirteen. The degree of dissociation of hexaphenylethane is increased by an *o*-tolyl group almost as much as by an α-naphthyl group. The alkyl group may, of course, also contribute resonance energy, but the extension of the resonance theory to include alkyl groups awaits elaboration. It is quite evident from this work that the addition of an orthoalkyl group, and especially of two such groups (as in tetra-*o*-tolyldiphenylethane) is far more effective in promoting dissociation than a large increase in resonance energy. It should be pointed out that the α-naphthyl group contributes about as much steric effect as an *o*-tolyl group.

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Summary

Magnetic measurements at several temperatures and concentrations have been made on toluene solutions of the following hexaarylethanes: hexaphenylethane, di-*o*-tolyltetraphenylethane, di-α-naphthyltetraphenylethane, and tetra-*o*-tolyldiphenylethane. The results show that the entropy change of dissociation is not independent of substituent, and they support the "steric" rather than the "resonance" theory of free radical stability. The results also show that ebullioscopic measurements may be useless for free radical studies, and that the color of the solution is in no sense an accurate measure of free radical concentration.

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[21] Bent and Ebers, THIS JOURNAL, **57**, 1242 (1935).

[22] By "contributing" structures is meant those structures which actually contribute to the stability of the free radical, not including those which are also found in the undissociated ethane.