

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Studies on the Dissociation and Disproportionation of Some Hexaarylethanes

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Previous communications from this Laboratory^{1a} have given the heats of dissociation of hexylphenylethane, di-*o*-tolyltetraphenylethane, di- α -naphthyltetraphenylethane, and tetra-*o*-tolylidiphenylethane. Rate constants and activation energies have been given for the disproportionation of di-*o*-tolyltetraphenylethane.² To these results the present paper adds heats of dissociation and other thermodynamic constants for di-*o*-chlorophenyltetraphenylethane and for di- β -naphthyltetraphenylethane. Rate constants are given for the disproportionation of di-*p*-tolyltetraphenylethane. All the previously published results on heats of dissociation have been recalculated to correct an error in the method of calculating degrees of dissociation. Reference to this error has already been made.² Some of the data in Table I are not directly comparable with those published in 1941 because more experience with the magnetic susceptibility method has led us to reject certain data which we formerly believed were accurate. The conclusions drawn from the corrected results do not differ greatly from those originally reported, but all the reliable data, old and new, have been assembled in one table in the present paper.

Experimental

The magnetic measurements and the preparation of free radicals have already been described.^{1,2} Again the authors are indebted to Professor Carl S. Marvel of the University of Illinois for supplying the triarylmethyl chlorides. All solutions were in toluene.

Results

All results on the five ethanes are summarized in Table I. Table II shows the best average values for free energy, heat and entropy changes for the various ethanes, as derived from the data of Table I.

These results confirm the general conclusions previously reached. It appears that the entropy change associated with dissociation is not independent of substituent, although the difference between hexaphenylethane and the other ethanes is not so large in this respect as previously reported.

It is also confirmed that the heats of dissociation are substantially independent of the substituent. On the other hand, large differences in percentage dissociation are produced by what must obviously be steric effects. However, the difference in de-

(1) Ward Byerly died at Oak Ridge, Tennessee, January 13, 1943.

(1a) Preckel and Selwood, *THIS JOURNAL*, **63**, 3397 (1941).(2) Selwood and Preckel, *ibid.*, **65**, 895 (1943).

TABLE I

APPARENT DEGREE OF DISSOCIATION AND EQUILIBRIUM CONSTANTS FOR SOME HEXAARYLETHANES IN TOLUENE SOLUTION AT SEVERAL CONCENTRATIONS AND TEMPERATURES

The data are given in the following order: ethane, molal concentration, temperature, degree of dissociation $[\alpha]$, and equilibrium constant, $K \times 10^8$.

Hexaphenylethane.—0.0163 *M*; 60°, 0.200, 3.27; 70°, 0.257, 5.81; 80°, 0.296, 8.09.—0.0231 *M*; 60°, 0.199, 4.58; 70°, 0.241, 7.08; 80°, 0.300, 11.9.—0.0497 *M*; 60°, 0.134, 4.12; 80°, 0.204, 10.4.

*Di-*o*-tolyltetraphenylethane*.—0.0156 *M*; 30°, 0.426, 19.7; 40°, 0.518, 34.7; 50°, 0.622, 63.7.—0.0397 *M*; 30°, 0.349, 29.7; 40°, 0.433, 52.4; 50°, 0.523, 91.2; 60°, 0.601, 143; 70°, 0.644, 209; 80°, 0.704, 266; 90°, 0.699, 257.—0.0649 *M*; 10°, 0.184, 10.7; 20°, 0.243, 18.5; 30°, 0.312, 36.6; 40°, 0.395, 66.8; 50°, 0.485, 118.

Di- α -naphthyltetraphenylethane.—0.0109 *M*; 10°, 0.285, 4.94; 20°, 0.483, 19.7; 30°, 0.562, 31.4; 50°, 0.743, 93.5.—0.0278 *M*; -10°, 0.150, 2.96; 0°, 0.203, 5.73; 10°, 0.271, 11.2; 20°, 0.351, 21.1; 30°, 0.459, 43.2; 40°, 0.553, 76.0; 50°, 0.615, 109.—0.0410 *M*; 20°, 0.324, 25.4; 30°, 0.373, 36.3; 40°, 0.488, 76.1; 50°, 0.570, 123.

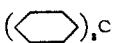
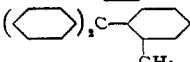
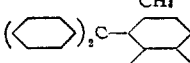
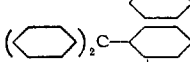
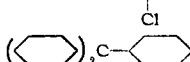
*Tetra-*o*-tolylidiphenylethane*.—0.0239 *M*; -10°, 0.678, 137; 0°, 0.728, 186; 10°, 0.802, 311.—0.0699 *M*; -10°, 0.692, 435; 0°, 0.777, 757.

*Di-*o*-chlorophenyltetraphenyl*.—0.0399 *M*; -10°, 0.043, 0.31; 0°, 0.062, 0.65; 10°, 0.083, 1.19; 20°, 0.115, 2.37; 30°, 0.152, 4.32; 40°, 0.196, 7.60; 60°, 0.325, 24.9.

Di- β -naphthyltetraphenylethane.—0.0246 *M*; 30°, 0.105, 1.22; 40°, 0.143, 2.34.—0.436 *M*; 30°, 0.0938, 1.69; 40°, 0.119, 2.53; 50°, 0.161, 5.42; 60°, 0.211, 9.88; 80°, 0.333, 29.1.—0.0821 *M*; 30°, 0.0656, 1.51; 40°, 0.089, 2.85; 50°, 0.123, 5.72; 60°, 0.142, 8.13; 70°, 0.192, 14.9.

TABLE II

PROBABLE VALUES FOR THE PERCENTAGE DISSOCIATION (100 α FOR 0.03 MOLAL SOLUTION AT 20°), THE FREE ENERGY, HEAT, AND ENTROPY CHANGE

Free radical	100 α for 0.03 <i>M</i> solution at 20°	ΔF_{20} , kcal./ mole	ΔH_{20} , kcal./ mole	ΔS_{20} , cal./ mole °C.
	1.7	4.7	10.9	21.2
	30	2.4	11.2	30.0
	34	2.2	10.4	28.0
	11.5	3.1	11.2	26.2
	2.5	4.2	12.0	26.6

gree of dissociation produced by an α -naphthyl group as compared with an o -chloro group might be interpreted as being due to resonance. The difference between α -naphthyl and β -naphthyl supports the resonance theory of free radical stability.

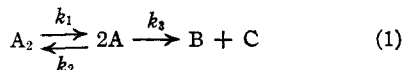
The results obtained on di- o -tolylphenylmethyl are of little significance because of the high rate of disproportionation shown by this radical.

We turn now to a rate study on the disproportionation of p -tolylidiphenylmethyl. The problem is one of some difficulty because the solutions must be prepared and handled below 0° . It is complicated in another way. In our previous study on the disproportionation of o -tolylidiphenylmethyl the ethane was at least 90% dissociated at the beginning of each run. But the degree of dissociation for p -tolylidiphenylmethyl is much less, and the changes in paramagnetism are correspondingly slight.

In Fig. 1 we show free radical concentrations plotted against time. The initial concentrations of ethane, and the temperatures at which disproportionation was observed are as follows: 0.0632 molal at 10° , and 0.0632 molal at 25° . For time intervals not in excess of ten hours these results give reasonably consistent velocity constants.

No difficulty is found in calculating the free radical concentration at any time, from the magnetic data, by the method previously used. But there is a difficulty in calculating the velocity constants because of the equilibrium, ethane \rightleftharpoons 2 radicals. The constants have been evaluated in the following way: Let $[A_2]$ be the concentration of the ethane, $[B]$ and $[C]$ those of the disproportionate.

We have



$$d[A]/dt = k_1[A_2] - k[A]^2 - k_3[A]^2 \quad (2)$$

and

$$k_1/k_2 = [A]^2/[A_2] \quad (3)$$

eliminating A_2

$$d[A]/dt = -k_3[A]^2 \quad (4)$$

and integrating

$$1/[A]_2 - 1/[A]_1 = k_3(t_2 - t_1) \quad (5)$$

where $[A]_2$, $[A]_1$ are concentrations of free radical at times t_2 , t_1 .

Rate constants derived in this way from the first few hours of disproportionation are as follows: 0.0632 M at 10° , $k_3 = 12.92$; 0.0632 M at 25° , $k_3 = 41.8$. We find the activation energy to be 13.1 kcal. per mole of free radical. It seems probable that this is a maximum value, because disproportionation of o -tolylidiphenylmethyl required an activation energy of only 11.4 kcal. per mole, and the experiments and calculations in that case were much less complex.

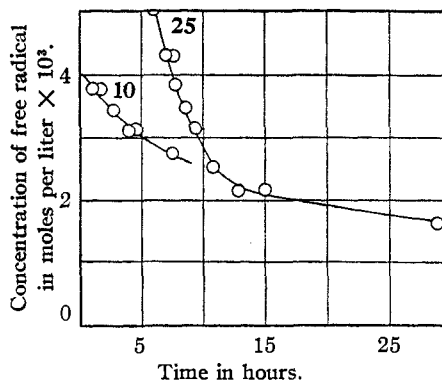


Fig. 1.—Disproportionation of p -tolylidiphenylmethyl.

An interesting observation was made during the work on p -tolylidiphenylmethyl. It will be recalled that the complete disproportionation of o -tolylidiphenylmethyl leaves the solution colored almost the same as when the free radical is present. The disproportionation of the p -tolyl also leaves the solution strongly colored *provided that the reaction is carried out in the dark*. If the disproportionation is carried out in the light, the loss of color parallels the loss of paramagnetism. But in the dark the solution remains colored even though all the free radical is destroyed. If now the solution is exposed to light the color fades in a few moments.

An attempt was made during this work to obtain the activation energy of the dissociation process by magnetic measurements on certain ethanes. The experimental difficulties proved insurmountable.

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