polymerized under the same conditions, since they act as poisons to the catalytic decomposition of hydrazine.

3. Polymerization is proportional to the palladium employed, to hydrazine and monomer concentrations at low values of these, becoming independent of these at higher concentrations.

4. The degree of polymerization is proportional to the monomer concentration and insensitive to hydrazine concentration and amount of palladium employed.

5. Chain initiation of polymerization occurs in only a very small fraction of the processes of catalyzed hydrazine decomposition.

6. A mechanism involving the growth of solid polymer by interaction of monomer with a free radical within a solid particle has been suggested, the growth being initiated by a reaction at the catalyst surface.

7. Chain transfer processes with monomer and hydrazine are indicated.

8. The experiments show that, under favorable circumstances, chain reactions may be initiated at catalyst surfaces and projected into the surrounding liquid media for propagation.

PRINCETON, NEW JERSEY RECEIVED MARCH 8, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Diamagnetic Correction for Free Radicals

BY P. W. SELWOOD AND ROBERT M. DOBRES

Calculations of free radical concentrations from susceptibility measurements involve a correction for the underlying diamagnetism of the free radical. In substituted triphenylmethyls this correction may be comparable in magnitude with the paramagnetic contribution, although, of course, opposite in sign. It is not possible to measure this diamagnetic correction directly, but considerable confidence has nevertheless been attached to the usual methods for estimating the correction. Two methods have commonly been used. These are, first, an application of Pascal's constants and, second, a direct measurement on the corresponding methane, followed by a small correction for one hydrogen. The satisfactory agreement between these two methods is the principal factor which has given confidence in the procedure.

There are in the literature some indications that magnetic measurements sometimes give anomalous results on free radicals. Solutions of the Chichibabin hydrocarbon,[1] although highly reactive and strongly colored, have been reported on the basis of susceptibility measurements, as being not over 2% dissociated to a biradical. But the *ortho–para* hydrogen conversion[2] on solutions of this substance suggest about 10% dissociation. There is also the anomaly that solutions of hexa-*p*-biphenylethane have been shown to be considerably less dissociated,[3,4] on the basis of magnetic measurements, than the pure crystalline solid seems to be. Cryoscopic measurements on this ethane have given contradictory results.[5,6]

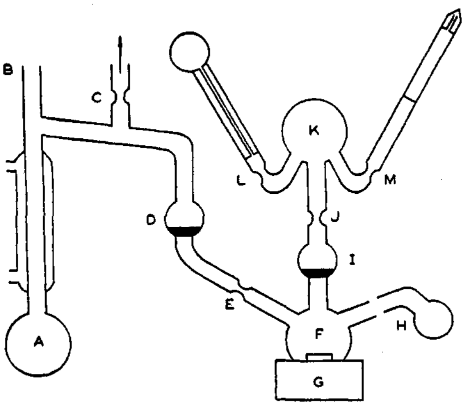

Fig. 1.—Apparatus for preparation and handling of free radicals.

Experimental

Preparation of Materials.—Tri-*p*-biphenylmethyl chloride and tri-*p*-*t*-butylphenylmethyl chloride were obtained through the courtesy of Professor C. S. Marvel of the University of Illinois.

Toluene was extracted with concd. sulfuric acid, washed with water, then with 5% bicarbonate solution, then with water again. It was refluxed over sodium for several hours, then distilled.

Technical pyrene was dissolved in benzene, filtered and twice crystallized.

Solutions of the free radicals were prepared in the apparatus shown in Fig. 1. The apparatus was cleaned, then rinsed with distilled water made faintly alkaline, and thoroughly dried. Toluene and clean sodium slices were introduced into A, which was then cooled to −75°, permitting sealing off at B. The triarylmethyl chloride was placed in F, the molecular silver in a side-arm bulb which was then sealed at H. The toluene was refluxed over the sodium for about one hour. This liquid was cooled to −75° and maintained at this temperature while the entire system was evacuated. The system was sealed off from the vacuum line at C. When A was immersed in tepid water and D, a sintered glass filter, was packed with Dry Ice, the toluene distilled into F which was immersed in a Dry Ice–acetone-bath. A seal was then made at E.

The solute present in F was dissolved with the aid of a magnetic stirrer G. All operations involving the hexaarylethanes were carried out in the dark. Molecular

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[1] Müller and Müller-Rodloff, *Ann.*, **517**, 134 (1935).

[2] Schwab and Agliardi, *Ber.*, **73B**, 95 (1940).

[3] Müller, Müller-Rodloff and Bung, *Ann.*, **520**, 251 (1935).

[4] Marvel, Shackleton, Himel and Whitson, THIS JOURNAL, **64**, 1824 (1942).

[5] Schlenk, Weickel and Herzenstein, *Ann.*, **372**, 1 (1910).

[6] Bachman and Kloetzel, *J. Org. Chem.*, **2**, 356 (1937).

silver, in 15-fold excess, was added gradually by tilting the apparatus, over a period of 4 to 24 hours. The solution was then filtered into K through a sintered-glass disc I.

The lower part of the system was disconnected by sealing at J. The magnetic sample tube and the pycnometer were rinsed with the solution, filled to desired height, and sealed at M and L, respectively.

Susceptibility and Density Determinations.—These were done substantially as previously described.[7]

Analysis of Samples.—Solutions were analyzed for total solute, for extent of reaction of the triarylmethyl chloride with silver, and for unreacted triarylmethyl chloride in the filtered solution.

Total solute concentration was found as follows: a portion of solution was transferred in carbon dioxide or nitrogen to a stoppered flask. The flask and solution were weighed. The solvent was then distilled off, to constant weight at 100°. Nitrogen was admitted to the residue, and the flask and contents were reweighed.

The per cent. conversion was found as follows: The residue from filtration, during the preparation step, contained principally silver chloride and excess silver. This residue was washed out of the reaction vessel with benzene, then filtered. It was repeatedly extracted with 1:1 ammonia water, and filtered, together with washings from the reaction vessel, until the filtrate no longer gave a test for chloride ion. Silver chloride was precipitated from the filtrate and determined gravimetrically. This determination was used to find the weight of triarylmethyl chloride which reacted, and this in turn compared with the original weight of triarylmethyl chloride introduced, permitted calculation of the extent of reaction.

If all the hexaarylethane formed had been soluble, no further analytical data would have been required, but with hexa-*p*-*t*-butylphenylethane this was not true. It was therefore necessary to determine what fraction of the total solute was unreacted triarylmethyl chloride. This was done by a modified micro-Carius determination as follows: The solid remaining from the total solute determination was scraped from the vessel, and about 0.3 g. of it was weighed into a Carius tube. Powdered C. P. silver nitrate was added together with about 10 cc. of C. P. fuming nitric acid. The tube was sealed and heated gradually over a period of about five hours to 225–250°, at which temperature it was held for several hours. The tube was cooled and opened, and the contents washed into a beaker. The mixture was digested until clear. The silver chloride was then determined gravimetrically. The filter was always cleared of silver chloride by 30% potassium iodide solution, washed and reweighed to correct for possible glass splinters introduced during opening of the Carius tube. A further correction was made for the fact that the hexaarylethane, having been exposed to air, contained peroxide.

With the data described above it was felt that the solutions could be characterized with considerable confidence.

Results

The susceptibility of toluene from 0 to 150° is given in Table I. These data are based on the value[8] $\chi_{25°} \times 10^6 = -0.7060$.

The results in Table I were obtained with both ends of the differential susceptibility tube filled with toluene.

Susceptibility data for three solutions containing hexa-*p*-biphenylethane are given in Tables II, III and IV. The degree of dissociation, α, was calculated as described elsewhere.[3] These calculations assume additivity of susceptibilities for all molecular species present. The diamagnetic correction for the free radical tri-*p*-biphenylmethyl was calculated from Pascal's constants to be -0.66×10^{-6} per gram. That for tri-*p*-*t*-butylphenylmethyl was -0.74×10^{-6}. In these tables χ_S is the susceptibility per gram of solution.

TABLE I

SUSCEPTIBILITY OF TOLUENE AT SEVERAL TEMPERATURES

Temp., °C.	Density g./cc.	$-\chi \times 10^6$
0	0.8855	0.7056
10	.8762	.7058
20	.8669	.7059
25	.8623	.7060
30	.8577	.7061
40	.8483	.7063
50	.8389	.7066
60	.8294	.7069
70	.8199	.7072
80	.8102	.7077
90	.8001	.7083
100	.7896	.7094
110	.7795	.7102
130	.7590	.7120
150	.7384	.7138

TABLE II

APPARENT DISSOCIATION OF HEXA-*p*-BIPHENYLETHANE (A)[a]

Weight fraction total solute 0.0160; fraction of solute which is ethane, 0.940; weight fraction ethane in solution, 0.0150; weight fraction chloride in solution, 0.0010; molal concentration of ethane, 0.0161_6.

Temp., °C.	Density, g./cc.	$-\chi_S \times 10^6$	α
0	0.8885	0.6693	0.814
10	.8791	.6706	.815
20	.8700	.6721	.811
30	.8612	.6733	.812
40	.8518	.6743	.819
50	.8425	.6760	.809
70	.8234	.6783	.807

[a] It was found that toluene solutions of hexa-*p*-biphenylethane and of hexa-*p*-*t*-butylphenylethane undergo, in the dark, slow irreversible reactions at moderately elevated temperatures. These reactions are between solute and solvent. Their kinetics will be described in a future paper.

TABLE III

APPARENT DISSOCIATION OF HEXA-*p*-BIPHENYLETHANE (B)

Weight fraction total solute, 0.00964; fraction of solute which is ethane 0.916; weight fraction ethane in solution, 0.00884; weight fraction chloride in solution, 0.0008; molal concentration of ethane, 0.0094_6.

Temp., °C.	Density, g./cc.	$-\chi_S \times 10^6$	α
0	0.8873	0.6845	0.787
10	.8781	.6853	.791
20	.8689	.6861	.791
25	.8643	.6866	.788
30	.8597	.6869	.793
40	.8503	.6880	.780
50	.8410	.6889	.777
60	.8316	.6901	.754

Data for hexa-*p*-*t*-butylphenylethane are given in Tables V, VI, and VII. This proved to

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(7) Haller and Selwood, THIS JOURNAL, **61**, 85 (1939).

(8) Preckel and Selwood, *ibid.*, **63**, 3397 (1941).

TABLE IV

APPARENT DISSOCIATION OF HEXA-*p*-BIPHENYLETHANE (C)

Weight fraction total solute, 0.0134; fraction of solute which is ethane, 0.935; weight fraction ethane in solution, 0.0125: weight fraction chloride in solution, 0.0009; molal concentration of ethane, 0.0134.

Temp., °C.	Density, g./cc.	$-\chi_s \times 10^6$	α
0	0.8884	0.6758	0.78$_6$
10	.8791	.6764	.80$_4$
20	.8698	.6781	.78$_6$
30	.8609	.6791	.78$_8$
40	.8512	.6804	.78$_0$
50	.8418	.6808	.80$_2$

be a difficult compound with which to work. Conversion of the methyl chloride never exceeded 82%, the ethane had a very low solubility, and the solution was sensitive to light. The absolute degrees of dissociation are, therefore, much less reliable than those reported above, but the relative values at different temperatures seem to be significant.

TABLE V

APPARENT DISSOCIATION OF HEXA-*p*-*t*-BUTYLPHENYLETHANE (A)

% conversion of chloride, 79.5; weight fraction of total solute, 0.00581; fraction of solute which is ethane, 0.670; weight fraction ethane in solution, 0.00389; weight fraction chloride in solution, 0.00192; molal concentration of ethane, 0.00475.

Temp., °C.	Density, g./cc.	$-\chi_s \times 10^6$	.α
0	0.8864	0.6950	0.7$_9$
10	.8764	.6963	.7$_3$
20	.8671	.6968	.7$_3$
25	.8626	.6871	.7$_2$
30	.8581	.6972	.7$_3$
40	.8486	.6979	.7$_1$
50	.8392	.6986	.7$_0$

TABLE VI

APPARENT DISSOCIATION OF HEXA-*p*-*t*-BUTYLPHENYLETHANE (B)

% conversion of chloride, 81.6; weight fraction of total solute, 0.0064$_9$; fraction of solute which is ethane, 0.659; weight fraction ethane in solution, 0.00428; weight fraction chloride in solution, 0.0022$_1$; molal concentration of ethane, 0.00523.

Temp., °C.	Density, g./cc.	$-\chi_s \times 10^6$	α
0	0.8863	0.6967	0.6$_2$
10	.8768	.6973	.6$_1$
20	.8675	.6977	.6$_1$
30	.8585	.6980	.6$_2$
40	.8490	.6986	.6$_1$
50	.8396	.6992	.6$_1$
60	.8302	.6996	.6$_2$

TABLE VII

APPARENT DISSOCIATION OF HEXA-*p*-*t*-BUTYLPHENYLETHANE (C)

% chloride converted, 72; weight fraction total solute, 0.0113; fraction of solute which is ethane, 0.657; weight fraction ethane in solution, 0.0074; weight fraction chloride in solution, 0.0039; molal concentration of ethane, 0.0091.

Temp., °C.	Density, g./cc.	$-\chi_s \times 10^6$	α
20	0.8682	0.6927	0.57
30	.8590	.6931	.58
40	.8497	.6937	.58
50	.8403	.6944	.58

The color of both ethane solutions was noted. Between room temperature and 100° there was no perceptible change of color. Below 0° the colors became lighter.

For reasons to be described below, recrystallized pyrene was investigated. The magnetic susceptibility of this compound was found to be the same in the powdered solid state (random orientation), and in toluene solution.

Discussion and Results

All magnetic results on both ethanes give the same anomalous result, namely, that the ethanes are less than 100% dissociated but that the dissociation has no temperature dependence. This result is supported by the observations on the colors of both ethane solutions, which are in sharp contrast to the strongly thermochromatic behavior of nearly all other hexaarylethanes.

There are several possible explanations for these anomalous results. One explanation is that the molecules of radical and of ethane, owing to their high molecular anisotropy, assume a preferred orientation in the magnetic field. The greatest molecular diamagnetism would thus be perpendicular to the field in a manner similar to that in which graphite flakes assume preferred orientations in a magnetic field. But the highly conjugated hydrocarbon pyrene was found to have the same susceptibility in toluene solution as in the solid powder where the molecules in the discrete powder particles were of necessity at random orientation to the field. There is the possibility that the degree of dissociation is actually about 80%, that ΔH is near zero, and that the change of free energy is due to a substantial entropy change. This explanation seems less well supported by the evidence than does the explanation given below. Another possibility considered is that the toluene solvent suffers a change of diamagnetism. Such solvent effects are considered unlikely in view of the exhaustive investigation reported by Angus.[9]

A more reasonable explanation involves resonance stabilization and its relation to molecular diamagnetism. The current theory of resonance stabilization implies that additional resonance in the radical stabilizes it with respect to the ethane. The additional resonance is brought about by an increase of electronic currents from those normally produced in isolated aromatic rings. But this is precisely the condition which leads to enhanced diamagnetism perpendicular to the plane of the rings. The molecular anisotropy of aromatic groups is well established both by theory and experiment. The anisotropy of conjugated ali-

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[9] Angus and Tilston, *Trans. Faraday Soc.*, **43**, 221 (1947).

phatics is equally well established by experiment. An explanation for the anomalous results reported here is that the resonance stabilization of triarylmethyls is accompanied with an increase of diamagnetism perpendicular to the rings, in other words, with an increase of molecular anisotropy in the free radicals. An explanation of this sort has been suggested by Wheland.[10]

If this explanation is correct, then it is clear why neither Pascal's constants nor a measurement on the corresponding methane can ever give the true diamagnetic correction. Neither the Pascal's constants method nor the methane method are structurally comparable to the free radical itself because the additional electronic currents are ignored in the one case, absent in the other.

In order to explain the results observed in this work, it is necessary to assume that the diamagnetic correction has been underestimated by from 65 to 120%. If an enhancement of diamagnetism actually occurs it is likely to be only in the direction perpendicular to the plane of the rings. The observed results could, therefore, be explained on the basis of a 195 to 360% increase in the principal molecular susceptibility normal to the plane of the rings. This increase is large, and unfortunately there seems to be available no method by which the electronic currents may be estimated in the resonating bonds joining the rings to the methyl carbon. There is as yet no magnetic theory for aliphatic conjugation, and this is essentially the problem involved. However, it is to be noted that a 300% anisotropy is by no means unusual. In fact, this is approximately the anisotropy produced in benzene itself by one resonating electron. If one free electron may be thought of as circulating around the whole structure of any triarylmethyl, then it is easy to imagine such a substantial increase of diamagnetism. Further support for this explanation is gained from the decrease of the necessary diamagnetic increment with increasing temperature. It is well known that resonance produced diamagnetic anisotropy is diminished with rising temperature.

It will be noted that this explanation serves for the anomaly previously mentioned in connection with the Chichibabin hydrocarbon. If the diamagnetic correction is thus underestimated it becomes clear why a direct susceptibility measurement on this hydrocarbon could be interpreted as indicating no dissociation, while an *ortho–para* hydrogen determination which involves no diamagnetic correction could yield a more accurate result.

It is somewhat more difficult to explain the reported 100% dissociation of hexa-*p*-biphenylethane in the solid. Possibly the fitting of the free radical molecules into the crystal lattice involves sufficient distortion to reduce the electronic currents and hence the molecular anisotropy. But it is not clear if this could be done and yet leave sufficient resonance energy to stabilize the radical.

It is a pleasure to acknowledge the support of the United States Rubber Company in connection with this work.

Summary

Magnetic susceptibility measurements on toluene solutions of hexa-*p*-biphenylethane and hexa-*p*-*t*-butylphenylethane suggest that resonance stabilization of triarylmethyls is accompanied by a substantial increase of molecular diamagnetism. This observation throws some doubt on quantitative magnetic studies on free radicals.

EVANSTON, ILLINOIS RECEIVED JANUARY 28, 1950

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[10] G. W. Wheland, "Advanced Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 696.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Photochemical Studies. XLIII. Propiolactone[1]

BY ROBERT H. LINNELL AND W. ALBERT NOYES, JR.

The photochemical decomposition of β-propiolactone does not seem to have been investigated previously. Data essential for establishing the details of the mechanism could not be obtained for this compound. Its vapor pressure at 51° is only 10 mm. so that studies of the vapor could not be made without using higher temperatures. Polymerization and other thermal reactions make the compound unstable under such conditions. The photochemical data were obtained by irradiation of the liquid.

Experimental

The β-propiolactone was obtained from the B. F. Goodrich Company and was synthesized from ketene and formaldehyde.[2] It polymerizes slowly at room temperature but can be kept satisfactorily at 5° or below. The physical properties have been listed.[3] The material used in these experiments was vacuum distilled from a temperature of 25° and condensed at 0°, the middle fraction was retained, and it was stored at 0°; $n^{25}\text{D}$ 1.4104, lit. 1.4110.[3]

Chloroform used as a solvent for obtaining the absorp-

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[1] This work was supported in part by Contract N6onr-241, Task I, with the Office of Naval Research, United States Navy.

[2] F. E. Küng, U. S. Patent 2,356,459 (1944); T. R. Steadman, *ibid.*, 2,424,589 (1947); T. R. Steadman and P. L. Breyfogle, *ibid.*, 2,424,590 (1947).

[3] T. L. Gresham, J. E. Jansen and F. W. Shaver, THIS JOURNAL, **70**, 998 (1948).