[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BOSTON UNIVERSITY]

Ionization Equilibria in Liquid Sulfur Dioxide. II. The Electronic Influence of the Phenyl Group[1]

BY NORMAN N. LICHTIN AND HERBERT GLAZER

The equivalent conductances of mono-*m*- and mono-*p*-biphenylyldiphenylchloromethane have been measured in liquid sulfur dioxide at 0.1° over a wide range of concentrations. Equilibrium constants (K_{exp}) and limiting conductances (Λ_0), calculated by Shedlovsky's method, are 3.12×10^{-5} and 175, respectively, for the meta compound and 23.2×10^{-5} and 190, respectively, for the para compound. The significance of the results relative to the electronic influences of the phenyl group is discussed.

Introduction

It has long been recognized that a phenyl group is capable of attracting electrons from an alkyl or substituted alkyl group.[2–4] Although early papers[2–4] ascribed an intrinsic electron attracting ability to the phenyl group, it is usually possible to adequately explain its electronic influence in terms of its ability to distribute electrical charges or odd electrons.

Wheland,[5] however, has pointed out that there are theoretical reasons for expecting that a carbon atom of a phenyl group should be more electronegative than a saturated carbon by virtue of electronic interactions not associated with the resonance distribution of charge into the benzene ring. The large body of evidence[6,7] on metalation of benzene by alkylsodium compounds can be interpreted as supporting this conclusion.[5]

Relatively unambiguous evidence on the quantitative aspects of this influence is very sparse. This is particularly so because of the coexistent resonance interaction usually present. A striking example of this complication arises in consideration of the thermodynamic dissociation constants of acetic acid ($K_{25^\circ} = 1.75 \times 10^{-5}$),[3] phenylacetic acid ($K_{25^\circ} = 4.88 \times 10^{-5}$)[3] and diphenylacetic acid ($K_{25^\circ} = 11.5 \times 10^{-5}$).[3] How much of the effect of the phenyl group is due to a fundamental electron attracting influence and how much to hyperconjugative distribution of negative charge into the benzene ring (thereby leaving a partial positive charge close to the carboxyl group in the acids and anions) cannot be determined. Other evidence is uncertain on different grounds. Thus, the comparison[5] of the acid strengths of trimethylboron[8] and triphenylboron,[9] with ammonia as reference base, is partially invalidated by the fact that data on the phenyl compound are for the solid complex where crystal forces may be more significant than the strength of the nitrogen–boron bond. Hammett[10] has assigned a sigma value of +0.218 to *m*-phenyl. This should constitute excellent quantitative information on the "non-resonance" electronic influence of the group, but is rendered less valid by the statement of the workers[11] who carried out the measurements (rates of acid hydrolysis of aryl sulfates) on which the sigma value is based, that their rate constants for *p*- and *m*-biphenylyl sulfates are "more uncertain... for potassium *m*- and *p*-phenylphenylsulphate and the corresponding phenols are difficultly soluble in water."

Less subject to question is the finding by Hatt, *et al.*,[12] that the migratory aptitude of the *m*-biphenylyl group in the pinacol rearrangement is 0.4 (phenyl = 1). They also reported the migratory aptitude of *p*-biphenylyl under identical conditions, to be 3.7, and speculatively ascribed the low value for *m*-biphenylyl to "steric opposition to migration." Examination of Fisher–Hirschfelder–Taylor models of the pinacolones resulting from migration of phenyl or *m*-biphenylyl and of assumed cyclic activated complexes, reveals very little difference between the steric oppositions to migration for the two groups. It is noteworthy in this connection that the migration aptitude of *m*-tolyl has been found to be 1.95.[13] It thus appears that although *p*-phenyl, which is so situated that it can participate in the distribution of a positive charge in the activated complex, acts as an electron supplying group in this reaction, *m*-phenyl, which cannot participate in such resonance, acts as an electron withdrawing group.

We have determined thermodynamic dissociation constants for mono-*m*- and mono-*p*-biphenylyldiphenylchloromethane in liquid sulfur dioxide at 0.1° in order to obtain further quantitative information on the electronic influence of the phenyl group.

Experimental

Synthetic. Mono-*m*-biphenylyldiphenylchloromethane.—*m*-Bromobiphenyl was prepared by a modification of the procedure of Marvel, *et al.*[14] In the present work the reaction mixture was worked up after the arylation reaction by adding 90–100° ligroin (5 cc. per cc. of benzene employed), separating by filtration the heavy tarry precipitate which formed, and chromatographing the clear red filtrate on a column composed of two parts by volume of Al_2O_3 ("Alorco" 80 mesh) and one part of "Cellite." The column was eluted with 5 to 1 ligroin–benzene until the originally yellow eluate became orange. The orange eluate was discarded and the combined yellow percolate and eluate freed of solvent by distillation. The crude product was distilled with superheated steam and then vacuum-distilled

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(1) Taken in part from the A.M. Thesis of Herbert Glazer.

(2) F. Ashworth and G. N. Burkhardt, *J. Chem. Soc.*, 1793 (1928).

(3) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).

(4) C. K. Ingold, *ibid.*, **15**, 239 (1934).

(5) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 175–177.

(6) P. Schorigin, *Ber.*, **41**, 2723 (1908); **43**, 1938 (1910).

(7) A. A. Morton, E. L. Little and W. O. Strong, THIS JOURNAL, **65**, 1339 (1943).

(8) H. C. Brown, H. Bartholomay and M. D. Taylor, *ibid.*, **66**, 435 (1944).

(9) E. Krause, *Ber.*, **57**, 813 (1924).

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(11) G. N. Burkhardt, C. Horrex and D. I. Jenkins, *J. Chem. Soc.*, 1657 (1936).

(12) H. H. Hatt, A. Pilgim and E. F. M. Stephenson, *ibid.*, 478 (1941).

(13) W. E. Bachmann and J. W. Ferguson, THIS JOURNAL, **56**, 2081 (1934).

(14) C. S. Marvel, E. Ginsberg and M. B. Mueller, *ibid.*, **61**, 77 (1939).

as described by Marvel, *et al.*[14] A 23% yield of golden-yellow product, $n^{20}\text{D}$ 1.6407 was obtained. This was converted to mono-*m*-biphenylyldiphenylcarbinol as described by Marvel, *et al.*,[15] melting range 104.8–106.5°. The carbinol was converted to the chloride by means of acetyl chloride (freshly distilled from dimethylaniline) as described by Marvel.[15] The product was recrystallized using all-glass equipment protected from atmospheric moisture, once from 90–110° ligroin (dried over CaH_2), once from a solvent composed of 1 part by volume of benzene (dried over CaH_2), 3 parts 35–60° petroleum ether (dried over CaH_2) and acetyl chloride (a few drops) and finally from benzene–petroleum ether (1 to 4) yielding not quite white crystals, melting range 86.0–87.0°.

Anal.[16] Calcd. for $C_{25}H_{19}Cl$: C, 84.61; H, 5.40; Cl, 9.99. Found: C, 84.4; H, 5.5; Cl, 9.9.

Mono-*p*-biphenylyldiphenylchloromethane.—*p*-Bromobiphenyl (Eastman Kodak Co., m.p. 90.5–91.8°) was converted to *p*-biphenylyllithium. The filtered ethereal solution then reacted with benzophenone in the usual way.[15] The carbinol was recrystallized, first from benzene 90–110°, ligroin (1 to 1) and then from acetic acid–water (2 to 1) giving a product with melting range 136.4–137.2° (uncor.); yield of pure product: 50% (based on benzophenone). The carbinol was converted to the chloride by the procedure employed for the meta compound and recrystallized, using all-glass equipment protected from atsmospheric moisture, twice from 90–110° ligroin (dried over CaH_2) and twice from a solvent composed of one part of benzene (dried over CaH_2) to two parts of 35–60° petroleum ether (dried over CaH_2). The white product has a melting range of 147.0–147.8° (uncor.).

Anal.[15] C, 84.7; H, 5.4; Cl, 9.8.

Measurements.—Most of the procedures and apparatus were similar to those previously reported.[17]

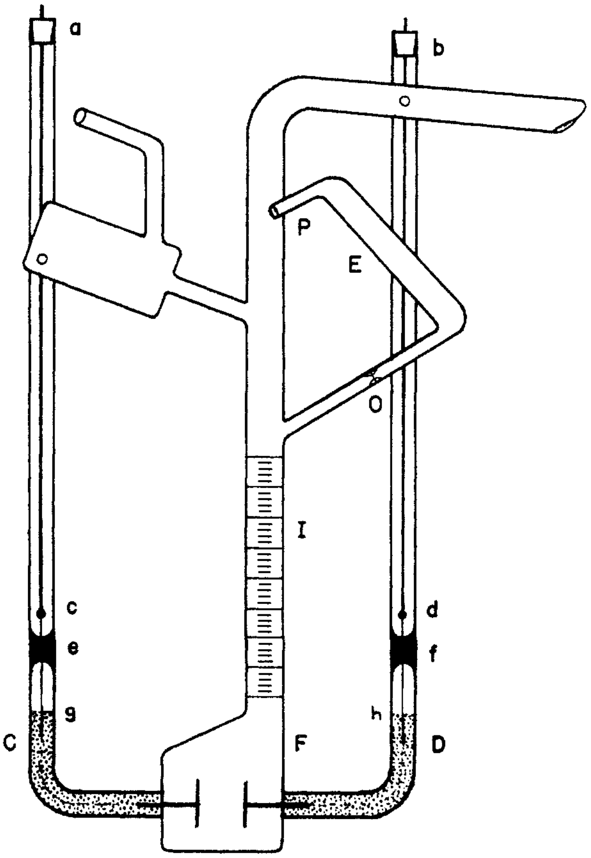

Fig. 1.—Electrode arm of conductivity cell.

The conductivity cell was modified somewhat so as to reduce drainage errors and otherwise increase the precision of the dilution process[17] and to conform more closely to the recommendations of Jones and Bollinger[18] on cell construction (Fig. 1). Thus the glass electrode supports were eliminated and the graduated neck (I) sealed to the electrode bulb (F) in an eccentric manner so that no shoulder was present along the surface over which the solution was drained during the dilution process. The graduated neck was part of a Pyrex semi-micro buret, reading directly to 0.05 ml. The dilution bulb (E) was ring sealed to the electrode bulb and the orifice (P) constricted to about 3 mm. so as to give a more precise cut-off. The calibration mark (O) was placed at a point where the inside diameter of the tube was constricted to about 2 mm. The electrode arms (C and D) were spaced 13.5 cm. apart, the maximum compatible with convenient use of the cell. These arms were filled with mercury to g and h. The horizontal tungsten electrode supports were sealed through the walls of the electrode bulb with vacuum-tight seals and extended into the mercury columns. Platinum wires were sealed through glass plugs at e and f and dipped into the mercury. These wires were fastened at c and d to heavy copper wires which were brought out of the electrode wells at a and b through water-tight seals.

The thermostat consisted of a kerosene-filled copper vessel surrounded by refrigerating coils separated from it by a one-inch air gap, all contained in a well insulated box. A thermoregulator, heater, stirrer and Beckmann thermometer were immersed in the kerosene-bath. For all the runs reported in this paper, the temperature was 0.118 ± 0.015°.

All measurements were made using a bridge employing a Campbell–Shackleton ratio box (Leeds and Northrup Co., cat. no. 1553) as the fixed arms. The variable resistance arm consisted of an 11,111.1-ohm six-decade box (Leeds and Northrup Co., cat. no. 4764) in series with a 100,000-ohm decade box (Leeds and Northrup Co., special construction) and with a variable capacitance (Leeds and Northrup, cat. no. 1185) in parallel. An audio frequency oscillator (Hewlett-Packard Co., Model 200A) with a frequency range from 35 to 35,000 c.p.s. was employed. Resistance readings were made at 2000 c.p.s. but were insensitive to a tenfold increase in frequency for the measurements reported here.[19] The bridge output was amplified by a 40 DB amplifier (Hewlett-Packard Co., Model 450A). An oscilloscope (Dumont Laboratories, Inc., Type 274A) was used as a null-point detector in the manner described by Jones, *et al.*[20] The bridge was assembled as described in Leeds and Northrup Bulletin D.B. 620. Resistance beyond the bridge capacity was measured with the aid of a 10,000-ohm shunt.

"Anhydrous grade" sulfur dioxide supplied by The Matheson Co.[21] was employed. The solvent was transferred into the cell by means of an all-glass vacuum system to which the cell was sealed for filling. The sulfur dioxide was passed sequentially through 18-inch columns of $CaCl_2$ and indicating Drierite, condensed in a bulb filled with glass helices and distilled, through a trap maintained at 0°, into the cell where it was condensed in the electrode bulb. The specific conductivity of the solvent, determined separately for each run, varied from 1.95×10^{-7} to 3.13×10^{-7} mho cm.$^{-1}$.

The procedures followed in carrying out runs and the precautions observed were essentially the same as those previously reported[17] except that pressures of between 0.001 and 0.01 mm. were routinely used in pumping the system.

The volume of the electrode bulb was determined directly with water with a precision of three parts in ten thousand. The volume of the dilution bulb was determined by filling the electrode bulb with water (at 0°), rotating the cell so that the water filled the dilution bulb and the excess flowed into the reservoir bulb, returning the cell to its normal position, adding a known weight of water to the cell and finally reading the total volume (again at 0°) on the graduated arm. The volume of the dilution bulb was then obtained by dif-

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[15] C. S. Marvel, M. B. Mueller and E. Ginsberg, THIS JOURNAL, **61**, 2008 (1939).

[16] Microanalysis by Dr. C. K. Fitz.

[17] N. N. Lichtin and P. D. Bartlett, THIS JOURNAL, **73**, 5530 (1951).

[18] G. Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

[19] Polarization effects characterized by great sensitivity of measured resistance to frequency, were encountered as long as silicone high vacuum grease was employed in the stopcocks through which the sulfur dioxide passed. This was completely eliminated on removal of the silicone.

[20] G. Jones, K. J. Mysels and W. Juda, THIS JOURNAL, **62**, 2919 (1940).

[21] This material is 99.988% SO_2, containing 0.002% moisture and 0.01% non-condensable gases according to the supplier's data sheet.

ference. This procedure, which is functionally the same as the dilution procedure followed in the runs, gave a precision of one part in one thousand. The dilution-bulb volume (18.73 ml.) was such as to give a dilution factor of approximately 2.3. The cell constant was determined with potassium chloride using the data of Jones and Bradshaw.[22]

The same cell was used in all the runs reported here with one exception but this run was in excellent agreement with others for the same compound (mono-*m*-biphenylyldiphenylchloromethane).

Data

Figure 2 shows semilogarithmic plots of equivalent conductance (Λ) *vs.* dilution (V). Tables I and II summarize the smoothed equivalent conductance data from large scale plots of these curves, each point of these tables being taken from a part of a curve in the immediate vicinity of experimental points.

Equilibrium constants ($K_{\text{exp.}}$) and limiting conductance values (Λ_0) were calculated from the data of Tables I and II by Shedlovsky's method[23,24] as described in the preceding paper[17] of this series and are presented in Table III. Figure 3 shows the Shedlovsky plots for the compounds of this research. Since the data of Ziegler and Wollschitt[25] for mono-*p*-biphenylyldiphenylchloromethane agreed fairly well with the present work, the Shedlovsky method was applied to their data for the di- and tri-*p*-phenyl derivatives of triphenylchloromethane. The linear plots obtained are shown in Fig. 4 and the equilibrium constants and limiting conductance values derived therefrom are included in Table III.

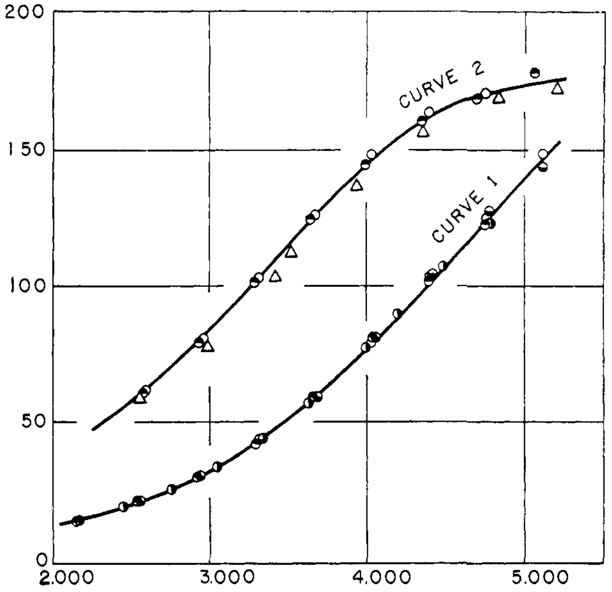


Fig. 2.—Conductivity data for mono-*m*-biphenylyldiphenylchloromethane (curve 1) and mono-*p*-biphenylyldiphenylchloromethane (curve 2) at 0.1. Different circles indicate independent runs. Triangles are from the data of Ziegler and Wollschitt.[24]

TABLE I

MONO-*p*-BIPHENYLYLDIPHENYLCHLOROMETHANE AT 0.1°

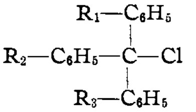
C, moles per liter × 10^4	Λ, mhos sq. cm./mole
26.60	60.5
11.22	80.0
5.31	100.4
2.188	125.0
1.000	146.0
0.473	161.0
.1778	171.4
.0950	174.5

TABLE II

MONO-*m*-BIPHENYLYLDIPHENYLCHLOROMETHANE AT 0.1°

C, moles per liter × 10^4	Λ, mhos sq. cm./mole
31.63	20.7
13.03	30.0
5.62	42.0
1.799	66.0
1.334	73.5
0.708	90.6
.398	106.8
.2122	124.5
.0842	150.0

TABLE III



$$R_1{-}C_6H_5 \quad R_2{-}C_6H_5{-}\underset{R_3-C_6H_5}{\overset{|}{C}}{-}Cl$$

R_1	R_2	R_3	Λ_0, mhos cm.²/mole	10^5K_{exp}	ΔF°_0 kcal./mole
H	H	H[a,b]	208	4.3	+5.49
H	H	*m*-C_6H_5[c]	175	3.12	+5.63
H	H	*p*-C_6H_5[c]	190	23.2	+4.54
H	*p*-C_6H_5	*p*-C_6H_5[b,d]	169	99	+3.75
p-C_6H_5	*p*-C_6H_5	*p*-C_6H_5[b,d]	164	290	+3.17

[a] *Cf.* Ref. 17. [b] At 0.0°. [c] At 0.1°. [d] Calculated from the data of Ziegler and Wollschitt, ref. 25.

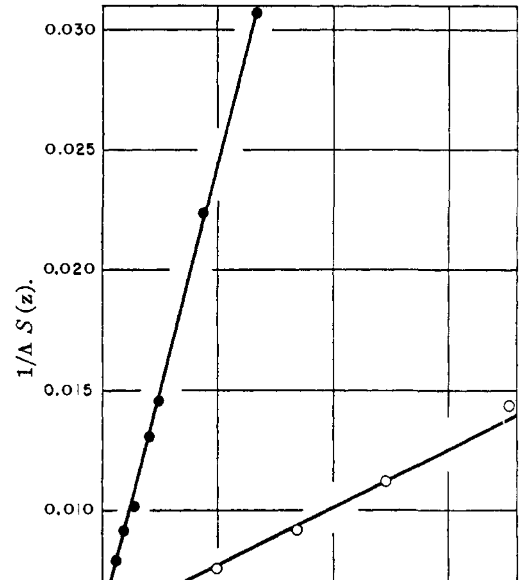


Fig. 3.—Shedlovsky plots for mono-*p*-biphenylyldiphenylchloromethane, ○, and mono-*m*-biphenylyldiphenylchloromethane, ●.

Discussion

It has previously been demonstrated[17] that the experimental dissociation constants (K_{exp}) for trityl chloride and those ring substitution derivatives which are weaker electrolytes, or stronger by no more than a factor of about ten, are directly

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[22] G. Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

[23] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

[24] R. M. Fuoss and T. Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

[25] K. Ziegler and H. Wollschitt, *Ann.*, **479**, 108 (1930).

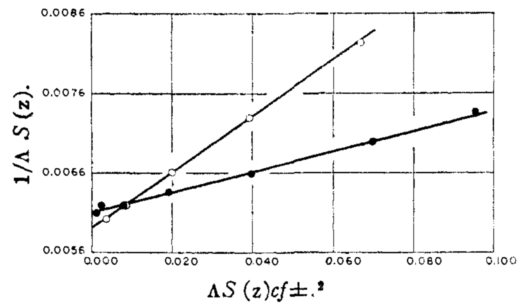

Fig. 4.—Shedlovsky plots for di-*p*-biphenylylphenylchloromethane, ○, and tri-*p*-biphenylylchloromethane, ●, from the data of Ziegler and Wollschitt.[25]

proportional to the unavailable equilibrium constants (K_1) for the ionization of the covalent chlorides (whatever the exact state of these may be in liquid sulfur dioxide solution) with a constant proportionality factor. The two compounds of this research fall within this range. Their experimental equilibrium constants therefore supply information bearing directly on the influence of the phenyl groups on ionization of the chlorides without complications arising from ion-pair equilibria.

The possibility that the influence of the *m*-phenyl substituent may be due to steric factors is disposed of by consideration of models. This group cannot sterically influence the approach of the chloride ion to the carbonium ion nor of solvent molecules to the chlorine of the un-ionized molecule. If *m*-phenyl has any steric effect, it should be to increase the extent of ionization, since its very slight interference with the *o*-hydrogens of the rings joined to the central carbon atom when the latter is tetrahedral is partially relieved when it becomes trigonal. In the propeller-like configuration of the carbonium ion, suggested by Lewis, *et al.*,[26] steric interaction of the *m*-phenyl group with other portions of the molecule is particularly small. The observed influence of *m*-phenyl, like that of *p*-phenyl, must be due to an electronic effect.

The promotion of ionization brought about by introduction of *p*-phenyl into triphenylchloromethane must be due to the resonance stabilization of the carbonium ion by this group. It is noteworthy, however, that in spite of the three major symbolic structures contributed to the hybrid by each *p*-phenyl, this group has a smaller influence than *p*-methyl or *p*-*t*-butyl.[17] It is also significant that the factors by which K_{exp} increases on successive introduction of *p*-phenyl groups (5.8, 4.3, 2.9) are much more nearly the same than the corresponding factors for *p*-*t*-butyl groups (18.9, 4.5, 2.4). Since the *p*-phenyl compounds are weaker electrolytes than the corresponding *p*-*t*-butyl compounds, the factor of proportionality between K_{exp} and K_1 must be more nearly constant for the former series.[17] The successive introduction of even less effective electrolyte-strengthening groups or electrolyte weakening groups (*e.g.*, *m*-phenyl) should show identical influences for each group. This prediction will be tested in future work.

Introduction of the *m*-phenyl group decreases the extent of ionization. The decrease is small, but is about ten times the precision of the measurements. This influence cannot be explained in terms of the conventional resonance participation of the phenyl group. It is not unreasonable to conclude that a phenyl group attached to the benzene ring exerts a small but unmistakeable fundamental electron-attracting influence.

There are at least two other interpretations which must be considered. One of these is that, somehow, the presence of a positive charge in one benzene ring decreases the extent of its resonance interaction (of the kind present in biphenyl) with the other. There seems to be no precedent for such an assumption. The second would ascribe the electronic influence of the group not simply to the group itself but to the solvated group. It is possible that association with a solvent molecule might render the phenyl group electron-attracting either because of an induced dipole or because of the transfer of an electron to the solvent molecule (as has been suggested for solutions of aromatic compounds in liquid sulfur dioxide[27]). This sort of influence should be more important in the un-ionized molecule than in the positive ion. Although this possibility is unattractive, it cannot be ruled out by the evidence. It is quite apparent that these two alternative interpretations can also be extended to the migration aptitude of *m*-biphenylyl in the pinacol rearrangement.

The influence of *m*- and *p*-phenyl substituents on the degree of ionization of triphenylchloromethane in liquid sulfur dioxide is in striking contrast to the effect of analogous substituents on the free radical dissociation of hexaphenylethane in benzene solution.[14,15,28,29] The equilibrium constant at 25–28° for dissociation of *sym*-tetraphenyldi-*m*-biphenylylethane has been reported to be about three quarters of that for *sym*-tetraphenyldi-*p*-biphenylylethane, and both to be more than ten times as great as that for hexaphenyl ethane.[29]

Comparison of the influences of *m*- and *p*-phenyl on the free radical dissociations has led workers in this field to the conclusion[15] that "the number of resonance forms of the free radical must play a rather minor part in determining the degree of dissociation of these hexaarylethanes." Examination of Fisher–Hirschfelder–Taylor models of *sym*-tetraphenyldi-*m*-biphenylylethane and diphenyl-*m*-biphenylylmethyl radical makes it appear most unlikely that this striking effect of *m*-phenyl is largely due to a steric factor.

This effect can be explained on the basis of resonance stabilization of the radical if the contributions of dipolar symbolic structures are taken into account. The unpaired electron can be distributed to all six carbon atoms of the *m*-phenyl group in the following manner

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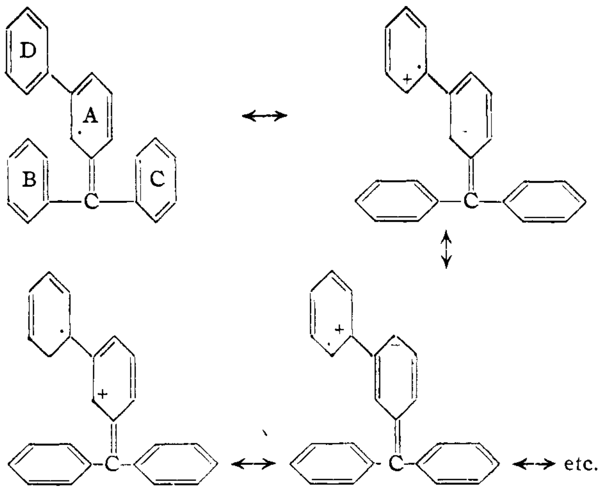
(26) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **64**, 1777 (1942).

(27) J. Weiss, *J. Chem. Soc.*, 250 (1942).

(28) C. S. Marvel, J. W. Shackelton, C. M. Himel and J. Whitson, THIS JOURNAL, **64**, 1824 (1942).

(29) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 694.



With a given charge in ring D there are 216 symbolic structures with the opposite charge in ring A,[30] the same number with the opposite charge in ring B and in ring C, respectively; with the charge on the central carbon, there are 144 contributing forms, yielding a total of 792 symbolic structures. There must be an equal number with opposite polarity, giving 1584 forms of similar stability. With a *p*-phenyl group there are an equal number of analogous dipolar contributions in addition to the 12 non-polar structures in which the odd electron is distributed into the *o*- and *p*-positions of the *p*-phenyl group. The evidence that one *m*-phenyl has an only slightly smaller influence than one *p*-phenyl indicates that the dipolar forms contribute significantly to the radical.

There is some evidence indicating that dipolar contributions are more important in free radicals than in molecules with no odd electrons. Thus the dipole moment of 1-picryl-2,2-diphenylhydrazyl radical (4.92 *D*) is appreciably greater than that of the corresponding hydrazine (3.59 *D*).[31] It has been suggested[32] that this is due to dipolar contributions being more important in the free radical. Importance has also been ascribed to dipolar contributions to the activated complexes for free radical copolymerizations where the alternating effect is dominant.[33]

The present treatment would not seem capable of fully explaining the report[14,28,29] that hexa-*m*-biphenylylethane is considerably more highly dissociated than hexa-*p*-biphenylylethane. It has been suggested[34] that Pascal's constants are not accurate when applied to estimation of the diamagnetic susceptibility of a free radical and that the hexa-*p*-substituted compound is completely dissociated in solution. This conclusion may apply equally well to the meta isomer. Although this throws doubt on the accuracy of the dissociation constants for the *sym*-bis-biphenylyltetraphenylethanes, there can be little question that they are of comparable magnitudes.

Acknowledgment.—The authors gratefully acknowledge a Frederick Gardner Cottrell Grant from the Research Corporation which made this work possible.

(30) These calculations take into account Kekulé resonance; *e.g.*, in rings B and C in this case.

(31) J. Turkevich, P. F. Oesper and C. P. Smyth, THIS JOURNAL, **64**, 1179 (1942).

(32) Ref. 5, p. 198.

(33) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 244 (1950).

(34) P. W. Selwood and R. M. Dobres, THIS JOURNAL, **72**, 3860 (1950).

BOSTON, MASS. RECEIVED MAY 17, 1951

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Copolymerization. The Effect of Reaction Conditions on the Monomer Reactivity Ratios for the System Styrene–*p*-Chlorostyrene–Stannic Chloride

BY C. G. OVERBERGER, LESTER H. ARNOLD AND JOHN J. TAYLOR

This work was undertaken in order to study the effect of reaction variables on the monomer reactivity ratios of a typical copolymer system catalyzed by a cationic catalyst. Such data were not available but are very necessary before additional quantitative or semi-quantitative copolymerization data obtained with cationic catalysts, can be interpreted. In the system styrene, *p*-chlorostyrene, stannic chloride; we have demonstrated that: (1) an actual copolymer is probably obtained; (2) the effect of dielectric constant on the monomer reactivity ratios is small. With a range of dielectric constants from approximately 2.2 to 29.7, the effect is smaller than the accuracy of the chlorine determinations; (3) the effect of known, small amounts of water on the monomer reactivity ratios is small; (4) the effect of catalyst concentration on the monomer reactivity ratios for the system *p*-chlorostyrene-α-methylstyrene is negligible; (5) the reactivity ratios determined at 30°, 0° and −20° for the styrene-*p*-chlorostyrene system are not appreciably different.

Since the development of the copolymer composition equation,[1] a large amount of copolymerization data has been obtained in the form of reactivity ratios. For the most part, these data[2] have been obtained for radical-catalyzed copolymerizations. Within the past five years, a number of copolymer systems have been described catalyzed by cationic catalysts. Most of these data have usually consisted of one experiment with a 50–50 monomer mixture. For the most part, these data have satisfied the intention, namely, as a diagnostic test for determining the mechanism of polymerization with free-radical and ionic catalysts.[3] On examination of the literature, one is aware, however, of the sparsity of any quantitative or even semi-quantitative data[4] available for cationic-catalyzed copolymerization. It is the purpose of this paper and succeeding ones to obtain such information.

The determination of relative reactivities of

(1) (a) T. Alfrey and G. Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944); (c) F. T. Wall, *ibid.*, **66**, 2050 (1944).

(2) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

(3) C. Walling, E. R. Briggs, W. Cummings and F. R. Mayo, THIS JOURNAL, **72**, 48 (1950).

(4) For notable exceptions, see Table 18, reference 2.