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Ionization and Dissociation Equilibria in Liquid Sulfur Dioxide. V. *o*-, *m*- and *p*-Chloro and *o*-Methyl[1] Derivatives of Triphenylchloromethane at 0.175

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Thermodynamic constants measuring the equilibria of free ion formation have been calculated by means of the Shedlovsky or Shedlovsky–Kay procedures from conductivity data for solutions in sulfur dioxide in the dilution range 2000 to 70,000 liters per mole at 0.175°. $K_{exp} \times 10^5$ is 1.06, 0.153, 1.26, 0.122 and 62.5 for the mono-*o*-chloro, mono-*m*-chloro, mono-*p*-chloro, tri-*p*-chloro and mono-*o*-methyl derivatives of trityl chloride, respectively. Quantitative ion-pair theory has been used to calculate constants measuring the equilibrium of ionization to ion-pairs of these solutes. Relative magnitudes of these ionization constants are very similar to the relative magnitudes of K_{exp}. The influence of a single *o*-methyl or *o*-chloro-substituent on the ionization equilibrium is very similar to that of the corresponding *p*-substituent. Calculations employing an extended Hammett equation indicate that the version of the Newman–Deno triarylcarbonium ion model in which only two rings are involved in charge distribution is as consistent with these and other data on ionization equilibria in liquid sulfur dioxide as is a model involving charge delocalization to all three rings. Calculations involving distribution to only one ring yield less satisfactory results.

Introduction

The investigation of *dissociation* equilibria in liquid sulfur dioxide of ion-pairs which associate as a consequence of only electrostatic forces[2,3] has clarified and provided support for the use of conductivity data for solutions in this medium in the quantitative evaluation of the influence of groups on the equilibria of *ionization* of triarylchloromethanes.[4] The measurements reported herein represent our first examination of the effects of *ortho* and of halogen substituents.

Experimental

Solvent, conductivity cell, bridge assembly and procedures have been described previously[5] as has the vacuum line.[2] Temperature control was improved by regulating the thermostat[5] with a Thermocap[6] relay activated by a mercury-filled capillary (1 mm. i.d.) attached to a 100-ml. bulb filled with toluene. The sensing clip of the relay was mounted on a screw which made it possible to set the temperature to within 0.005° very easily. The temperature of the bath cycled over approximately 0.01° (total range) in routine use.

Synthetic work was carried out with emphasis on purity. All-glass equipment was used throughout and moisture and oxygen were excluded whenever necessary. In particular, conversion of triaryl carbinols to chlorides and subsequent purification was accomplished under nitrogen in a special all-glass apparatus. Reagents were in most cases recrystallized or distilled before use. Ether and solvents employed in crystallization of triarylmethyl chlorides were dried over sodium wire. Otherwise solvents were dried over calcium hydride. Magnesium was Dow Chemical Co. sublimed grade, freshly turned before use.

Mono-*o*-chlorotriphenylchloromethane.—*o*-Chlorotoluene ($n^{20}D$ 1.5257) was converted to *o*-chlorobenzoic acid by oxidation with potassium permanganate. The acid, recrystallized from toluene (m.r. 141–142°)[7] was esterified in the presence of H_2SO_4, with the aid of toluene to remove water azeotropically, to yield ethyl *o*-chlorobenzoate, b.r. 128–131° at 21–22 mm., $n^{25.4}D$ 1.5192, which was dried over Drierite. An ethereal solution of phenylmagnesium bromide was filtered through glass wool and the ether replaced by sufficient benzene to yield an approximately 1 *M* solution. To this was added the ester in a ratio of 1 to 5 moles of Grignard reagent. The mixture was stirred on the steam-bath for several hours, decomposed with cold saturated aqueous ammonium chloride and steam distilled. Crude mono-*o*-chlorotriphenylcarbinol[8] was recrystallized from 1:1 ligroin–petroleum ether and twice from ligroin to yield white crystals melting at 91.5–92.0°. The Grignard reaction, when carried out in anisole or ether, yielded oils which did not crystallize. The carbinol (5 g.) was converted to the chloride[8] by refluxing for half an hour with 3 ml. of acetyl chloride diluted with 5 ml. of petroleum ether and 9 ml. of benzene. The filtered solution was cooled and the resulting crystals filtered and washed by trituration with petroleum ether. The white crystals filtered and washed by trituration with petroleum ether. The white crystals melted at 135.3–136.0°. *Anal.* Calcd. for $C_{19}H_{14}Cl_2$: C, 72.85; H, 4.50; alkyl bound Cl, 11.32. Found: C,[9] 72.7; H,[9] 4.4; alkyl bound Cl,[10] 11.28.

Mono-*m*-chlorotriphenylchloromethane.—*m*-Chlorobenzoic acid (m.r. 154.0–154.6°) prepared by oxidation of *m*-chlorotoluene was converted to the ethyl ester, b.r. 137–140° at 60 mm., and then to mono-*m*-chlorotriphenylcarbinol[11] essentially as described for the *o*-isomer. The resulting yellow oil was induced to crystallize by dissolving it in acetic acid and triturating the partially frozen solution with a few ml. of petroleum ether. Recrystallization from the latter solvent gave a pale yellow solid melting at 52.0–53.5°. The crystalline carbinol was not obtained from the reaction of *m*-chlorophenylmagnesium bromide with benzophenone. The carbinol (5 g.) was refluxed for 1 hr. with 2 ml. of acetyl chloride diluted with 2 ml. of methylene chloride and 2 ml. of petroleum ether. The hot solution was filtered and most of the solvent removed with aspirator vacuum. Addition of 2 ml. of petroleum ether yielded mono-*m*-chlorotriphenylchloromethane[11] melting at 58.0–59.6°. *Anal.* Found: C,[9] 72.4; H,[9] 4.8; alkyl bound Cl,[10] 11.30.

Mono-*p*-chlorotriphenylchloromethane.—The corresponding carbinol was prepared by the reaction of equimolar amounts of benzophenone and *p*-chlorophenylmagnesium bromide in benzene solution and was worked up essentially as described for the *o*-isomer. The resulting yellow oil solidified on trituration with cold petroleum ether and was recrystallized sequentially from methanol-water (9:1), petroleum ether–ligroin (5:1) and petroleum ether–methylene chloride (5:1) to yield white crystals melting at 84.8–85.5°. The carbinol (4.75 g.) was refluxed with 10 ml. of acetyl chloride–petroleum ether (1:1) for 1 hr. The hot solution was filtered and cooled to yield the white chloride.[11] Recrystallization from petroleum ether–methylene chloride (12:1) and petroleum ether containing a few drops of acetyl chloride yielded white crystals melting at 88.8–89.7°.

Anal. Found: C,[9] 72.7; H,[9] 4.5; alkyl bound Cl,[10] 11.38.

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[1] Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956. Based on a dissertation submitted by M. J. Vignale in fulfillment of a requirement for the Ph.D. degree granted at Boston University in June, 1956.

[2] N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 160 (1956).

[3] N. N. Lichtin and P. Pappas, Abstracts 130th Mtg. Amer. Chem. Soc., Atlantic City, N. J., September, 1956, p. 10R.

[4] *Cf.* N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 164 (1956), for a discussion and references to earlier work.

[5] N. N. Lichtin and H. Glazer, THIS JOURNAL, **73**, 5537 (1951).

[6] "Lab" model, Niagara Electron Laboratories.

[7] All melting points were obtained with Anschütz-type thermometers.

[8] M. Gomberg and D. D. Van Slyke, THIS JOURNAL, **33**, 531 (1911).

[9] Microanalysis by K. Ritter, Basel 2, Switzerland.

[10] Estimated by acidimetric titration of ethanolized solution, a procedure which was precise to about two parts in one thousand.

[11] C. S. Marvel, J. C. Dietz and C. M. Himel, *J. Org. Chem.*, **7**, 392 (1942).

Tri-*p*-chlorophenylchloromethane.—Tri-*p*-chlorophenylcarbinol[12] was prepared from ethyl carbonate and *p*-chlorophenylmagnesium bromide following procedures like those employed for the mono-*o*-chloro compound. The yellow oil resulting after steam distillation was crystallized from ligroin. Two recrystallizations from 95% ethanol yielded almost white crystals melting at 95.6–95.8°. The carbinol (5.9 g.) was refluxed for 1 hr. with 10 ml. of 1:1 acetyl chloride–petroleum ether, yielding white crystals melting at 110.6–111.4°.

Anal. Calcd. for $C_{19}H_{12}Cl_4$: C, 59.72; H, 3.17; alkyl bound Cl, 9.28. Found: C,[9] 59.4; H,[9] 3.5; alkyl bound Cl,[10] 9.26.

Mono-*o*-methyltriphenylchloromethane.—A sample of the corresponding carbinol, provided by Professor M. S. Newman, was recrystallized from 95% ethanol to yield white crystals melting at 97.4–97.8°.[13] This was treated in ether solution with anhydrous hydrogen chloride and the product recrystallized twice from ether. The white crystals melted at 138.6–139.5°.[13]

Anal. Calcd. for $C_{20}H_{17}Cl$: C, 82.03; H, 5.84; Cl, 12.11. Found: C,[14] 81.8; H,[14] 5.9; Cl,[14] 12.14.

Data

Conductivity measurements were obtained at 0.175 ± 0.005° for solutions ranging in dilution from about 1000 to 70,000 liters per mole. The results of representative single runs are assembled in Table I. At least two independent runs were performed with each solute. Individual data points at dilutions above 2000 liters per mole were employed in the solution of Shedlovsky's equation[15] with the aid of Daggett's tables of the Shedlovsky function S(z).[16] The method of least squares was applied with $1/\Lambda S(z)$ as dependent variable to yield $1/K(\Lambda^0)^2$ and $1/\Lambda^0$, the slope and intercept, respectively, of the Shedlovsky line.[17] This procedure did not yield acceptable results with the data for the mono-*m*-chloro and tri-*p*-chloro derivatives, the two weakest electrolytes. In these cases, the Shedlovsky intercepts ($1/\Lambda^0$) could be excluded on the basis of comparison with other solutes. Specifically, the resulting values of Λ^0 were much too small. This difficulty is associated with the lengthy extrapolation and the large slope (*ca.* 20) of the Shedlovsky line. This problem, which is general for very weak electrolytes, has been treated recently by Shedlovsky and Kay[18] who have developed a modification of the Shedlovsky equation which treats solvent conductivity as a disposable parameter and which requires prior knowledge of Λ^0. Since data for independent evaluation of Λ^0 for these two solutes were not available,[19] a successive approximation procedure was employed. A value of Λ^0 was estimated from its magnitude for related solutes and introduced, together with data which were not corrected for experimentally determined solvent conductivity, into the Shedlovsky–Kay calculation (which itself involves successive approximations) to obtain a "solvent conductivity." The latter was then used to "correct" raw data and secure values of Λ which were then introduced into the Shedlovsky calculation. The value of Λ^0 thereby obtained, if significantly different from that assumed initially, was then employed in a repetition of the Shedlovsky–Kay calculation. The resulting value of the "solvent conductivity" was not found to differ significantly from that obtained in the first cycle of calculations. Values of K_{exp}, Λ^0 and related quantities are presented in Table II.

TABLE I

CONDUCTANCE DATA OF REPRESENTATIVE SINGLE RUNS[a,b]

$V \times 10^3$ Mono-*o*-Cl	Λ	$V \times 10^3$ Mono-*p*-Cl	Λ	$V \times 10^3$ Tri-*p*-Cl	Λ
2826	31.1	1385	25.3	1486	7.82
4522	38.0	2224	31.1	2400	9.59
11590	55.8	3572	38.0	3882	11.88
18560	66.9	5736	46.3	10170	18.03
29810	79.3	9215	56.1	16480	22.5
47750	92.3	14790	67.1	26730	27.8
		23770	79.2	43310	34.1

$V \times 10^3$ Mono-*m*-Cl	Λ	$V \times 10^3$ Mono-*o*-CH_3	Λ
848.4	6.97	2796	138
1744	9.72	4544	149.5
3589	13.58	7383	159
7381	18.82	12010	167
15170	26.3	19550	173.5
31200	36.4	31830	178
64180	50.6	51850	181

[a] V in liters mole^{-1}, Λ in mhos cm.^{2} mole^{-1} and corrected for solvent conductivity which fell in the range 0.57–1.39 × 10^{-7} mhos cm.$^{-1}$. [b] Solutes are named as derivatives of trityl chloride.

TABLE II

EXPERIMENTAL EQUILIBRIUM CONSTANTS AND RELATED DATA

Solute[a]	Λ^0, mhos. cm.^{2} mole^{-1}	$10^5 K_{\text{exp}}$, moles/l.	$(K_x/K_H)_{\text{exp}}$	Data points employed	Probable error,[b] % Slope[c]	Intercept[c]
Unsubstituted[d]	207	4.15	(1.000)	18	1.1	1.3
Mono-*o*-chloro	182	1.06	0.26	18	0.5	1.4
Mono-*m*-chloro	185	0.153	.037	12	1.7	14.5
Mono-*p*-chloro	185	1.26	.30	24	0.3	1.0
Tri-*p*-chloro	178	0.122	.029	11	1.0	9.9
Mono-*o*-methyl	190	62.5	15.1	18	1.1	0.2
Mono-*m*-methyl[d]	201	9.5	2.3	7	1.1	0.7
Mono-*p*-methyl[d]	196	77	18.6	13	4.1	0.5

[a] Indicated as derivatives of trityl chloride. [b] *Cf.* H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 502. [c] Of the Shedlovsky line. Where the Shedlovsky–Kay procedure was used, these refer to the last repetition of the Shedlovsky calculation in this procedure. [d] From reference 4.

Discussion

Calculation of Ionization Constants.—In order to employ complex equilibrium data of the type summarized in Table II as a measure of the influence of structure on *ionization* equilibria, an analysis of K_{exp} in terms of ionization and dissociation equilibria according to equations 1 and 2 has been assumed.[2,4,5,20] Here RCl represents the covalent molecule, and $\overbrace{R^+Cl^-}$ represents the ionized but undissociated pair.

$$RCl \underset{}{\overset{K_1}{\rightleftarrows}} \overbrace{R^+Cl^-} \overset{K_2}{\rightleftarrows} R^+ + Cl^- \qquad (1)$$

$$K_{\text{exp}} = (R^+)(Cl^-)/[(RCl) + (\overbrace{R^+Cl^-})] = K_2/(1 + 1/K_1) \qquad (2)$$

$$K_1 = K_{\text{exp}}/(K_2 - K_{\text{exp}})$$

Magnitudes of K_2 have been estimated[4] with the aid of Bjerrum's equation[21] and the assignment of equivalent radii of closest approach based on the

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[12] O. Fischer and W. Hess, *Ber.*, **38**, 338 (1905).

[13] A. Bistrzyski and J. Gyr, *ibid.*, **37**, 1245 (1904).

[14] Semimicro analysis by C. K. Fitz, Needham, Mass.

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

[16] H. M. Daggett, THIS JOURNAL, **73**, 4977 (1951).

[17] Unless specifically defined, the symbols employed in this article have the meanings assigned by H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, pp. XIII–XXVII.

[18] T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

[19] Investigation of the corresponding bromides would provide them since these solutes would be strong enough electrolytes to afford accurate values of Λ^0 and the relationship, $\Lambda^0_{Ar_3CCl} = \Lambda^0_{Ar_3CBr} + \Lambda^0_{KCl} - \Lambda^0_{KBr}$, could then be employed.

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

[21] *Cf.* reference 17, pp. 42–46.

assumption[22] that disk-shaped cations occupy a spherical region defined by the largest van der Waals radius about the center of gravity of the ion. These Bjerrum radii were estimated for the present cases from Fisher–Hirschfelder–Taylor models in which chlorine atoms were weighted with mercury so as to give the appropriate mass ratio with respect to C–H. The rings were oriented symmetrically in as flat a "propellor" alignment as possible although considerable variation in the dihedral angle between rings has only a small influence on the location of the center of gravity. The center of gravity of the plane projection of such a model was located by the point of intersection of plumb lines dropped from two or more points of suspension of the model. The longest radius about this center of gravity was then measured on a plane projection of the model and taken as a reasonable estimate of the equivalent Bjerrum radius. Resulting values of cationic radii (r^+), K_2, K_1 and $(K_x/K_H)_1$, the ionization constant relative to its value for trityl chloride, are presented in Table III.

Comparison of Tables II and III reveals that the magnitudes of the two kinds of relative equilibrium constant are quite similar for each solute. Thus, for these compounds, structural effects on the equilibrium of ionization are reflected with considerable accuracy in K_{exp}. This follows from eq. 2a and two conditions, namely, that K_2 varies but little and that K_1 is much smaller than unity for the series of solutes. It should be emphasized that the relative values of K_1 would not be altered appreciably for this series by considerable variation in K_2 provided that these conditions are maintained.

TABLE III

ESTIMATED DISSOCIATION AND IONIZATION CONSTANTS

Solute	r^+, Å.	10^3K_2,[b] moles l.$^{-1}$	10^3K_1	$(K_x/K_H)_1$[c]
Unsubstituted[a]	6.5	2.88	14.6	(1.000)
Mono-*o*-chloro	7.5	3.41	3.12	0.214
Mono-*m*-chloro	7.2	3.25	0.471	.0322
Mono-*p*-chloro	7.4	3.36	3.76	.257
Tri-*p*-chloro	8.0	3.71	0.329	.0225
Mono-*o*-methyl	6.7	2.98	266	18.2
Mono-*m*-methyl[a]	6.6	2.92	33.7	2.31
Mono-*p*-methyl[a]	7.4	3.36	297	20.3

[a] These are 0.5 Å. less than values estimated previously,[4] a difference which alters K_2 and K_1 less than 10%. [b] Calculated from Bjerrum's equation[21] with $\mathring{a} = (r^+ + 1.8)$ Å., where 1.8 Å. is the radius of chloride ion.

K_1 is the quantity appropriate to a discussion of the influence of structure on equilibrium of ionization and is herein employed for this purpose. Justification for confidence in this treatment has been presented previously[4,20] and will be supplemented.[22] This analysis and also the unusual procedure employed in evaluating K_{exp} for this solute is supported by the observation that the Hammett σ-value calculated from K_1 for the *m*-chloro compound with the aid of the previously determined[4] ρ-value of -4.41[23] is $+0.338$ and differs very little from the accepted value ($+0.373$) for this substituent.

Interpretation of K_1 Data.—The data yield a σ-value of $+0.133$ for *p*-chloro. This is significantly less than the standard value ($+0.227$). This difference is undoubtedly a consequence of direct participation of *p*-chloro in charge distribution and is analogous to other negative deviations from standard values of sigmas calculated for *p*-substituents in triaryl carbonium ions.[4,24]

The effects of both *o*-chloro and *o*-methyl on the ionization equilibrium are very similar to the effects of the analogous *p*-substituents and widely different from those of the corresponding *m*-substituents. Distribution of the positive charge of the carbonium ion into these *o*-substituents is thus clearly indicated. Apparently a single *o*-methyl or chloro substituent is not capable of altering the conformation of the carbonium ion in such a way as to interfere seriously with charge delocalization (but *vide infra*).

It is worthy of comment that these and other[4,24] data on triarylcarbonium ion equilibria provide additional evidence for the conclusion[25] that the special influence of groups in the *o*- and *p*-position is not related to an "alternating" character of the inductive effect. It does not appear possible to rationalize the negative deviations of σ-values calculated for *p*-methyl,[4,24] *p*-t-butyl,[4] *p*-chloro,[24] *p*-methoxyl[24] and *p*-amino[24] by means of this sort of theory.

On the basis of the latter consideration, the data for the *o*-methyl compound also reinforce those[4,20] for *m*- and *p*-alkyl triarylcarbonium ion equilibria as evidence for the importance of both C–C and C–H hyperconjugative participation[20] in charge distribution. Whatever role the solvent[26] may play in determining the order of alkyl group effects, the large difference between the effects of *o*- and *p*-alkyl as against *m*-alkyl does not seem capable of rationalization in terms of interaction with the solvent. Clearly, in triarylcarbonium ions, hyperconjugation is the most potent mode of electron release by alkyl groups.

Current concepts relating to substituent effects are more than sufficient to account for the small differences between the effects of a given substituent placed in the *o*- and *p*-positions. A particularly attractive approach employs the clear distinction between field and inductive effects for which Roberts has provided trenchant evidence.[27] Thus, the inductive effect of the chloro-substituent should operate more effectively from the *o*-position and reduce the degree of ionization below that of the *p*-isomer whereas the field effect should render the *p*-substituted isomer less ionized. If the resonance effect of *o*- and *p*-substituents are the same,[27b] it follows that the inductive effect of chlorine somewhat more than compensates for the field effect. The same analysis applied to the methyl substituted

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[22] Data providing a test of this assumption have been collected by Mr. Peter Pappas in these laboratories and will be published.

[23] This value was obtained using slightly larger values of K_2. The difference is compensated sufficiently through use of a revised value of K_1 for the unsubstituted compound in the calculation of sigmas.

[24] N. C. Deno and A. Schriesheim, THIS JOURNAL, **77**, 3051 (1955).

[25] J. D. Roberts, R. A. Clement and J. J. Drysdale, *ibid.*, **73**, 2181 (1951).

[26] W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956).

[27] (a) J. D. Roberts and R. A. Carboni, THIS JOURNAL, **77**, 5554 (1955); (b) *ibid.*, footnote 10.

isomers indicates that, for this group, the field effect is slightly more important. The observed order for both substituents, namely, $(K_1)p > (K_1)o$ is, however, also consistent with a small degree of steric inhibition of resonance in the *o*-isomers. In addition there may be small differences in resonance effects of *o*- and *p*-groups. Clearly no single interpretation of *ortho vs. para* effects is uniquely successful.

It is interesting to compare in detail some of these results in sulfur dioxide solution with measurements[24] of the equilibria of hydrolysis of symmetrically trisubstituted triphenylcarbonium ions in aqueous sulfuric acid at 25°. These reveal a similar relationship between the effect of *o*- or *p*-methyl substituents and that of *m*-methyl. Relative ionization constants corresponding to equation 3 calculated from these data are 1.78 × 10³, 1.90

$$K_{\mathrm{rel}} = \frac{(\mathrm{Ar_3C^+})((\mathrm{C_6H_5})_3\mathrm{COH})}{(\mathrm{Ar_3COH})((\mathrm{C_6H_5})_3\mathrm{C^+})} \qquad (3)$$

and 1.18 × 10³ for the tri-*o*-, *m*- and *p*-substituted compounds, respectively. Clearly, steric inhibition of resonance is not evident in the data relating to the tri-*o*-methylcarbonium ion. If, on the basis of Deno's evidence for roughly equal effects of successive *p*-methyl substituents, similar equality is assumed for the *m*- and *o*-isomers, relative ionization constants can be estimated for the monomethyl substituted isomers. These are 12.1, 1.24 and 10.6 for the *o*-, *m*- and *p*-compounds, respectively. The degree of similarity to the corresponding relative ionization constants presented in Table III is striking, but this point should not be belabored because of the relatively low precision of the sulfuric acid data and the inaccuracies involved in assigning exactly equal influences to groups when, in fact, the data show quite appreciable variations.

Almost identical influences of successive identical groups are, however, characteristic of K_1 values obtained in this and earlier work in liquid sulfur dioxide. This is relevant to further consideration of the nature of charge delocalization in triarylcarbonium ions. Pertinent data have been described[4] previously for *p*-*t*-butyl, *p*-phenyl and *m*-phenyl substituents. The magnitude of the relative equilibrium constant for the tri-*p*-chloro-compound, 0.0225, differs relatively little from the cube of its magnitude for the mono-*p*-chloro compound, 0.0170, in essential agreement with the earlier data. The data for the *p*-substituted triphenylchloromethanes are consistent[25] with a triarylcarbonium ion model in which all three aryl groups are equally able to participate in charge distribution (model A), *e.g.*, the propeller model proposed by Lewis, Magel and Lipkin.[29] Newman and Deno[24,30] have, however, presented evidence, obtained with solutions in sulfuric acid, in support of a triarylcarbonium ion model in which only one or two aryl groups participate in charge distribution. It is of interest to compare the results in liquid sulfur dioxide with the latter type of model. The effect on K_1 of introduction of successive *p*-substituents can be calculated on the basis of these models by means of a rather obvious modification of the Hammett equation. This treatment, which differs from that employed by Deno, takes cognizance of the fact that the value of the substituent constant for a group directly involved in charge delocalization differs from its value when not so participating. Thus, the effect of a group not directly involved in delocalization of charge would be determined in part by its normal Hammett σ-value and the Hammett ρ-value, −4.41, which has been determined[4] from K_1 for *m*-substituted triphenylchloromethanes. In addition, if the substituent can, when the ring to which it is affixed is directly involved in charge delocalization, increase the resonance stabilization, a statistical factor will enter. In the limit of highly effective participation, the maximum statistical increment corresponding to introducing second and third identical substituents would be factors of 2 and ³/₂, respectively, if only one ring participates in charge distribution (model B). If two rings are involved (model C), introduction of a second substituent would have no statistical influence while a third substituent would augment K_1 by a factor of 3. In the later case, also, introduction of a second substituent would be associated with a change in K_1 measured not by the normal Hammett sigma but by a constant appropriate to direct participation in distribution of positive charge. We follow Deno[24] in signifying such constants by σ_R. They can be evaluated most directly from the effect on K_1 of the introduction of one substituent. Equations 4–9 indicate the operations performed in obtaining the substituent factors summarized in Table IV. The superscripts indicate the number of substituents.

TABLE IV

FACTORS FOR *p*-SUBSTITUENTS

X	K_1 ratio	K_1 factors Calcd.[a] with model B	C	Exptl.
t-Bu	K_1^{2x}/K_1^{x}	14.8	16.8	14.4
C_6H_5	K_1^{2x}/K_1^{x}	1.83	4.2	3.9
	K_1^{3x}/K_1^{2x}	1.37	2.7	3.9
Cl[b]	K_1^{3x}/K_1^{x}	0.030	0.077	0.088

[a] Standard Hammett σ-values are from H. Jaffe, *Chem. Revs.*, **53**, 222 (1953). [b] σ_R = +0.133, calculated from the data for the mono-*p*-chloro compound and the relationship: $K_1^{x}/K_1^{H} = -4.41\ \sigma_R$.

The ratios calculated for model C are in distinctly

model B—only one ring involved in charge distribution

$$\log(K_1^{2x}/K_1^{x}) = -4.41\sigma + \log 2 \qquad (4)$$
$$\log(K_1^{3x}/K_1^{2x}) = -4.41\sigma + \log 3/2 \qquad (5)$$
$$\log(K_1{}^{3}\mathrm{x}/K_1^{x}) = -4.41(2\sigma) + \log 3 \qquad (6)$$

model C—two rings involved in charge distribution

$$\log(K_1^{2x}/K_1^{x}) = -4.41\sigma_R = \log(K_1^{x}/K_1^{H}) \qquad (7)$$
$$\log(K_1^{3x}/K_1^{2x}) = -4.41\sigma + \log 3 \qquad (8)$$
$$\log(K_1^{3x}/K_1^{x}) = -4.41(\sigma_R + \sigma) + \log 3 \qquad (9)$$

better agreement with the experimental ratios than are those calculated for model B. The data in liquid sulfur dioxide appear to be about as consistent with model C as with one in which charge is delocalized to all three aryl groups. Similar calculations performed with the data of Deno and Schriesheim[24] corresponding to successive introduction of *p*-

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(28) A. Streitwieser, THIS JOURNAL, **74**, 5288 (1952).

(29) G. N. Lewis, T. T. Magel and D. Lipkin, *ibid.*, **64**, 1774 (1942).

(30) M. S. Newman and N. C. Deno, *ibid.*, **73**, 3644 (1951); N. C. Deno, J. Jaruzelski and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

methoxyl groups into triphenylcarbinol do not yield as satisfactory agreement with experimental ratios. Thus models B and C yield calculated ratios that in no case agree with corresponding experimental ratios of $K_{\mathrm{R}}{}^{+}$ to within a factor of three. With *p*-methyl as substituent, according to model B, $K^{3x}_{\mathrm{R}^+}/K^{x}_{\mathrm{R}^+}$ equals 68 while the experimental value is 48. Model C yields a ratio of 170 in this case. Deviations from expectations based on model A are even greater. Part of the evidence which has been offered[24] in support of model B and/or C is the small dependence on the nature of the substituent of the ratio of $K_{\mathrm{R}}+$ values for di- and triphenylcarbonium ions symmetrically substituted with identical substituents. Such behavior can, however, be rationalized in terms of model A.[31] Furthermore, inductive and field effects should produce substantial substituent-dependent variation in this ratio for ions of type B or C.

Neither the data on ionization equilibria in liquid sulfur dioxide nor hydrolysis equilibria in aqueous sulfuric acid provide a basis for unequivocal choice of model A or B and/or C. The present data are, however, least consistent with B.

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(31) This was pointed out to us by Prof. W. F. Sager as follows: "The constancy is really just one way of expressing the fact that the ratio of rho's for the two reactions is 3/2. A little simple algebra shows that either of these conditions implies the other. If the charge dispersal to the rings is extensive, if the stabilizing effect is proportional to the charge on the ring and if the substituent does not drastically alter the ring charge, then a value of 3/2 would be expected for the ratio of rho's. Similar considerations do not predict a constant ratio of $K_{\mathrm{R}}{}^{+}$ values for diarylphenylcarbonium and diarylcarbonium ions, as does model C, in cases where the aryl group is more effective than phenyl in stabilizing the ion. Deno's results show that the ratios are 4.47 for OCH_3, 6.0 for CH_3 and 6.7 for H. However, the third assumption made above requires that Deno's constant ratio should break down for ions in which the substituent is capable of bearing much of the charge. The large deviation found in the case of the dimethylamino substituent is in accord with this."

BOSTON 15, MASS.

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The Mechanism of Dye Formation in Color Photography. III. Oxidative Condensation with *p*-Phenylenediamines in Aqueous Alkaline Solutions[1a,b]

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The kinetics of the oxidative condensation of *p*-phenylenediamine and *p*-aminodialkylanilines with derivatives of α-naphthol in the *p*H range of 8 to 12 has been investigated by means of a steady-state flow method. The rates are proportional to the concentrations of the quinonediimines and of the naphtholate ions. It is suggested that the rate-determining step of the over-all reaction is the formation of the leuco dye by a bimolecular reaction of the above species. This is followed by rapid conversion of the leuco dye to the respective dyes. With different quinonediimines, approximate proportionality was found between rates of deamination and rates of coupling with a given coupler.

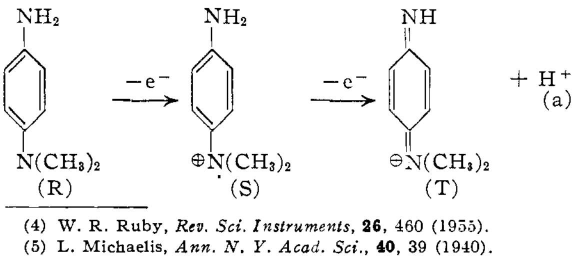
I. Introduction

In present-day color photography, the image dyes are most commonly formed by oxidative condensation (coupling) between *p*-phenylenediamine derivatives (developing agents), usually *p*-amino-N,N-dialkylanilines, and various compounds containing active methylene or methine groups (couplers), silver halide being the oxidant. The reaction as a whole, from the oxidation of the developer to the deposition of the dye, is heterogeneous, and can be very complex; the couplers may be present in various physical states in dilute aqueous solutions, as colloids, or as finely dispersed solid or liquid particles. The various phases of the process will be discussed separately. The subject of this paper is the homogeneous reaction between oxidized *p*-aminoalkylaniline and coupler in dilute aqueous solution.

In most of the previous research on coupling reactions, AgX was used as the oxidant.[2,3] This work has been reviewed adequately by Vittum and Weissberger.[2] Because of the complications just mentioned, such techniques[2,3] are not the most suitable ones for determining the mechanisms of the coupling reaction. For this purpose, the techniques used must produce the oxidized developing agent at a high rate and must be suitable for the observation of rapid reactions. Accordingly, ferricyanide was used as the oxidizing agent and most of the reactions were observed in the flow machine for rapid reactions designed by Ruby.[4]

II. Reactants

1. Developing Agents.—According to Michaelis,[5] the oxidation of *p*-phenylenediamines, R, takes place in two steps, each involving the removal of one electron, first to the semiquinone, S, then to the quinonediimine, T.



(R) (S) (T)

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[3] K. S. Lyalikov, B. A. Tsarev, Ya. L. Leibov and V. N. Kurnakov, *Otdel. Khim. Nauk*, **2**, 38 (1954).

[4] W. R. Ruby, *Rev. Sci. Instruments*, **26**, 460 (1955).

[5] L. Michaelis, *Ann. N. Y. Acad. Sci.*, **40**, 39 (1940).